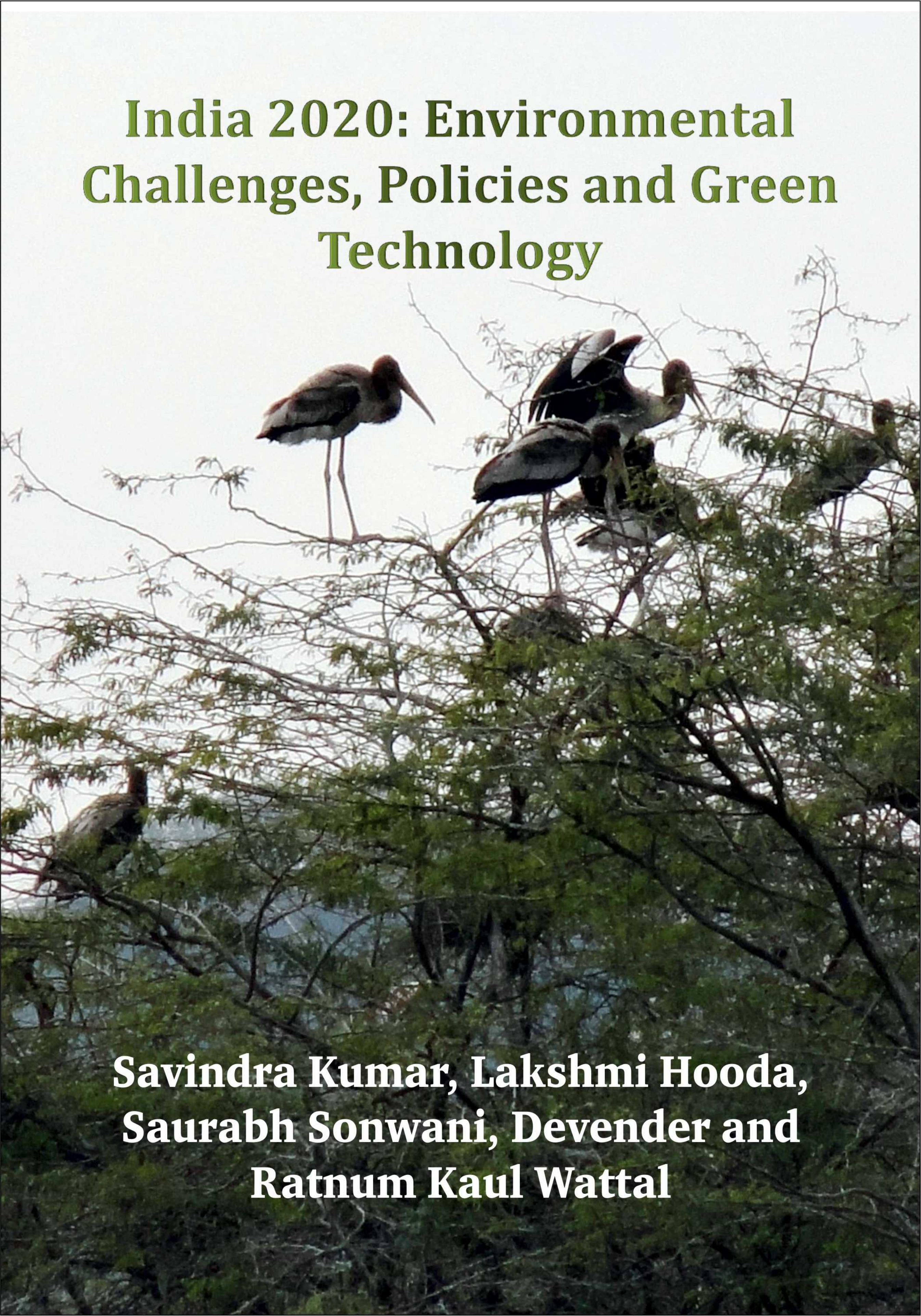

India 2020: Environmental Challenges, Policies and Green Technology

Savindra Kumar, Lakshmi Hooda, Saurabh Sonwani, Devender and Ratnum Kaul Wattal

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INDIA 2020: ENVIRONMENTAL CHALLENGES, POLICIES AND GREEN TECHNOLOGY

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PREFACE

Water is a natural resource which is depleting at an alarming rate across the globe. Rapid population growth, unsustainable industrial activities together with immense human interference with the natural resources, has led to present water-crisis. There is confrontation among nations, states and societies due to the gap between demand and supply. Water pollution and poor water management strategies have brought us to the brink of water shortage. Access to clean water and adequate sanitation is at present, a global problem. According to UNICEF and the World Health Organization, report in 2019 around 2.2 billion people around the world lack safely managed drinking water services and 4.2 billion people do not have safely managed sanitation services. Intensive water use in agriculture, non-eco-friendly manufacturing process and poor land use practices across the globe are withdrawing or contaminating groundwater at an alarming rate. Concurrent with the ecological dimensions of the water crisis there are issues related with public health, since a lot many diseases are water-borne, particularly in the developing world. Existing systems need to be modified, or new systems need to be created, so as to achieve wider access to clean drinking water, as well as to provide for effective redressal of public health concerns. The questions that confront the world today are to ensure adequate supply of clean water not only for present generation but also need to leave enough for future generations. How can equitable access be ensured and by whom? What will be the effect of climate change on the quantity and quality of water? Could the water crises be a likely cause of third world war? How is this problem to be addressed? The agenda for sustainable development was adopted globally in 2015 with the aim to end poverty and it has also included a dedicated goal on water and sanitation. The need of the hour is to introduce and implement water resource management at all levels. Water governance requires an ethical approach. Water management policies will have a profound effect on biodiversity loss as well as socio-cultural changes such as, forced migration and resettlement.

There is marvellous work going around globally attempting to address the problem of water scarcity, pollution, alternate green technologies to combat water pollution and strategies to protect water cycle in a manner that degradation of environment is taken care of. It was this fact which made us realize the need for a review of existing challenges and their redressal mechanisms in terms of green technologies, policies, governance and ethics. The available literature has been reviewed to provide in-depth knowledge about the water crisis that is looming large.

Keeping these challenges in mind, the book comprises of 14 chapters in a logical sequence and mentions significant components of the environmental challenges, policies and green technologies. The book begins with a brief account of the environmental issues of the present times and water sustainability being one of the major crises. It also discusses the ethical issues in addressing the environmental challenges. The need of the hour is to come up with technological as well as value-based interventions to mitigate environmental challenges in order to ensure a safe future for the generations to come. The main cruces of the book revolve around the water cycle, impact and remediation of contaminants /chemicals generated through various anthropogenic activities which lead to degradation of the environment, especially the hydrosphere. The sustainable development goals (SDG) adopted in 2015 were taken into consideration during drafting this book. The water crisis, challenges and implications are also mentioned in detail with possible and sustainable solutions. The book provides in depth information about restoration of degraded wetlands, phytoremediation, sustainable agriculture based on use of plant growth promoting rhizobacteria, acid rains and their environmental impact. Attention has also been drawn to the new technologies of biochar and use of seaweed liquid extracts to achieve environmental sustainability.

On the whole the book tries to cover all aspects of water crisis, mitigation strategies and ethical issues related with this natural resource. In our opinion, the book will be of great help to students of environmental sciences, scientists, and researchers as well as to non-government organizations trying to address the problems of water scarcity, pollution, creating awareness about sustainable clean water, wetland revival and several other water related issues.

Acknowledgment

It gives us immense pleasure in putting on record the contribution of all those who have helped us in the compilation of this book. It was indeed a very enriching experience. First of all, we would like to extend our deep sense of gratitude to all the authors for their contributions to this book. We are indeed grateful to all the reviewers for their valuable comments during the course of compilation.

We wish to convey out heartfelt gratitude to the Principal, Zakir Husain Delhi College, for all the support and encouragement. We gratefully recognise the overwhelming support and constant cooperation from the members of Department of Environmental Studies, Nature and Environment Society, and Department of Botany. Thanks, are also due to Imperial publications for their technical expertise in bringing this book to its present form.

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Editors

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WATER CRISIS AND ENVIRONMENTAL ETHICS

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"*Water and air, the two essential fluids on which all life depends, have become global garbage cans*".
(Jacques Yves Cousteau)

Abstract
Today the world is grappling with a growing number of environmental challenges as a result of the lax behaviour of mankind. Increase in global population and rapid industrialisation, without due regard to the judicious use of natural resources, has overburdened the ecological system. In particular, the effect of this crisis on water systems is acute, and has ramifications for ecological systems and public health, and has led to rise in conflicts among stakeholders. The question arises that when we do not have enough resources for our generation, how can we think of leaving anything for our children? The threat of an environmental collapse is imminent. Specific policy initiatives, their strict implementation and the practice of ethics are required to deal with such contradictory challenges at war footing.

1. Introduction

Population explosion together with human interference and industrial revolution has resulted in the emergence of serious new environmental problems on a global scale. These problems include, global climate change; worldwide loss of biodiversity, forests, and wetlands; long-range transport of toxic substances; decline of coastal ocean quality; distorted water cycles and degradation of the world's freshwater and ecological systems.

Climate change has brought with it, extremes of rains, floods, pollution and eventual scarcity of potable water on the planet earth. The earth is a watery place. About 71 percent of the earth's surface is water-covered, in the form of oceans, rivers, lakes, springs and glaciers. Besides, due to the water cycle, it is available in the form of water vapour in the atmosphere, ground water, aquifers and above all in all the living beings. In Arthur C. Clarke's words "How inappropriate to call this planet earth when it is clearly Ocean". Oceans hold 96.5% of earth's water.

Fresh water sources are depleting due to extensive urbanisation. Population explosion results in increased demand for limited resources , enormous waste generation and disposal leading to pollution of water bodies. Water-intensive agricultural practices, textile, paper and pulp manufacturing, and land use practices throughout the globe are over-utilizing and contaminating groundwater at an alarming rate. Rivers across the nation are getting polluted due to discharge of municipal waste as well as industrial discharge. State of affairs is no better with the oceans which are also not being spared from dumping of waste. Despite all this there is not enough sensitization towards these environmental challenges among masses. We are not able to perceive how the burning of fossil fuels in the United States may affect distant people-and an even more distant and abstract posterity. We must be able to connect the impact of coal and oil burning in one country on temperatures in many others. We need to visualize concretely how the use of certain pesticides in one part of the world is threatening, through long-range air transport, human health and the environment in other places around the globe. We also must see that high levels of consumption of paper in the developed world are leading to the destruction of forests in the developing world. Cyclones or hurricanes too have similar far reaching effects. Water pollution in one part of the world is showing far reaching effects in other parts of the world. These environmental damages may show displacement of its ill effects over time or space. Also, marine ecosystems in coastal areas around the world are being seriously threatened by urbanization and the aquatic pollution. A recent loss of coral reefs is a matter of grave concern. Humans are also endangering marine food supplies by overexploiting fish stocks. These are some of the environmental challenges which need immediate redressal.

It should also be noted that rapidly depleting fresh water supply disproportionately affects the poor. Almost a billion people do not have adequate drinking water, and diminishing fresh water supplies especially threaten poor people who are trying to grow crops on arid land. Concurrent with the ecological dimensions of the water crisis are public health concerns. The brunt of polluted water being source of the spread of water-borne diseases is particularly felt in the developing world. Existing systems need to be modified, or new systems need to be created, so as to achieve more, access to clean drinking water, as well as to provide for effective societal responses to public health concerns.

This is a global emergency. Our planet is facing a severe ecological crisis and the need of the hour is to care for our common home. It is time that we define certain guidelines which elaborate upon what is right and wrong from the ecological perspective. It should be more of a moral binding than legal compulsion. We have witnessed water conflicts arising between various stakeholders. The conflict may be due to resource depletion and hence conflicts between today's generation and future generations or between users of water who are faced with its scarcity, in particular between upstream and downstream populations. The conflict also appears between different types of usage (irrigation, industrial use, household use, etc.) and so forth. Ethics cannot offer "best solutions". They can only help to better understand the normative structure of water conflicts and support deliberations about responsible solutions.

Many questions confront the world today. How can we ensure that an adequate supply of clean water is available, both for today and for future generations? How do we ensure equitable access to all? How should it be managed, and by whom? How will quality and quantity of fresh water be affected by climate change? Will clean water be the bone of contention for the twenty-first century like petroleum was for the twentieth, a source of geopolitical power and conflict? Will social change concerning water use, come through technological innovation or through cultural and value change, or some combination of both?

Since its inception in the early 1970s, environmental ethics as a discipline has focused on the way humans treat the natural world. In 2012 during World Water Forum the need for water ethics was discussed. The Agenda for Sustainable Development was adopted in 2015, with the ultimate aim to end poverty by 2030. The 2030 agenda includes 17 Sustainable Development Goals (SDGs) and 169 targets. The SDGs are global and universal with the vision to "leave no one behind" and "seek to realize the human rights of all." The SDGs include a dedicated goal on water and sanitation (SDG 6) that aims to "ensure availability and sustainable management of water and sanitation for all." While SDG 6 broadens the Millennium Development Goal on drinking water and basic sanitation (MDG 7) to include the entire water cycle, target 6.5, implements integrated water resources management at all levels, including through transboundary cooperation (Génevaux, 2018). According to Target 6.3 "By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally".

It is therefore very essential to educate present generation about their moral obligations towards the environment they live in. It is their responsibility to preserve the composition of the environment for future generations.

The world is presently facing multiple environmental challenges. To be able to address these challenges the need of the hour is to ensure sustainable use of resources and treat all components of the environment ethically. Cooperation is required for their redressal not only locally, but internationally. We need ethics in place for environmental justice.

2. Types of Environmental Challenges

1. THE ISSUE OF RESOURCES

For a very long time, people have worried that we will run out of things we depend on, such as oil, fresh water, and minerals (Ehrlich, 1968). Resources, like wood and fish can replenish themselves quickly; others, such as oil, coal, and minerals, regenerate at much slower rates. Still other resources, such as the genetic material particular to each species, can be permanently lost (Wilson, 1992). This clearly indicates that earth has a very restrictive regenerative capacity (Kunstler, 2005).

2. NATURAL ENVIRONMENTAL SINKS

The self-cleaning ability of earth is because of its biophysical processes. The waste like carbon dioxide generated is absorbed by photosynthesis. Excessive amount of waste generated results in increased toxicity since it crosses earth's absorptive capacity. Almost 50 years ago, Carson (1962) explained how our overuse of pesticides was making it difficult for the earth to break down harmful substances such as DDT. Today, for example, carbon dioxide and other greenhouse gas emissions are way beyond the absorptive capacity of the oceans and forests, earth's natural sinks to absorb such substances and of the atmosphere to wash them out of its system. This is ultimately adversely affecting the global climate.

3. TRANSFORMATION OF LANDSCAPES

There is yet another type of challenge being faced and that is about the pace at which transformation of landscapes and ecosystems is occurring. Environmentalist value vast expanses of natural habitats with minimum human interference (Shabecoff, 2003). Such areas are places of rich biodiversity and provide ample opportunities for research and recreation. Urbanization has encroached on these areas of wilderness thereby affecting the flora and fauna of so-called natural places. This has resulted in loss of ecosystems. It is very essential to protect these ecosystems in the interest of the services they provide and the future value they represent.

In other words, these challenges are threats to resources, sinks and landscapes. Resources are pulled out from earth; waste is dumped into land/sea or land ecosystems are exploited. All this is happening globally according to specific pattern of power game. The rich and resourceful countries are overutilizing the natural resources, generating tremendous waste without worrying about the consequences of resource depletion and ill effects of decomposition of enormous waste (Peluso and Watts, 2001).

3. Displacement Across Space

Exhausting natural resources from other people's land with the aim of conserving/protecting their own are actually displacing environmental burden across space to protect their own. Japan, (Wapner and Matthew, 2009) imports significant amounts of wood from South East Asia but is unwilling to allow its own forests to be cut. Japan is maintaining its forest reserves since 1970's as a national treasure. However, neither it wishes to give this status to forests abroad nor attempts to meet its timber requirement through sustainable timber harvesting. (Samejima, 2020).

Displacement is a matter not only of shifting the effects of environmental degradation but also of moving people themselves. The history of protecting lands is full of cases in which marginalized people are removed to establish reserves and parks.

1. Native Americans in the United States were displaced in order to create Yosemite, Yellowstone, Grand Canyon, and Glacier National Parks (Fisher, 2003; Spence, 1996).

About 70,000 people were displaced, from the Koshi Tappu wetland in Nepal into an area virtually without any resources to create a Ramsar site (Matthew and Upreti, 2007). People are also displaced for large projects that transform landscapes, such as dam construction (Nayak, 2010).

2. In addition to resources, land, and people, sinks are also displaced across space. Waste is also being exported to economically weaker and politically less powerful countries. Britain uses nuclear power to generate one quarter of its energy needs and produces plutonium and other radioactive materials to service its nuclear weapons arsenal (British Broadcasting Corporation, 2003). However, it has not been able to come up with technology for the safe disposal of its nuclear waste. As a result, England is disposing its nuclear waste in the Irish-sea a practice which is being resented by its neighbouring countries like Norway and Ireland. (Singer, 2002).

The earth's diversity of species is a resource in that it provides a robust genetic base from which to develop new food crops and medicines, and a panoply of life forms for human enjoyment and scientific research. Practices associated with habitat destruction, the introduction of exotic species, hunting, and climate change are wiping out vast numbers of species (Wapner and Mathew 2009). The rate at which species are disappearing, the time is not very far when we will witness another round of massive extinction on earth. The most significant impact, however, is on future generations. Loss of biological diversity permanently narrows the range of genotypes available for ecological stability and diminishes the variety of life forms that can be researched or enjoyed. Loss of biological diversity involves displacing the finitude of resources. Resource displacement across time is a more general issue when one considers patterns of consumption. Many resources can regenerate themselves. However, extreme demand on these leads to unsustainable resource use.

"Wilderness is a resource which can shrink but not grow" (Leopold, 1989). Once wilderness is altered, it loses its integrity as a land untrammelled by humans. One could extend this thought to forests, farmlands, and even gardens in the sense that, once such areas are paved over or significantly altered, they can rarely grow back to their original state.

4. Displacement of sinks across time

The build-up of greenhouse gases has already altered the global climate system, and many predict that this will become more dramatic as global average temperatures rise even higher, sea levels climb, agricultural yields decrease, biodiversity diminishes, and storms become more violent with the continual build-up of greenhouse gases in the future (Wapner and Mathew, 2009) . When we burn fossil fuels that contribute to the build-up of greenhouse gases and overwhelm the capacity of water and forest sinks to absorb carbon, we implicitly choose to displace the sink problem across time. Should we not reduce our fossil-fuel consumption today, we will be passing on the experience of climate change to future generations. Displacement across time is no surprise. It happens because, like displacement across space, there are people available to be exploited.

David Brower explained, "We don't inherit the earth from our fathers, we borrow it from our children" (Brower and Chapple, 1995), and borrowing it in a meaningful way means ensuring that future generations have the same opportunities that we do. Everyone has an ecological footprint. Everyone uses natural resources, produces waste, and occupies land. The footprint of the globalized rich is much bigger than that of the localized poor. If the earth's carrying capacity was infinite, this might not be a problem. However, given that the earth's ecosystem does have limits, distributing rights to its bounty becomes a challenging moral issue.

The environmental justice movement points out, the phenomenon of environmental racism i.e. the disproportionate impact of environmental hazards particularly toxic waste dumps and polluting factories on people of low-income communities. Thus, the poor or politically weak tend to bear the brunt of environmental assaults, such as adverse health impacts (Cole and Foster, 2001). Sustainable development should keep in mind the concerns of the environmental justice as well. It is very essential to respect local and environmental practices. Long term planning is required whereas indiscriminate and destructive human practices need to be stopped. What is required is to live more sustainably and ethically at the same time. Global environmental problems raise very serious ethical issues: for example, a global climate change will hurt the poorest on the planet, seriously reduce the quality of life for future generations, and threaten plants and animals around the world. Is this right or just, particularly if those who are most harmed are least responsible for the problem?

Looking at the present scenario we need to undertake ecologically correct and ethically responsible water management strategies to secure the future of generations that come after us. Controlling water wastage and contamination is a major ethical issue. Here we will have to monitor the human induced water loss and contamination. We indiscriminately pollute water bodies because we are not paying for the costs incurred in controlling damages caused by it. The extent of pollution should be within waters self-cleansing ability. We will have to remember that water is not a commodity but a natural resource which needs to be used and conserved very judiciously. We have witnessed disputes over water not only between states with in the country but also between different countries. Quality of water in the rivers is far below the prescribed standards. This is aggravating the water crisis. The only hope and possible alternative appear to reuse and recycle treated waste water. This would address the problem of pollution and scarcity simultaneously by making non potable water available to masses. The focus of ethics is therefore not on water in isolation, but on the water cycle and how the cycle connects the land and the atmosphere. The notion of a “watershed” has this connotation, connecting water, the soil, and the biotic community, thereby making a difference to this planet.

Let’s not forget “The earth is what we all have in common”. Wendell Berry

5. Conclusion

The issue of water scarcity is a fact, but efforts can still be made to mitigate further damage. We need to increase our national sustainability efforts on all fronts to take charge of the deteriorating environmental conditions. This is only possible by the combined contribution of government policies and their proper implementation, as well as public participation at the grassroot level. Public participation in turn can be brought in with active support from live media and non-governmental organizations who can help with sensitization towards the issue of water scarcity. Through a combination of initiatives, it can ensure that we have a sustainable present and yet we can leave behind adequate resources for the future generation.

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WATER CRISIS IN INDIA: CHALLENGES AND IMPLICATIONS

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Abstract

Sources of the water crisis in India are diverse, and unraveling them, is a fiddly piece of work. The water crisis is universal and perennial in nature, and for a second most populated country like India, it is a decisive issue. India has started witnessing severe water crisis where accessibility and affordability to the safe water supply are threatened. The rapidly growing economic activities have excessively utilized and contaminated water resources in India. Besides, lack of availability of water resources for large sections of the population, contamination in water also raises questions on the existence of livelihood of people dependent on these water resources and the sustainability of varied ecosystems existing in these water bodies. In this background, the present study analyses the water crisis in India by bifurcating it into two segments - water scarcity and water pollution. For water scarcity- withdrawal of groundwater; falling precipitation; rapid population growth; irrigation, industries and municipal withdrawals and river disputes have been held responsible whereas, for water pollution- mismanaged irrigation practices, industrial wastes and untreated sewage disposal are considered as a major source of pollution.

Keywords: Water resources, water pollution, water scarcity, industries, agriculture.

1. Introduction

Water is essential for the existence of life on earth. The ravenousness of mankind is slowly turning water resources from public to private good. Water is used for multiple purposes such as domestic uses, drinking, irrigation, generation of hydroelectricity, and industrial purposes, etc. According to the United States Geological Survey (USGS), nearly 97% of water is present in the oceans, which are saline in nature, and the remaining 3% of water is fresh. The freshwater is distributed amongst icecaps and glaciers in the Arctic and Antarctic region (68.7%), surface water (0.3%), and groundwater (30.1%). Out of surface water, 87% is contained in lakes and rest in rivers and swamps (Shiklomanov, 1993), which means that only 1% of total water found on earth is usable by human beings. Water being the foundation of life, the scarcity of it is currently affecting one-fifth of the world's population, and a quarter of the world population faces a shortage of technology to retrieve freshwater from rivers and ponds (Xiao-jun et al., 2014). This scarcity of water is a severe problem, which is an after-effect of an increase in population and development in industrial and agricultural sectors (Manju and Sagar, 2017). The *World Water Development Report 2019: Leaving*

No-one Behind indicates that three out of ten people worldwide do not have access to safe drinking water, and six out of ten are deprived of safely managed sanitation services.

In India, clean/hygienic water is not less than an extravagance for the large section of the population. Currently, around 1.3 million people in India are suffering from water scarcity, which is evident from the poor health statistics of a large part of the population due to the water crisis. About 70% of the water supply in India is perilously polluted with sewage effluents (World Resources Report, 2017). The current state of the water crisis in India is critical as it has reached its maximum level of exploitation. Demand for water resources beyond the saturation level causes the water crisis. India is susceptible to issues related to the water crisis and growing urbanization has undoubtedly added to the existing water crisis in India. In most of the cities, water supply is available for few hours only. India has lost most of its significant reservoirs, with many of them possessing half the volume it is supposed to have. Many efforts have been made by the government to address the issues related to the water crisis. In most cases, it has been addressed adequately by the programs like Swachh Bharat Mission (SBM). This mission has largely improved the water-related issues such as clean drinking water, sanitation, hygiene in rural India. Jal Shakti Abhiyan (JSA) was launched to accelerate progress on water conservation activities in the most water-stressed blocks and districts of India. JSA has delivered over 3.5 lakh water conservation measures in 256 districts. Out of these, 1.54 lakh are of water conservation and rainwater harvesting measures, 20,000 relate to the rejuvenation of traditional water bodies, over 65,000 are reuse and recharge structures, and 1.23 lakh are watershed development projects. An estimated 2.64 crore people have already participated in the Abhiyan, making it a Jan Andolan (Economic Survey, 2019-20).

2. Review of Literature

Goldman (1991), in his study on the desert, found that the two main uses of water in the desert are to cultivate crop in order to fulfill the local needs and to grow fodder for the animals. His study found that in Jodhpur, capitalist farmers can divert enough water supply in their fields due to their relations at higher levels. In contrast, the small farmers remain to deprive of even an essential supply of water. Analyzing the role of retting of coconut husk on Kadinamkulam backwaters in Kerela, Nandan (1995) asserted that along with the destruction of greenery, this retting is polluting Kerela's backwater and producing unpleasant smell in the surrounding regions. Concerning global water scarcity, Biswas (1996) has emphasized on the effective use of the water available locally, since other purification methods will be very costly. The author opined that the storage tanks are the best option for the storage of water. The study recommended the utilization of run-off water by possible available means and suggested that expansion of vegetation cover is an essential tool for retention of water by soil. Ambekar (1999), in his analysis, found water pollution responsible for the spread of epidemics in India, particularly in the Kolhapur district of Maharashtra. Clean drinking water for people has been considered as a priority by the author. The author held Municipal Corporation responsible for the substandard progress towards controlling water pollution.

In an interesting study by Goldar and Banerjee (2004), a positive relationship was found between rainfall and water quality, while for water quality and industrialization, irrigation intensity and fertilizer, a negative correlation was confirmed by the study. Municipal and industrial wastewater, leaching, and run-off and soil weathering were identified as primary factors adversely affecting the water quality of the Gomti river by Singh et al., (2005). Saleth (2011) considered water harvesting, new storage, water recycling, and desalinization as an effective way to work towards water management, particularly in areas prone to the water crisis. Babbar et al., (2012), in their study, have hailed the performance of the Decision Support system (DSS) in controlling water quality and propose the implementation of DSS for India. In an intriguing study by Bharucha et al., (2014), the reasons for the water crisis have been directed towards the rising demand for water resources rather than the shortage of supply.

Narsimha and Sudarshan (2018) warned of severe health consequences from the usage of water-rich in fluoride in the north-eastern part of Basara, Telangana. A direct positive relationship was found between water scarcity and livelihood of people by Rangarathan et al., (2018), where the water crisis is associated with deterioration in the standard of living of people. Their study found that people who are engaged in agriculture earn 50 percent less than what they would have earned in case of any other alternative occupation. The study considered water scarcity as an essential reason for forcing farmers out of agricultural activities and directing them towards another occupations. Kumar et al., (2019) found the quality of water in northern India not fit for consumption due to industrial activities. They further warned of severe health consequences arising from the consumption of this water. The water crisis has been considered as a structural limitation by Likhacheva (2019). The study by Singh et al., (2020) found that the water of river Ganga is unsuitable for drinking, aquatic life, and even irrigation except for Bithoor and Sarsayaghat, which experienced moderate effects.

3. Analysis

It is a tedious task to investigate about water crisis in India, which is a multidimensional aspect. The present study analyses the water crisis by dividing it into two segments: (a) Water scarcity and (b) Water pollution.

It is not easy to estimate which of them is a more significant menace. The reasons determining both the factors are almost different, but in combination, they are influential enough to create a considerable pandemonium at the country level, which is observable in India nowadays. Rapidly growing economic activities in India, continue to threat the sustainability of water resources, mainly through mismanaged agricultural practices, industrialization, and other related economic actions.

3.1. WATER SCARCITY

There are many facets of water scarcity in India and multiple factors responsible for infuriating water scarcity, which is day by day becoming more intimidating. Growing urbanization further raises alarm for the sustainability aspect of water resources. Some of the significant factors held responsible in this regard are Groundwater, Precipitation, Population growth, Irrigation, Industries and Municipal Withdrawals River disputes

3.1.1. Groundwater

Groundwater is one of the most significant natural water resources which has excessively been used for drinking and irrigation purposes, particularly in arid and semi-arid regions of the world (Adimalla and Li, 2018; Adimalla et al., 2018a; Li et al., 2018a). Shen et al., (2010) reported that more than 1.5 billion people directly or indirectly rely on groundwater for drinking purposes in the world. Because of insufficient supply of surface water, demand for groundwater resource has massively been increased not only in the semi-arid region of India but also in the world for the last two decades, particularly for drinking and irrigation purposes (Adimalla and Li, 2018; Adimalla and Venkatayogi, 2018; Li et al., 2018b). The contamination of groundwater has rapidly increased in areas that have witnessed a surge in industrialization, population growth. This is followed by urbanization, accelerated agricultural activities, heavy use of agricultural inputs, etc. (Adimalla and Venkatayogi, 2017; Subba Rao et al., 2017; Adimalla et al., 2018b). Therefore, groundwater contamination, water quality for drinking and irrigation purposes, geochemical occurrence and distribution has widely been analysed throughout the world (Khan and Jhariya, 2017; Adimalla and Venkatayogi, 2018; Abd El-Aziz, 2017; He et al., 2018; He and Wu, 2018; Narsimha and Sudarshan, 2013, Adimalla and Qian 2019).

Over the years, India has witnessed a rapid reduction in the groundwater level due to overuse and insufficient replenishment. India utilizes around 250 billion m^3 per year of groundwater, which is more than 25 percent of the global total. The significance of groundwater is evident from the fact that around 60 percent of irrigated agriculture and 85 percent of drinking water for rural India is supplied from groundwater. Hence, groundwater is undoubtedly an essential lifeline for rural India. (AQUASTAT, 2010; Sishodia et al., 2016). Moreover, in the Indian context, about 85% of the population live in rural areas, and they depend mainly on groundwater for drinking and irrigation purposes (Adimalla and Qian 2019). In terms of total annual replenishable groundwater resources, Uttar Pradesh comes out to be the highest user of replenishable groundwater resources, followed by Andhra Pradesh, Madhya Pradesh, and Maharashtra (Fig.1).

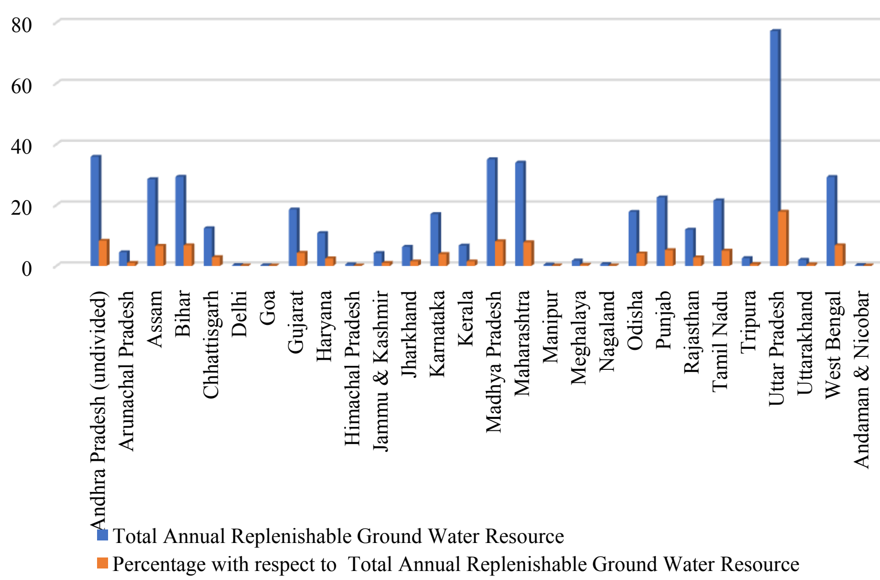

Fig.1: Total Annual Replenishable Groundwater Resources in Billion Cubic Metres
Source: Ministry of Water Resources, Open Government Data, New Delhi. https://data.gov.in/

The analysis of the district level availability of groundwater resources reveals a surge in the percentage of districts under critical zone from 3%in 1995 to 14%in 2011 due to overexploitation of groundwater resources (Table.1).

Table.1: District level Availability of ground water resource

Level of Groundwater Development	**Explanation**	**Percent of districts in 1995**	**Percent of districts in 2004**	**Percent of districts in 2009**	**Percent of districts in 2011**
0%-70% Safe	Areas which have groundwater potential for development	92	73	72	71
70%-90% (Semi Critical)	Areas where cautious groundwater development is recommended	1	9	10	10
90%-100% (Critical)	Areas which need intensive monitoring and evaluation for groundwater development	4	4	4	4
>100% (Over exploited)	Areas where future groundwater development is linked with water conservation measures	3	14	14	14

Source: Central Ground Water Board, PRS, 2016.

Today India has a significant portion of regions where groundwater is overexploited. In the northwestern part of India, the water table has gone down significantly. The increased in-depth level is attributable to both lacks of replenishment sources and overexploitation. Among the excessive usage, agriculture comes out to be a significant user of groundwater resources. Figure.2 shows that among various sources of irrigation ' Tube wells' turned out to be a major guzzler of groundwater resources followed by 'Canals' and 'Wells'. Among 'Size Class', Marginal class is on an average highest user of irrigation facilities.

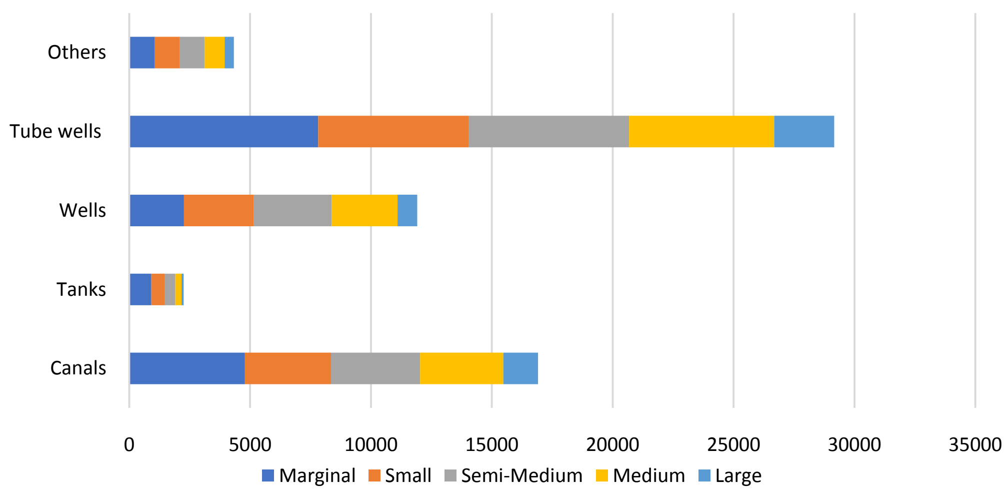

Fig.2: Areas irrigated by different source of irrigation by size classes (in hectares)
Source: Department of Agriculture, Cooperation and Farmers Welfare (Agriculture Census 2010-11)

Similarly, Fig. 3 captures the inefficiency and mismanagement in the use of water resources in irrigation practices in India. This is evident from the fact that the average amount of water used to produce the same amount of crop in India is much higher than in the case of most of the other countries where the same amount of crop is being produced by using less quantity of water. Such irrigation practices has over the period of time guzzled up the potentials of groundwater in India. Water utilization is particularly very high for cotton production in India.

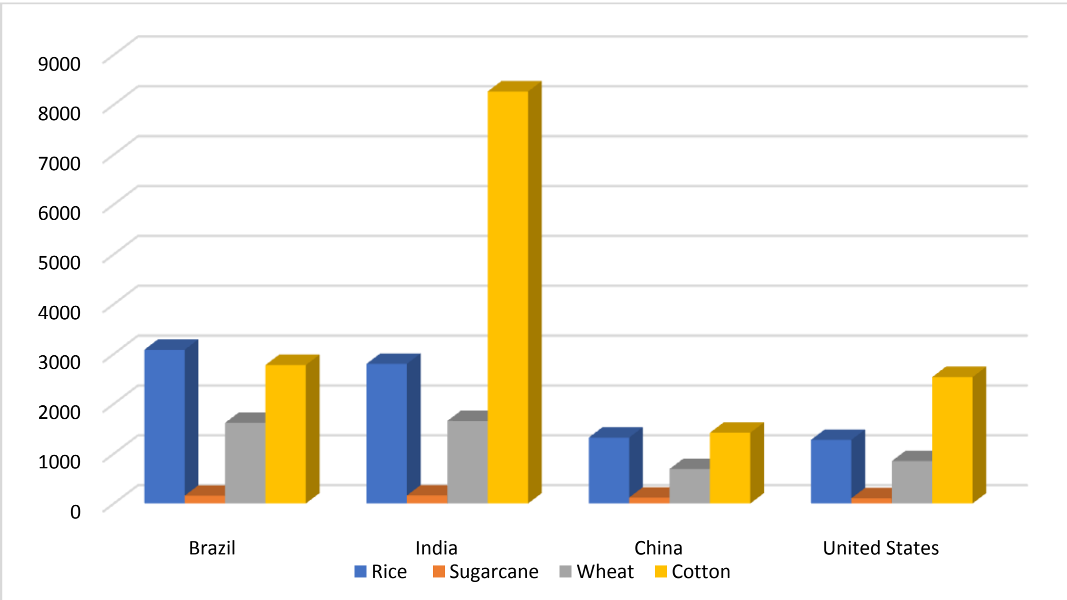

Fig: 3: Water use for producing same crop in different countries (in M3/MT).
Source: Department of Agriculture, Cooperation and Farmers Welfare (Agriculture Census 2010-11)

3.1.2. Precipitation

Precipitation is the primary source of groundwater replenishment in India. However, in the past few years, fluctuations in precipitation have adversely affected the groundwater table, irrigation facilities etc, especially in the northern part of the country. The amount of rainfall each year cannot be estimated as it mainly depends on monsoon which is highly unpredictable. This unpredictability has increased manifold after climate change and hence, its estimation remains one of the most perilous statistics for the researchers. From drought to flood, climate change threatens India with extreme rainfall events.

A research to analyse long term trend of annual and seasonal rainfall over different districts and meteorological sub-divisions of the country between 1901-2013 was carried by three IMD scientists named- Surinder Kaur, Sumant Kumar Diwakar and Ashok Kumar Das in 2017. Based on the rainfall analysis the researcher found that between 1961 and 2013, 64 districts (10.1%) experienced increasing trend of annual rainfall, whereas 85 districts (13.4%) witnessed a decreasing trend. The maximum number of such districts showing a fall in precipitation are located in Uttar Pradesh (32 districts) (Fig.4). Some of them are: Agra, Aligarh, Etawah, Firozabad,Gorakhpur, Kanpur, Mathura, Unnao, etc (Diwakar etal, 2017; Jamwal,2018). The changing rainfall pattern in India is a huge concern as the country's water and food security is at a risk. According to Mishra

(2017), India is a water stressed country. Almost 52% of its cropped area remains deprived of irrigation and some areas are chronically water stressed.

The declining trend is evident in most of the states in India (Fig.4). It is a critical issue since most of the districts which have experienced a declining trend belong to the agricultural belt of India. The lack of required rainfall is perilous for agricultural production as it provides livelihood to large section of population in India. Among all the states , Uttar Pradesh is the worst sufferer with 27 districts during 1901-2013 and 32 districts during 1961-2013. This declining trend of precipitation, apart from agriculture, threatens the sustainability of water bodies whose replenishment depends on precipitation.

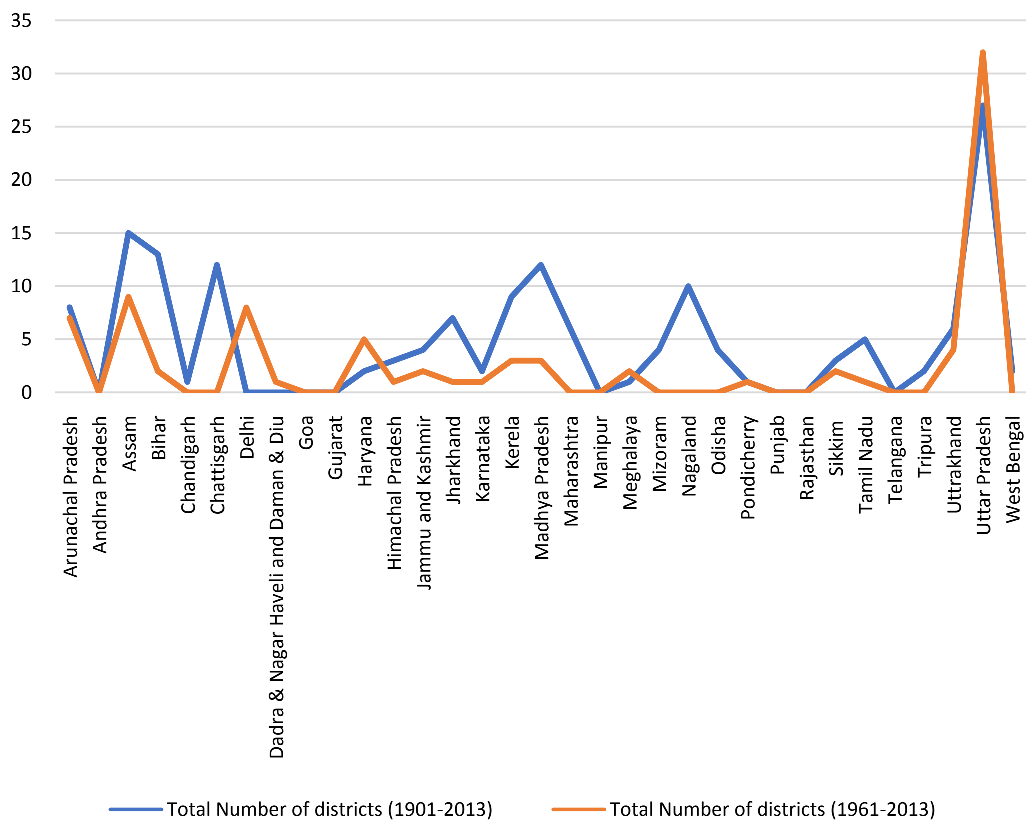

Fig.4 : Statewise number of districts showing decreasing trend (1901-2013) (Reproduce from Diwakar et. al., 2017).

3.1.3. Population Growth

India is witnessing accelerating demand for water resources due to rapidly growing population. As a result, the per capita water availability declined to 1544 cubic meters in 2011 from 1816 cubic meters in 2001 (Central Ground Water Board, 2019). This is also evident from Table.2 below, which shows that there has been a rapid decline in per capita availability of renewable internal freshwaster resources during the period 1962-2014. According to the World Bank (2020), renewable internal freshwater resources flow refers to internal renewable resources (internal river flows and groundwater from rainfall) in the country. Renewable internal freshwater resources per capita are calculated using the World Bank's population estimates.

Table.2 : Renewable internal freshwater resources per capita (cubic meters)

Year	Renewable internal freshwater resources per capita
1962	3,082.65
1967	2,778.63
1972	2,488.44
1977	2,216.4
1982	1,974.76
1987	1,764.1
1992	1,590.22
1997	1,444.7
2002	1,322.58
2007	1,222.1
2012	1,142.38
2014	1,116.08

Source: World Development Indicators, World Bank, Last updated on 8 April 2020.

In Table.2, it is noticeable that a steep fall in per capita availability of renewable internal freshwater resources has taken place, which fell from 3082.65 cubic meters in 1962 to 1590.22 cubic meters in 1992 to 1116.08 cubic meters in 2014. The overall decline was by around 64 % during the entire period. This is a worrisome issue. The growing population raises the demand for water used for various purposes and forms a genuine peril towards internal freshwater resources and sustainability of these water resources. Since the supply of water resources almost remains the same, so the per capita availability of renewable water resources goes down rapidly.

3.1.4. Irrigation, Industries and Municipal Withdrawals

These days there is an excessive utilization of water for agricultural, industrial, and municipal purposes. Here, the sector-wise utilization of water reveals that from 1973-77 to 2008-12, there has been a 94.68% increase in agricultural water withdrawal, 11.84 %increase in industrial water withdrawal and a whopping 391.22 %increase in municipal water withdrawal (Table.3). In this way, municipal water withdrawal turned out to be a significant guzzler of groundwater in India. Municipal water withdrawal is the water that is directly used by the population.

Table.3 : Sector-wise consumption of water in India

Sectors/Years	1973-1977	1978-1982	1983-1987	1988-1992	1998-2002	2008-2012
Agricultural water withdrawal (10^9 m3/year)	353.4	411.7	468	460	558.4	688
Industrial water withdrawal (10^9 m3/year)	15.2	12.6	11	15	10	17

Municipal water withdrawal (10^9 m3/year)	11.4	14.05	18.36	25	42	56
Total water withdrawal (10^9 m3/year)	380	438.3	497.4	500	610.4	761
Agricultural water withdrawal as % of total water withdrawal (%)	93	93.93	94.09	92	91.48	90.41
Industrial water withdrawal as % of total water withdrawal (%)	4	2.875	2.211	3	1.638	2.234
Municipal water withdrawal as % of total water withdrawal (%)	3	3.206	3.691	5	6.881	7.359
Total water withdrawal per capita (m3/inhab/year)	584.2	600.5	609	551.9	560.1	602.5

Source: Aquastat, Food and Agricultural Organisation (FAO), United Nations, 2020.

Sector-wise withdrawal of water as a percentage of total water withdrawal (Table.3) shows that both the agricultural as well as industrial sectors have witnessed a decline in withdrawal percentage. In contrast, municipal water withdrawal as a percent of total water withdrawal has more than doubled from 3% to 7.35%.

It can be observed that water utilization increased manifolds in the case of crops such as wheat and rice, where the green revolution was applied on a large scale (Table. 4). This has been one of the major reasons for the fall in the water table. FromTable.4 , it can be observed that the two crops which were mainly benefitted by the green revolution, i.e., wheat and rice, are the highest water utilizers in India. The water utilization in the case of wheat increased by 562.48% from 4300 (1000 ha) in 1958-62 to 28487 (1000 ha) in 2013-14. Similarly, in the case of rice, water utilization increased by 91.72% from 13000 (1000 ha) to 24924 (1000 ha) in 2013-14. While in the case of Barley, the water utilization fell by 59.74% during the same period. Maize, leguminous crops, and sugarcane witnessed an increase of 444.75%, 114.90% , and 209.13% respectively, during the period 1958-62 to 2013-17. Haryana, Punjab, and Uttar Pradesh were the primary beneficiaries of the benefits of the green revolution and these are also the regions in northern India which are facing severe groundwater crisis too.

3.1.5. River Disputes

Rivers have always been very close to people in India because they provide usable water, fishing, transportation, irrigation, etc. to a large section of the population. Rivers are an essential source of water for the agricultural, household, and industrial activities. India possesses one of the largest numbers of rivers in the world (ten), with rivers almost on every corner of the country. Despite this abundance, most of the State governments in India are facing perplex situations in combating growing river water disputes, namely, Krishna River Water Disputes, Kaveri River Water Dispute, Godavari Water Disputes, Mahadayi Water Disputes, Son Rihand Water Dispute, Ravi-Beas Dispute, etc. These disputes have sometimes led to even violent agitations in the states. In India, this is a significant issue since the majority of rivers in India are inter-state. These disputes are expected to increase with the rise in population.

Some of the major river water disputes are:

Krishna River Water Dispute: This is a very old dispute between Andhra Pradesh, Karnataka, and Maharashtra, which began in the year 1968. This dispute was over the construction of Almati Dam on Krishna river on which Andhra Pradesh government objected by arguing that the height of the dam will lessen the flow of water to Andhra Pradesh.

Kaveri River Water Dispute: The dispute over the sharing of water of the Kaveri river is between Tamil Nadu and Karnataka. Interestingly, this legal dispute dates back to 1892 and 1924. Karnataka declined to accept the ruling regarding Kaveri river water sharing given in the pre-independence period and asked for a much higher share. While Tamil Nadu showed its dependence on Kaveri river water by stating that it has a huge irrigation demand which is met primarily by Kaveri river water.

Godavari river water dispute: This is a dispute between Andhra Pradesh, Karnataka, Madhya Pradesh, Chattisgarh, and Odisha over the sharing of Godavari river water. After Telangana was formed, this dispute intensified mainly on the ground of Polavaram Projects. Further, the Godavari-Krishna river linking put forward by Andhra Pradesh also became a national issue for discussion. Andhra Pradesh proposed this to provide water for Karnataka and Maharashtra.

Narmada River Water Dispute: This dispute is between Maharashtra, Gujarat, Madhya Pradesh, and Rajasthan over the sharing of costs and benefits of dam construction on India's fifth longest river Narmada river. This has been one of the most controversial projects in India. Along with States Governments, large scale protests were held by environmentalists also. Even World Bank withdrew its funding proposal for Sardar Sarovar Dam in 1994.

Mahadayi River water dispute: This dispute is over the sharing of water of Mahadayi river (popularly known as Mandovi in Goa) with Karnataka. The dispute started over Karnataka's insistence on linking the Mandovi river with a tributary river of Krishna river in 2002. This was severely opposed by Goa, whose economy is dependent on the Mandovi river for several purposes.

Among all major rivers in India, Godavari river possesses the largest water resource potential followed by Krishna river, west flowing rivers from Tadri to Kanyakumari, Mahanadi, west flowing rivers from Tapi to Tadri, Narmada, Brahmani-Baitarni, Kaveri, and so on (Fig.5).

Table 4: Crop-Wise Utilization of Water in India

Water Utilization Crop-wise/Year	1958-1962	1963-1967	1968-1972	1973-1977	1978-1982	1983-1987	1988-1992	1993-1997	1998-2002	2003-2007	2008-2012	2013-2017
Total harvested irrigated crop area (full control irrigation) (1000 ha)	27980	30900	38190	43180	49876	55636	62470	66144	76187	76820	87259	92575
Irrigated cropping intensity (%)	112.5	114.8	121	122.8	123.2	130.7	131.7	NA	131.1	129.8	140.1	140
Harvested irrigated temporary crop area: Wheat (1000 ha)	4300	6200	10400	13600	15700	17876	19500	20654	NA	23498	NA	28487
Harvested irrigated temporary crop area: Rice (1000 ha)	13000	13400	14000	14800	16900	17843	19400	19633	NA	22428	NA	24924
Harvested irrigated temporary crop area: Barley (1000 ha)	1334	1316	1328	1524	910	668	NA	569	NA	472	NA	537
Harvested irrigated temporary crop area: Maize (1000 ha)	400	800	800	1100	1200	1233	1200	1314	NA	1411	NA	2179
Harvested irrigated temporary crop area: Leguminous crops (1000 ha)	1899	NA	NA	NA	2027	2288	2510	2441	NA	3326	NA	4081
Harvested irrigated temporary crop area: Sugarcane (1000 ha)	1674	2014	1874	2228	2289	2586	3180	3614	NA	4043	NA	5175

Source: Aquastat, Food and Agricultural Organisation (FAO), United Nations, 2020.

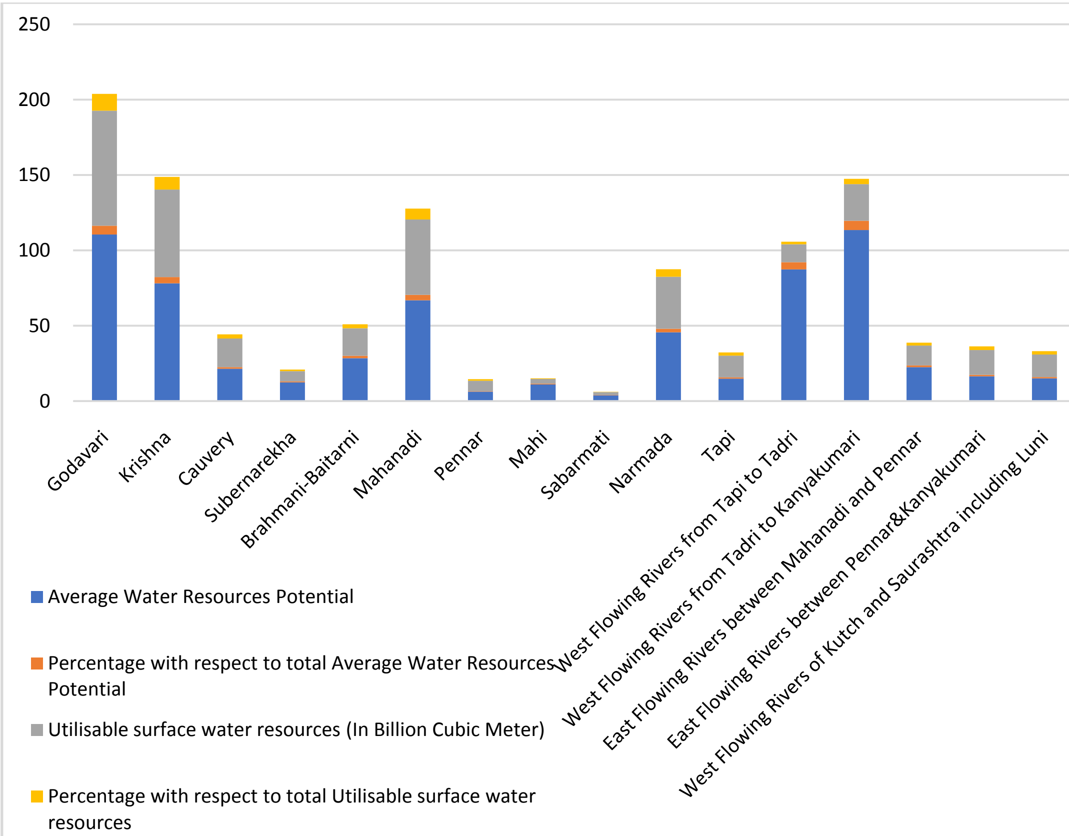

Fig. 5 Water resource potential of river basin in India (in BCM)
Source: Ministry of Water Resources, River Development & Ganga Rejuvenation, OGD, GOI, New Delhi (https://data.gov.in/).

3.2. WATER POLLUTION

Another way of analyzing the water crisis is through water pollution. Water scarcity accompanied by water pollution aggravates the already existing water crisis in India. This further reduces the availability of usable water for large sections of the population. Since, whatever, the water is accessible for the population, a substantial portion of that quantity is contaminated. India therefore is encountering severe water crisis due to contamination of water resources also with pollutants that are released during economic activities. The report, Central Pollution Control Board (2014), estimates that around 75%-80% of water pollution is by domestic disposal of wastes. Untreated perilous sewage flowing through river bodies has almost doubled in India, and water-borne diseases have gone up substantially.

Therefore, the primary sources of water pollution in India are:

1. Irrigation practices
2. Industries
3. Sewage Disposal

3.2.1. Irrigation Practices

Irrigation requirements substantially increased after the green revolution was introduced in India. Many tube wells, borewells using electricity were installed, which accelerated the pumping of groundwater and depleted the groundwater table. Post green revolution farmers (due to the lack of awareness regarding the proportion of inputs like fertilizers, weedicides, pesticides, high yielding variety seeds, etc., appropriate for a piece of land) in order to increase production used the maximum amount of the inputs along with higher irrigation provisions which in turn adversely affected the fertility of the soil and polluted the nearby water bodies where they were carried away by run-off of water. This agricultural run-off contains harmful chemicals that pollute the water and hence, makes it unfit for consumption purposes. Eutrophication is one of the common effects which can be observed on various water bodies, and one of the reasons is an agricultural run-off.

Further, such excessive use of inputs also polluted the groundwater through percolation. Hence, groundwater also gets un clean, which in the long run, adversely affects the health statistics of the population dependent on the consumption of these water sources. Punjab is a perfect example where people residing in green revolution zones are suffering from serious health complications even today.

Further, water available for irrigation purposes is obtained mainly from nearby water bodies or from groundwater, which sometimes supplies the same polluted waters in these agricultural fields. Crops produced from contaminated waters are found to possess a high level of toxic elements which is perilous for health.

3.2.2. Industries

Another major factor responsible for large scale water pollution of prominent water bodies in India is the release of industrial waste, which severely contaminates the water bodies and creates acute health threats in this regard. The main polluters are thermal power plants, leather industries, chemical and dye industries, plastic-based industries, sugar mills, pulp and paper mills, tanneries, and many more. Most of the rivers, ponds, lakes in India are unsympathetically polluted by these industrial organizations, which, apart from pollution, kill the ecosystem which exists in these water bodies and thereby, threaten environmental sustainability. There are many examples of ruthless carnage of water bodies by the harmful disposal of industrial wastes, and Yamuna river is one of the perfect examples of such human-made tyranny on nature.

The perilous impacts of industrial pollution are also observable in the form of poor water quality of the Ganga river. Singh et al., (2020) have considered industries as the worst besmirch of the Ganga river. The water of the Ganga river was found heavily stained with heavy metals and toxic chemicals as a result of discharge from industries. (Katiyar 2011; Madhulekha 2016; Hussain & Rao., 2018). According to Kumar et al., (2019), the groundwater in the industrial vicinity in northern India possess high amount of lead (Pb) and manganese (Mn) concentration, which makes it toxic and unfit for consumption purposes, in comparison to the quality of groundwater in southern India.

Several studies from India (Kumar et al., 2006; Krishna et al., 2009; Mondal et al., 2010; Chakrabarty and Sharma 2011; Singh et al., 2011; Mahato et al., 2016) and other parts of the world (Liao et al., 2005; Wang et al., 2005; Katsoyiannis and Katsoyiannis 2006; Leung and Jiao 2006; Zhou et al., 2008; Jan et al., 2010; Linhua et al., 2013; Wongsasuluk et al., 2014; Kumar et al., 2018) have held rapid industrialization and urbanization responsible for the presence of trace metal accumulation in water and soil.

3.2.3. Sewage Disposal

Sewage discharge is another key source of water pollution in India. Around 65-70 %of untreated urban sewage is directed towards water bodies. This, in turn, gives rise to several health-related problems in India and is particularly unsafe for the population who resides in the vicinity of these water bodies. Besides producing foul smell, this contaminated water is consumed by the nearby residents who, in turn, suffer from deadly health complications. India should try to strengthen its waste management system. The growing urbanization in India is further placing new threats for the provision of sewage disposal, which is expected to worsen as time passes. The untreated perilous sewage is unkindly dumped into the water bodies, which permanently damages their ecosystem. Further, the dumping of this sewage on land adversely affects the groundwater quality through percolation. This is a worrisome issue since groundwater is the prime source of drinking water for the people. Therefore, it is essential to put a check on the contamination of these water bodies particularly groundwater.

4. Challenges and Implications

For a second most populated country like India, the water crisis is a critical issue that is intensifying day by day. The main culprit being human-made activities responsible for water quality degradation. This is evident from the fact that most of the water bodies in India have started showing signs of adios. Major rivers in India, like Yamuna, and Ganga, have been ruthlessly utilized for the dumping of harmful waste released during the industrial processes and other such economic activities. This is a serious concern because these are the two major rivers in northern India. Most of the north part of India is already running out of groundwater supplies. These areas are also the green revolution regions and are now in the critical zone of water dilemma which needs immediate concern. Further, with the growth of the population in northern India, this water quandary is expected to intensify.

Growing interstate water disputes also complicates the prevailing water problem. With lots of resources and time wasted on these disputes, most of the cases remain unsolved. The adverse impact of water scarcity is also observable on the lack of irrigation in many parts of country. India, where majority of population depend on agriculture and agricultural based activities for their sustenance, lack of irrigation, is certainly going to place a difficult challenge for the policymakers in near future. Apart from reducing agricultural productivity, in the absence of required irrigation facilities, the use of contaminated water withdrawn from polluted nearby water bodies also contaminates the crops grown on these pieces of land. This in turn creates several health complications for the population who consume these products.

Persistently monsoon related issues are also expected to intensify the water crisis in India. Rivers and water reservoirs in India are continuously drying up due to a lack of precipitation. NITI Aayog (2018) has listed the name of 21 cities where groundwater would deplete by 2020. Chennai and Delhi are the most relevant examples where, despite best efforts, rapid industrialization and urbanization have guzzled up precious water resources.

The impact of this water crisis on human health seems to be vicious. India everyday witnesses large number of cases of cholera, hepatitis, typhoid, jaundice, diarrhoea etc. The largest number of death among water borne diseases was due to diarrhoea, recorded in the most populated state of India, Uttar Pradesh in the year 2017 (Fig.6). An important reason for the spread of water borne diseases in India is that a significant portion of Indian population lives in densely populated regions which again provides a scope for the spread of water-borne diseases. However, the introduction of Swachh Bharat Mission (SBM) has created awareness at a large scale even in the rural remote parts of India. SBM has a holistic approach which included both urban as well as rural areas. People have actively participated and are successfully practicing the teachings of SBM. In future SBM is expected to solve most of the health complications related with the consumption of unclean water in India, sanitation and hygiene.

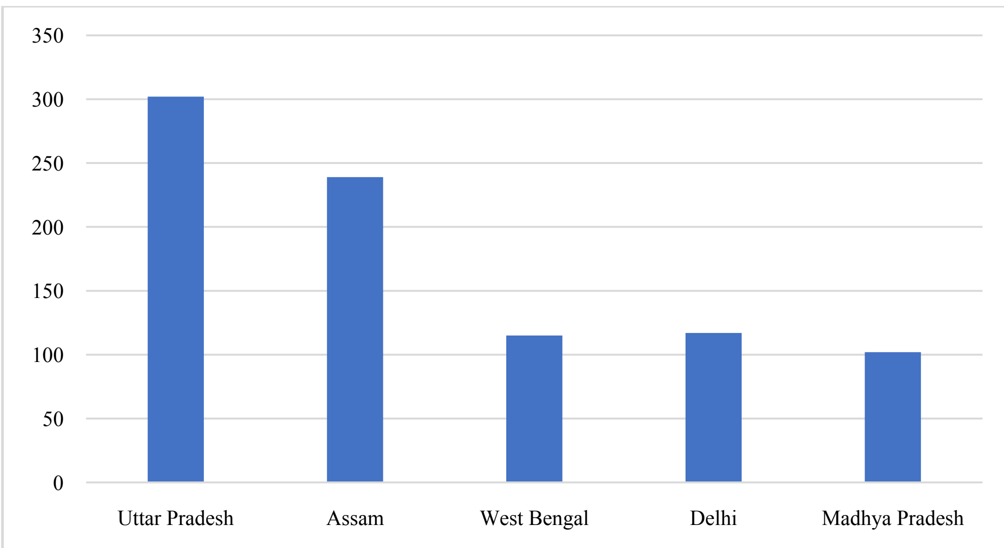

Fig.6: Death due to acute diarrhoreal diseases in India (2018)
Source: Data from CBHI , National Health Profile 2018, 13th Issue

5. Conclusion

The study investigates the water crisis in India in terms of water scarcity and water pollution. Water scarcity emerges due to the rapidly growing demand for water, while the supply remains the same. Lack of precipitation further aggravates the scarcity aspect. On the other hand, the disposal of untreated wastes is responsible for most of the pollution of water bodies in India. Human-made factors such as inefficient agricultural practices mainly associated with the green revolution, growing industrial activities, several water conflicts, untreated sewage disposal etc, are the main offenders for present-day water crisis in India. Our country is expected to become dryer in the near future e.g. Punjab, Rajasthan, Delhi, Uttar Pradesh are already suffering from this perilous condition. In many cities in India, water table is going down rapidly. People sometimes have to wait the whole day to get few litres of water. An important problem related to water pollution is the spread of water borne diseases. In a densely populated country like India, measures should be taken to promote cleanliness and hygiene in order to control these diseases particularly diarrhoea. SBM is expected to solve these issues if it is practiced extensively.

To deal with prevailing issues, steps such as the installation of water meters, restriction on the rampant installation of tube wells in agricultural fields, creating public awareness, substantial limitation on the use of groundwater by industrial sectors, strict government rules against the disposal of mainly industrial wastes in the river and other water bodies,etc should be taken in order to protect our water resources.

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WATER POLLUTION: CAUSES, IMPACTS, SOLUTIONS AND TREATMENT TECHNOLOGIES

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Abstract

Water pollution is the condition when harmful and toxic substances like chemicals, heavy metals, microorganisms contaminate water or water resources, degrade water quality and make it toxic. Due to booming population, urbanization and rapid industrialization, there is scarcity of clean water and water contamination is rising up. Wastewater is generally the used water being released from homes or from commercial, industrial, and agricultural activities (i.e. metals, solvents, and toxic sludge). The wastewater which is being released from homes remains untreated and although there is provision of treatment of wastewater coming out from various industries it is limited with primary treatment process only and is capable of polluting nearby water bodies. Agricultural runoff causes soil degradation and depletion of aquatic flora and fauna in water bodies, and there is no preventive measure. Due to the consumption of contaminated water, every year, more than one billion people worldwide get infected through water borne diseases such as cholera, dysentery and typhoid. As water pollution is rising on an alarming scale, it is important to control it at the primary source of contamination and hence, there is a need to emphasize on possible solutions through treatment technologies.

Keywords: Chemicals, Diseases, Environment, Toxic, Water pollution, Wastewater treatment

1. Introduction

Water is elixir of life which covers around 71% of the total earth's surface mainly, the water exists on earth in Sea and Oceans (97%) and only a little amount (3%) is fresh water. Most of the fresh water (about 2.7%) exists in the form of ice, groundwater and soil moisture, with only 0.3% in liquid form on the earth surface (Gleick, 1993a, 1993b, 1996). Out of this 0.3% liquid fresh water, mostly (around 87%) is contained in lakes, 11% in swamps, and only a little amount (2%) in rivers (http://www.blueplanet.nsw.edu.au/mi--water--distribution-of-water/.aspx). Water plays a significant role in the world economy, as it acts as a universal solvent and facilitates industrial cooling and transportation. Animal farming and agriculture are responsible for about 70% of freshwater utilization, whereas only 22% of fresh water is used by industry and about 8% is used for domestic purposes (World Watch Institute, 2004; Baroni, et al., 2007).

Water pollution occurs when harmful substances like chemicals, heavy metals and microorganisms etc. contaminate any lake, river, stream, ocean, aquifer, ground water or any other water body, degrading water quality and rendering it toxic to human consumption or the environment (Schweitzer and Noblet 2018). After contamination this polluted water is termed as waste water as it can't be used without further treatment. Based on its origin the wastewater can be categorized as commercial, industrial, sanitary, agricultural or surface runoff (Sanamdikar and Harne, 2012). Sewage water is contaminated with faeces or urine, the sewage generates from domestic residence, hospitals, industries and offices etc. Sewage includes domestic, municipal, and industrial liquid waste products. Domestic sewage contains a wide variety of dissolved and suspended impurities and is the primary source of various pathogens, potentially creating a direct threat to public health and water quality. As the water pollution is increasing alarmingly, in recent years, the awareness and concern about water conservation has increased at global level, and new approaches to conserve and protect water resources are considered worldwide (Sanamdikar and Harne, 2012; Shrirang and Chatterjee, 2014).

India and most of the other developing and underdeveloped nations are facing major problems with water pollution, predominantly due to untreated sewage. In India, rivers like Ganges, Yamuna and other major rivers flow through densely populated areas, and industrial belts, which pollute the rivers. Although governments have made some regulatory policies, however due to lack of stringent measures to check these norms, there is no success in controlling the water pollution (Shrirang and Chatterjee, 2014). The industrial and household effluents are directly released in the nearby water bodies which make them polluted and unfit for use. The present chapter emphasizes on possible solutions through treatment technologies for sewage and polluted water and its reuse that is the need of the hour.

2. Causes of water pollution

Water is known as a universal solvent therefore, it's able to dissolve more substances than any other liquid present on planet earth. That is why water is so easily polluted. Toxic substances from factories, farms and towns readily dissolve and mix with water, causing water pollution, the substances which pollute water are known as water pollutants or water polluting agents and may be of the following types Table. 1.

Table- 1. Major water polluting agents

S. No.	Polluting Agents	Examples
1.	Organic Pollutants	Detergents, Sewage, Insecticides, Pesticides, Herbicides and Petroleum etc.
2.	Inorganic Pollutants	Heavy metals, Chemical wastes, Ammonia etc
3.	Macroscopic Solid waste	Plastic, Paper, Glass pieces, Food waste etc
4.	Pathogens	Bacteria, Protozoans, Viruses etc.
5.	Others	Hot water discharge into various water bodies

3. Types and sources of water pollution

Water pollution can be classified mainly into two types as surface-water pollution and ground-water pollution. Marine pollution (plastic pollution & oil spills), thermal pollution and nutrient pollution are extensions of water pollution (Schweitzer and Noblet 2018). Water pollution sources are either point sources or non-point sources. Point sources have single identifiable cause of the pollution, such as a storm drain or a wastewater treatment plant. Non-point sources are more diffused, such as runoff insecticides, herbicides, pesticides and fertilizers (Moss, 2008).

4. Impacts of water pollution

Pollution is the result of the cumulative effect over a period of time. All living entities like plants and other organisms living in or being exposed to polluted water bodies can be impacted. The effects can damage individual species and impact the natural biological communities they are part of (Baroni, et al., 2007, Schweitzer and Noblet 2018). Waterborne diseases are caused by a variety of microorganisms/pathogens, bio-toxins, and toxic contaminants, which lead to devastating illnesses and also linked to significant disease, burden worldwide (Malik, et al., 2012) (Table- 2). The World Health Organization estimates that 58% of that burden or 8,42,000 deaths/year, are attributable to a lack of safe drinking water supply, sanitation and hygiene. (https://www.who.int/water_sanitation_health/publications/gbd_poor_water/en/)

Table- 2 Common waterborne diseases and their pathogens

S. No.	Disease	Pathogen	Types of pathogen
1.	Amebiasis	*Entamoeba histolytica*	Protozoan
2.	Ascariasis	*Ascaris lumbricoides*	Nematodes
3.	Campylobacteriosis	*Campylobacter jejuni*	Bacteria
4.	Cryptosporidiosis (oral)	*Cryptosporidium parvum*	Protozoan
5.	Cholera	*Vibrio cholerae*	Bacteria
6.	Cyclosporiasis	*Cyclospora cayetanensis*	Protozoan
7.	Desmodesmus	*Desmodesmus armatus*	Algae
8.	Dracunculiasis (Guinea worm disease)	*Dracunculus medinensis*	Nematodes
9.	Dysentery	*Shigella dysenteriae*	Bacteria
10.	*E. coli* Infection	*Escherichia coli*	Bacteria
11.	Encephalitis	*Viral encephalitis*	Virus
12.	Enteritis	*Serratia*	Bacteria
13.	Gastroenteritis	*Rotavirus*	Virus
14.	Giardiasis	*Giardia lamblia*	Protozoan
15.	Hepatitis A	*Hepatitis* A virus	Virus
16.	Legionellosis	*Shigella dysenteriae*	Bacteria
17.	Leptospirosis	*Leptospira*	Bacteria

18.	Microsporidiosis	*Microsporidia*	Protozoan
19.	Poliomyelitis (Polio)	*Poliovirus*	Virus
20.	Typhoid	*Salmonella typhi*	Bacteria

5. Possible solutions through treatment technologies

As we all know that water is most important for the survival of living beings; thus it is a necessity to explore the possible solutions for wastewater treatment using various technologies. There are various techniques which are being utilized to remove pollutants from wastewaters. Several standards and protocols have also been set and are well documented. The treatment strategies vary from source to source and the type of contaminants being released (Grady, Jr. et al., 2011). Thus, depending on type of effluent, various methods are available for removal of toxic, heavy metals and other contaminants from wastewater which are discussed below:

5.1 INDUSTRIAL WASTEWATER TREATMENT

The wastewaters from various chemical and pesticide industries usually contain several strong and toxic pollutants, organic and inorganic matter in various concentration, various acids, bases, colors, dyes etc. Therefore effluents from the chemical industries are carcinogenic, mutagenic, non-biodegradable and lethal/toxic in nature (Bury, et al., 2002). The treatment strategy of highly contaminated, lethal and toxic industrial wastewater is to treat them at the source or sometimes by applying appropriate onsite treatment strategies and also adopt processes based on molecular size and bio-degradable nature of the pollutants (Hu et al., 1999). The industrial effluents quality always depends on type of industry from where it is coming out for example the industry can be a food processing industry, a battery manufacturing unit, power plant, metal industry, mines, nuclear plants, paper and pulp industry, textile mills, tanneries etc (EPA, 1998). Wastewaters from chemical industries can be treated by some biological methods like activated sludge, rotating biological contactor (RBC), trickling filters and many other oxidation methods (Jobbagy et al., 2000; Grady, Jr. et al., 2011). The best strategy to treat industrial wastewater is to minimize waste at the production phase; that is why it's the first and most important step towards the waste production at production site (Carini, 1999; Alvarez et al., 2004). The solid waste can be removed by using simple sedimentation techniques, flocculation using alum or polyelectrolytes; filteration or if pore size is too less, ultrafilteration can also be done. The oil and greese can be removed using evaporators. The biodegradable organic compounds are separated using activated sludge, rotating biological contactor (RBC), trickling filters and many other oxidation methods (Meric et al., 1999: Jobbagy et al., 2000; Nykova et al., 2002; Grady, Jr. et al., 2011).

5.2 AEROBIC AND ANAEROBIC WASTEWATER TREATMENT

Aerobic and anaerobic wastewater treatment systems are based on the biological treatment methods used to breakdown the organic compounds into byproducts using micro-organisms. The aerobic treatment is done when the BOD and COD are relatively low and if they are high then anaerobic treatment is selected. Aerobic wastewater treatment is done in the presence of air for example in a pond and on the other hand anaerobic is done in closed digesters. As the conditions for both type of systems is different, thus different type of wastewater is being treated and in fact when the concentration of the organic compounds is very high, then both the treatments are paired. In such case, initially, the anaerobic treatment is done to reduce the concentration of organic contaminants and their level is brought down, organic treatment is done to further reduce the levels of BOD and COD. The final products of organic assimilation in aerobic treatment are carbon dioxide, water and biomass, while in anaerobic treatments they are methane, carbon dioxide and biomass (Grady, Jr. et al., 2011). In last few decades the use of anaerobic wastewater treatment plans has increased significantly. There are various positive effects associated with these processes such as, low sludge production removal of high pathogen and higher organic loading, methane gas production and low energy consumption (Nykova et al., 2002).

5.3 MUNICIPAL WASTEWATER TREATMENT

There are various methods used for the treatment of municipal wastewater which includes physical, chemical, and biological processes. All of these treatments remove contaminants from the wastewater and make it safe enough to be released into the environment. After sewage treatment the by-product is a semi-solid waste or slurry, called sewage sludge (Grady, Jr. et al., 2011). The sludge has to undergo further processing before the disposal or reuse. Sewage treatment generally involves three stages, called primary (physical), secondary (biological) and tertiary treatment (chemical) (fig. 1). Municipal wastewater treatment can also be done through construction of wetlands. This wetland technology treatment is a feasible and alternative process. An appropriate design of wetland should be more effective and able to maintain the wetland hydraulics, as it affects significantly the treatment process (Torrens, et al., 2009: Ghosh and Gopal, 2010). Although the wetland technology is an effective mean to combat municipal wastewater but it is the major challenge in developing and densely populated countries (Kivaisi, 2001; Massoud, et al., 2009; Zhang, et al., 2014; Stefanakis, 2015).

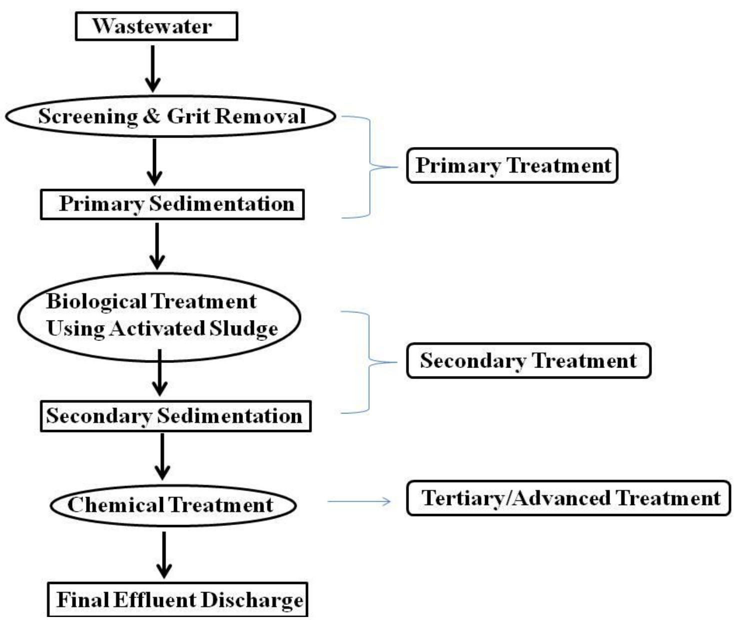

Fig.1 Generalized wastewater treatment plan

5.4 AGRICULTURAL WASTEWATER TREATMENT

The wastewater generated from agricultural practices is generally treated with certain management processes like a farm management program for controlling pollution from surface runoff that may be contaminated by excessive use of chemicals in fertilizer, pesticides, animal slurry, crop residues or irrigation water (EPA, 1998). Wastewater produced from bad agricultural practices is usually not contaminated with mineral elements, but also significant loads of organic substances like cellulose, starches and sugar. Wastewater from animal husbandry, cattle sheds, dairy, or fruit and vegetable production also contribute in a large amount (Moss, 2008; Grady, Jr. et al., 2011). The best practice which effectively can reduce the production of wastewater from agricultural activities is sustainable management.

5.5 ON-SITE SANITATION MANAGEMENT SYSTEM

The wastewater which is produced, if managed properly at its origin then a large volume of water from further contamination can be reduced. In on site sanitation, a water body or any other water resource can be managed and their conversion into polluted water can be avoided. The onsite management of effluents can be done by raising the awareness and making stringent laws and regulations. The Environmental Protection Agency (EPA) established the Clean Water Act (1972) and set strict guidelines for the release of effluents to reduce the contamination level in water bodies by industrial wastewater (https://www.epa.gov/laws-regulations/summary-clean-water-act). On-site wastewater management has its own advantages and disadvantages. The advantages are that it is low cost, has easy maintenance, planning and construction. The maintenance is easy and almost negligible investment is required. Also, there is less environmental disturbance and it can be used as a preliminary step in expanding urban areas. The disadvantages of this system can be listed as there is no well established policy related to installation, operation and maintenance in developing countries (http://cpheeo.gov.in/upload/uploadfiles/files/Guidelines%20for%20Decentralized%20Wastewater%20Management.pdf). Thus, it is difficult to standardize the technical designs to suit the local geography and climatic conditions. If it is not maintained properly it may lead to significant environmental consequences.

6. Conclusions

The sustainable utilization of the unique resource present on Earth i.e. Water is very important. If water is there then life is here on Earth. The anthropogenic activities are polluting the water and making it unfit for use. There is a need to develop such methodologies so that wastewater can be recycled and reused. Wastewater can be treated by a number of various ways. There are various methods which have proven to be an excellent treatment technology in many parts of the world. As various advancements have been carried out in wastewater treatment management systems now, it is necessary to make stringent rules and regulations to check the proper disposal and treatment of wastewater so that the water contamination and pollution can be controlled.

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ACID RAIN AND ITS ENVIRONMENTAL IMPACTS: A REVIEW

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Abstract

Acid rain is one of the important environmental threats and occurs due to the presence of certain acids in the atmosphere. Acidification of the rainwater is identified by the presence of sulphuric and nitric acids. Interaction of acid rain with environmental components results in their degradation. Acid rain reduces the soil fertility resulting in an adverse impact on the growth of the forest and crop fields. Acidification of the water bodies (lake/ponds) affects aquatic flora and fauna adversely. Acid rain also has some deleterious effects on human health, building and materials. The acid rain is responsible for the disturbance of several abiotic and biotic components of the ecosystem. Thus, the present review focuses on the causes, impacts and possible solution for the acid rain.

Key words: - Acid rain, Causes, Effects, Acidification, Control strategies

1. Introduction

The acid rain is considered as one of the Global ecological problems. It is considered as the precipitation of low pH water (pH range: 4.2-4.7) in the form of rain, snow, fog, hail or even dust. The term acid rain is first used by Robert Angus Smith in 1872 to describe the nature of rain around the industrial town of Manchester, UK (Smith, 1872). Wet deposition such as cloud water, rain, snow, hail, dew, fog or sheet) and dry deposition (SO_2, NO_x, other acid gas and particles) of acid components are responsible for the acid rain. Sulphuric and Nitric acids are considered as the major causes behind acidic rain whereas the formation of sulphuric acid and nitric acid in the atmosphere are the results of the atmospheric transformation reactions of the oxides of sulphur (SO_2) and oxides of nitrogen (NO_x) respectively. Several industries, motor vehicles, oil refineries and burning of fossil fuel are the important sources responsible for the generation of acid rain precursors. In the wet atmospheric conditions, these precursor gasses are converted in to sulphuric acid and nitric acid (as mentioned in the eq.1 and eq.2).

SO_2 +H_2O =H_2SO_4 (Sulphuric Acid)....................... (1)

NO_x+ H_2O =HNO_3 (Nitric Acid)............................ (2)

Acid rain is also known for its role in environmental damage and trans-boundary air pollution. Acid rain is a result of emission of SO_2 (fossil fuel combustion and metal smelter) and NO_x (released from the vehicular sources, industrial and power plant) forming sulphuric and nitric acid in precipitation. Acid rain has several adverse effects on ecological aspects (it harms flora and fauna both), biogeochemical cycles, soil quality due to nutrient leaching from top soil to sub soil and below sub soil in the presence of acid rain (Sonwani and Maurya, 2018). Apart from the above mentioned, acid rain also has several adverse impacts on human health such as itching, skin burn, respiratory problems (asthma, dry cough and irritation in throat), headache, brain damage and kidney problems. Degradation in building material (historical monument and sculpture all over the world), yellowing and weakening of fabrics are also results of acid rain exposure. Acid rain is the main reason for corrosion of several metals and structure made from it. It is also responsible for the loss of carved details and corrosion of copper, zinc etc.

2. Causes of Acid Rain

Figure 1 shows the cause and mechanism of the acid rain formation. Both natural and anthropogenic causes are responsible for the formation of acid rain in the atmosphere. But the combustion of the fossil fuel releases sulphur dioxide (SO_2) and nitrogen oxides (NO_x) which are significantly responsible for the formation of acid rain in the atmosphere (Sonwani and Maurya, 2018).

2.1 NATURAL SOURCES

Volcanic eruption is one of the main sources for the acid rain formation. Volcanoes release a large amount of gases responsible for the formation of the acid rain and other forms of precipitation (fog and snow) affecting the environment adversely. Forest fire, degrading vegetation and biological activities also release significant quantities of gasses producing acid rain. Dimethyl sulphide (C_2H_6S) is a major biological contributor to sulphur containing elements into the atmosphere. Anaerobic biological reactions in the soil/water and photochemical destructions are the important sources for the formation of atmospheric oxide of nitrogen in the atmosphere. Lightening activity produces nitric oxide (N_2O) which reacts with the water to form nitric acid which is an important constituent of acid rain.

2.2 ANTHROPOGENIC SOURCES

Several industries, (chemical, petrochemicals, pulp and paper) oil refineries, thermal power plant and emissions from the motor vehicles are the important sources that release the precursor gasses such as oxides of sulphur and oxide of nitrogen responsible for the formation of the acid rain (Saxena and Sonwani, 2019) The coal combustion used in the electricity generating plants is one of the biggest contributors for the production of gasses responsible for the acid rain. In the urban area, gaseous emissions from the industries and motor vehicles are the major sources for the acid rain formation. Such gasses react with the water, oxygen and other atmospheric chemicals to form several compounds such as sulphuric acid and nitric acid which result in the formation of acid rain. Under the influence of the meteorological parameters (such as wind speed, wind directions, temperature, relative humidity and mixing height) these atmospheric gasses transport at a larger distance and participate in the atmospheric transformation reactions responsible for the acid rain (Fig.1).

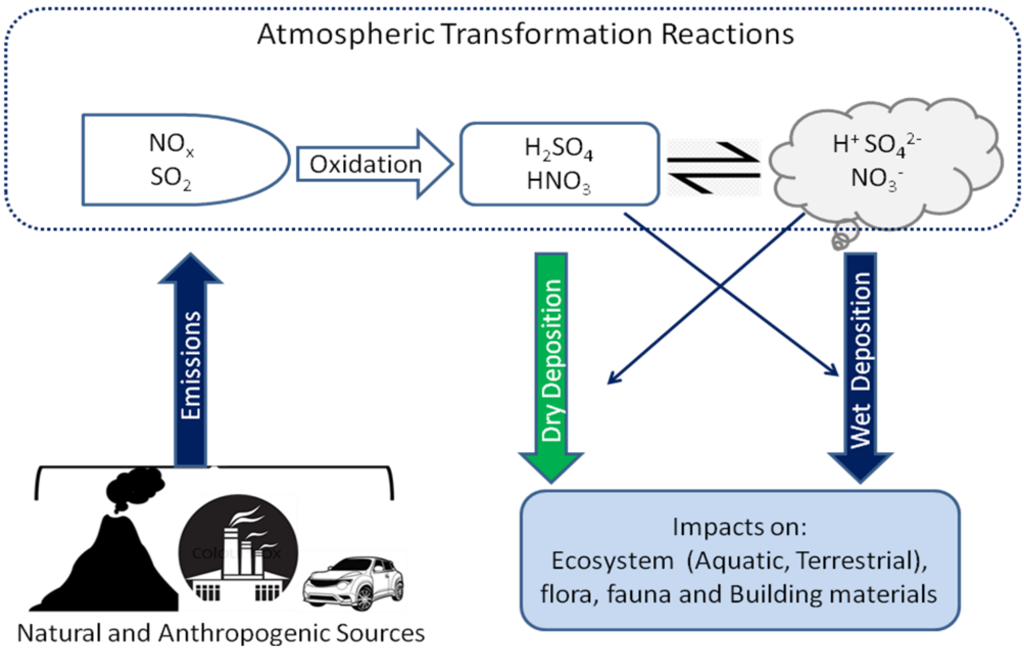

Fig. 1 Causes, formation mechanism and environmental impacts of the acid rain (Adapted from Sonwani and Maurya, 2018)

3. Effect of acid rain

In today's world due to rapid industrialization and to cope up with the demand of this exponentially growing population we have completely ignored the consequences of such actions on nature which ultimately resulted in causing serious damage to our environment. Acid rain is one such phenomenon caused due to acidification of rainwater by gases like sulphur dioxides and oxides of nitrogen and ozone to some extent. Such gases are not only released as a by-product from the burning of fossil fuels but also from motor vehicle exhausts (releasing NO_x) and smelters (releasing SO_2). These oxides react with each other and form hazardous substances in both dry and wet form which carried along with rainwater droplets and cause acid rain. Acid rain is a common term used for acid deposition in the form of rain, snow, hail etc. This acid precipitation has several profound effects on almost everything ranging from plants, soil to non-living objects like buildings. Here we will only discuss it's the effect on plants and crop fields.

In plants, acid precipitation causes foliar damage, create disturbance in plant physiological pathways like photosynthesis, nitrogen and sulphur metabolism, leaching of essential nutrients from leaves, cause hindrance in germination. (Varshney et al., 1979). Moreover, this acid precipitation causes soil acidification, improper nutrient supply etc.

The acidity of the rainwater is measured using a pH scale as low pH can damage biological membranes, electron transport system and other crucial phenomena essential for the survival of the plant.

3.1 EFFECTS ON CROP FIELD

Several studies mentioned the impacts of the acid rain on crop field (Singh and Agrawal, 2007, 2004). A wide range of responses are shown by crop plants in response to acidic rain. Table 1 showing the age wise changes in morphological characteristics in Simulated Acid Rain (SAR) treated *Triticum aestivum* var. *M213 & Sonalika* plants. Singh and Agarwal, (2004) conducted a field experiment in which they studied the effects of simulated acid rain of different pH i.e. 5.6 (control), 5.0, 4.5, 4.0, 3.0, using two cultivars of wheat (*Triticum aestivum*) *Malviya 213* (*M213*) and Sonalika. They used a split-plot design with cultivars as whole plots and SAR treatment was used as subplots. Five treatments of SAR were given (after 15 days of germination) i.e. 5.6, 5.0, 4.5, 4.0, and 3.0 within a time interval of 9:00-11:00 a.m. twice a week for 75 days. After 75 days six monoliths of 10x10x20cm^3 with intact roots were taken out. Two growth days i.e. 45 and 75 were taken and the samples were then thoroughly washed and several observations like leaf area (calculated using leaf area meter), shoot and root lengths, number of leaves, total biomass were made for each pH value. They found a significant reduction in root and shoot length at pH 3.0, the difference between both varieties is that *M213* showed a reduction in shoot length at both ages while Sonalika showed reduction at 75 days age. Whereas 13% and 15.5% root length reduction reported for *M213* and *Sonalika* respectively at pH 3. Similarly, leaf area declined at pH 4.0 & 3.0 in *M213* while 75 days age in *Sonalika* similar trend was observed in case of total biomass. Hence the magnitude of reduction was higher in *M213* as compared to that of *Sonalika*. Thus, different cultivars respond differently to different pH values of acid rain.

Table 1 Age wise changes in morphological characteristics in SAR treated *Triticum aestivum* var. *M213 & Sonalika* plants

Sonalika plants

Parameters	Age (Days) 45					Age (Days) 75				
	C	T1	T2	T3	T4	C	T1	T2	T3	T4
Root Length (cm)	9.83^{a}	8.97^{a}	8.97^{a}	8.25^{a}	8.08^{a}	10.45^{a}	9.58^{a}	9.25^{a}	9.17^{a}	8.73^{b}
	±0.68	±0.32	±0.21	±0.41	±0.35	±0.22	±0.47	±0.28	±0.40	±0.59
Shoot Length (cm)	19^{a}	18.37^{a}	18.22^{a}	17.8^{a}	17.58^{a}	79.45^{a}	78.67^{a}	76.33^{a}	73.17^{ab}	71.33^{b}
	±0.74	±0.44	±0.54	±0.64	±0.40	±1.11	±1.26	±1.38	±1.28	±1.34

M213 Plants

Parameters	Age (Days) 45					Age (Days) 75				
	C	T1	T2	T3	T4	C	T1	T2	T3	T4
Root Length (cm)	9.17^{a}	9.08^{a}	8.37^{a}	8.33^{a}	7.92^{a}	9.75^{a}	9.33^{a}	9.42^{a}	8.75^{a}	8.47^{b}
	±0.44	±0.27	±0.33	±0.28	±0.52	±0.38	±0.31	±0.31	±0.50	±0.51
Shoot Length (cm)	23.75^{a}	22.22^{a}	20.58^{a}	20.22^{a}	17.92^{a}	80.67^{a}	76.73^{a}	76.17^{a}	74.67^{ab}	70.5^{b}
	±0.81	±0.69	±1.04	±0.64	±0.72	±2.68	±0.52	±0.91	±1.15	±0.76

C= control; T1= pH 5.0; T2=pH4.5; T3= pH4.0; T4= pH3 (Table modified from Singh and Agarwal, 2004)

Acid rain can severely affect foliar parts of a plant. There are few crop plants which are resistant towards acid rain and noticed with profitable yield. In an experiment, some major crops of United States were allowed to grow in field chambers and exposed with simulated acid rain (pH 3.0, 3.5, 4.0 & control of pH 5.6) to identify the effects of acid rain on their yield, growth and foliar injury (Lee et al., 1981). Total above-ground portion and roots are usually determined at the time of harvest. Studies found that the acid rain unexpectedly increases the yield of crops (tomato, green pepper, strawberry, alfalfa, timothy, orchard grass). It was also mentioned that a group of monocotyledons are generally more affected than dicotyledons and different species showed different tolerance to acidified water (Lee et al., 1981; Singh and Agrawal, 2007; Lal, 2016).

3.2 IMPACT ON FOREST TREES

Effects of acid deposition on forest can be studied at two levels, firstly acid rain will damage foliar parts of the plant which will include direct damage to plant tissues like chlorosis, necrosis etc. and secondly through roots which is responsible for the stunted growth of tree including reduced canopy size (Tomlinson, 1983). It is worth mentioning that apart from the negative effects, acid rain also has some positive aspects in the forest ecosystem (Abrahamsen, 1984; Cowling and Dochinger, 1980). The positive and negative effects of the acid rain to forest ecosystem determine on the basis of the high/low productivity of the forest. Acid rain is considered as beneficial if it supports the productivity and vice versa.

This can be understood easily by taking an example consider a forest that is deficient in nitrogen (N) and sulphur (S) in that case moderate acid deposition will enrich the land with nitrogen and sulphur thereby causing productivity to increase. Similarly, if the land is already enriched with nitrogen and sulphur then acid deposition will lead to decrease in productivity (Johnson, 1982). An experiment was conducted where researchers sprayed acidic mist of pH 2.5 to a canopy of Sitka spruce which provided an overall of 48 Kg nitrogen and 50 Kg sulphur per hectare per year for three years. They observed a continuous decrease in the wood growth which is primarily due to the leaching of calcium ion causing membrane destabilization and foliar injury. Morphology and chemical composition of the soil is another important factor which decide the impact of the acid rain onto the forest and its productivity.

3.3 EFFECT ON SOIL

Soil is one of the essential ecological factors responsible to supply water and nutrients to the plants. Acid deposition adversely affects the soil quality by changing its pH levels, which ultimately disturb the soil nutrients concentration. Thus, acid deposition indirectly affects the ecosystem by changing soil chemistry. Increasing soil acidity negatively affects soil microflora population, accountable for the breakdown of soil organic matter into simple nutrients. Thus, acid rain harms the soil quality. Importantly, three important impacts of acid rain on soil reported are: (1) acid rain entering in the soil may be neutralized by the presence of the free bases such as $CaCO_3$ or Na_2CO_3, but during episodic acidification (melting snow or heavy rain downpour brings higher quantity of acidic deposition in soil) soil losses its buffering capacity (2) Acid rain removes the essential nutrients and minerals from the soil that are required for the plant growth (3) Acid rain leaches aluminium from the soil, which may be injurious to flora and fauna.

Due to the soil acidification cation (potassium, calcium and magnesium) exchange also happen under the influence of the hydrogen ions of acid rain. The dissolution of the soil minerals and salts resulting in the leaching of these minerals and salts from top soil to sub soil surface cause the mineral and salt deficiency in the top soil. This deficiency of the soil minerals and salts affect the soil fertility, which ultimately effects the growth of plants.

3.4 EFFECT ON AQUATIC ECOSYSTEMS

Aquatic ecosystem has wide range of abiotic and biotic components (autotrophs and heterotrophs). Acid rain lowers the acidity of the water bodies as water has low acid buffering capacity than soil, thus acid rain changes the chemistry of the lake. Thus, acid rain increases the acidity of the water bodies such as lakes and streams due to low buffering capacity of water and surrounding soil. Acid rain also releases aluminium from soil to the lakes and streams which is highly toxic to aquatic life including producers (algae, mosses and phytoplankton) and consumers. Phytoplankton is an important source of food for filter-feeding crustaceans and rotifers. Many of them are very sensitive to low pH level and thus disappear from water bodies after acid rain.

3.5 ACIDIFICATION OF LAKES/PONDS

Lakes are one of the important aquatic ecosystems supporting water life. Each abiotic and biotic component in any ecosystem has an important role and can affect directly or indirectly other related things in the ecosystem. Acid rain is one of the results of various anthropogenic activities which harm the environment. Lakes and pond have buffering capacity to balance their fluctuating pH levels which supports their aquatic life. So, the influx of acid in lakes/ponds can be maintained up to some extent. But when acid rain is precipitated in lakes/ponds for a long time, the concentration of nitrogen and sulphur compound increases in water resulting in loss of their buffering capacity and slowly its water becomes acidic there by resulting in the death of aquatic life and lakes both. The country like Norway has been suffering from acidification of lakes which has also reduced their freshwater availability. Most of the European countries, US and Canada are also suffering from these problems.

3.6 EUTROPHICATION OF LAKE

Eutrophication can be defined as the over enrichment of mineral and nutrients in the water bodies such as lakes and ponds. This excessive growth of algae in the lake called algal bloom which covers lake surfaces with green blanket. Eutrophication depletes the dissolved oxygen and increases the biochemical oxygen demand of water. It also blocks the sunlight and gaseous exchange from the lake water resulting in loss of underwater plant and animal species. Excess accumulation of the nitrogen, phosphate and organic compounds are the major causes responsible for the eutrophication of lake, whereas acid rain is another important reason behind eutrophication in lake. As acid rain reaches to the ground it easily solubilises several available nutrients present in the soil which ultimately reaches the nearby water bodies. Due to this continuous flow of such water leads to nutrient enrichment and cause eutrophication in lakes.

DAL JHEEL is the one of the famous lakes in Srinagar capital of Jammu & Kashmir. It is slowly dying due to eutrophication. Main reason for the eutrophication in Dal Lake is the disposal of 15 major drains of city containing sewage and organic waste of the city in lake which decreases the oxygen level and causes the algal bloom in the lake. Thus the fresh water availability for the cities as well as the aquatic life forms has decreased in the lake.

3.7 EFFECT ON BUILDING MATERIALS

Mainly the materials used in the buildings are marble, limestone, wood, cement, and metals (iron, aluminium, bronze etc). Acid rain affects these materials through two processes: **Dissolution** in which acid solubilises other solids or metals in to it and **Alteration** in which acid rain breaks or alters the solid physically.

3.7.1 Effect on marble and limestone

Acid rain has permanent effect on the marble and limestone because they are made up of calcium carbonate mainly called calcite. Such materials easily dissolve in the acid rain through the dissolution and form sulphates and nitrate of calcium which are highly soluble in water.

$$CaCO_3 + \text{Acid } (H_2SO_4, HNO_3) \rightarrow CaSO_4 + Ca(NO_3)_2 + CO_2 \text{ (Bubble off)}$$

They are later washed out by the rain water which leads to the degradation of limestone

3.7.2 Effect on cement and concrete

Acid rain effects cemented or concrete structures directly through the process of alteration, making the structures porous due to low pH (~3) and exposed to the moisture and leads to deterioration of the structure. Carbonation is the process through which acid rain affects the cemented structure which leads to corrosion, weakening and cracks in concrete which are very harmful for a building.

3.7.3 Effect on metals

Acid is very reactive towards metals. It easily corrodes or damages the surface of several metals such as iron, copper and zinc. Under the influence of acid rain, the acid reacts slowly and forms a corrosive layer on metal surface. This corrosion damages metal and reduces its strength and durability. Steel, bronze, zinc and nickel are some of the most vulnerable metals towards acid rain.

$$Fe(s) + H_2SO_4(aq) = FeSO_4(aq) + H_2 \text{ .... } (4)$$

$$Zn(s) + H_2SO_4(aq) = ZnSO_4(aq) + H_2 \text{ etc .... } (5)$$

3.7.4 Effect on Sculptures

Acid rain has significant effect on the monuments and sculptures made up of rocks, stones, wood, fabric and metals. Acid rain leads to the loss of many art sculptures every year. Acid rain affects sculptures in two ways:

Dry Acid– During dry conditions fumes of sulphuric acid deposit at the marble or limestone structure that are exposed to rain as well as shaded area and forms black crust over the surface which is called as gypsum. When it is washed with water, it leads to loss of material and weakening of that sculpture. The area which is protected from water this gypsum can be seen.

Wet Acid– Under normal weather conditions in acid mixes with rain water and reacts with calcite present in calcium carbonate which leads to corrosion of the materials.

Fig.2 Effects of the acid rain on Sculptures (Source: https://en.wikipedia.org/wiki/Acid_rain)

Some major monuments that are affected by acid rain are:

(a) Taj Mahal, Agra: Taj Mahal is one of the cultural UNESCO World Heritage Site and situated on the bank of the river Yamuna in Agra, India. It is also known as one of the Seven Wonders of the World. But under the influence of acid rain, the colour of the Taj Mahal is turning yellow day by day which leads to loss of its beauty. It's due to the presence of nitric acid and sulphuric acid in the rain deposited in the vicinity of Agra. These acids are the results of the transformation of atmospheric oxides of nitrogen and sulphur dioxide into nitric acid and sulphuric acid respectively. Such types of gases released by several industries located in the vicinity of Agra and Mathura. Vehicular emission also contributed to a large amount of the oxide of nitrogen into the atmosphere. The acid rain reacts with the calcite of marble resulting in yellowing of white marble of Taj. Due to continuous exposure marble loses its texture, broken spot and yellow tint form over the marble over time. Taj Trapezium case is linked to the Taj and the petition of this case was filled by M.C. Mehta, who mentioned that oil refinery at Mathura and industries located at Agra, emit a large amount of the toxic gasses responsible for the acid rain in the Agra region resulting in yellowing of white marble of Taj.

(b) Giant Buddha Statue, China: The world's largest Buddha statue situated in Mount Emei, one of the four sacred Buddhist Mountains of China. The statue has great religious belief and made up of carving a face on a sandstone rock of 71-meter height. Now, it is suffering from the black spot due to acid rain. Acid rain has destroyed the beauty of the statue and surface of the statue has become rough and porous. The cause of this acid rain is due to coal power plants near Mount Emei.

(c) Silver Bridge, Ohio River, U.S.: Silver bridge located in U.S over the Ohio River is famous for its unique aluminium paint. It collapsed in 1967 after a life of 40 years. According to some

investigators, the indirect reason for collapsing of bridge is the acid rain which slowly corrodes its paints and its joints leading to the weakening of shackles or cables.

4. Acid Rain Control Strategies

Acid rain is a global environmental problem and cannot be solved without any proper strategy. It may take several years to solve the problem. Till today few under developing countries can't even figure out the source of emission and receptor for the acid rain. These strategies can be divided into two parts 1. Source emission strategies which include strategies to control the emission of acidic gases from the source, to examine the emission from the sources, to check the sources whether they are working under the policy or norms made by the government or not like stack height, etc. 2. Receptor recovery strategies which include recovering the sites which are affected by the deposition of acid rain example: soil liming, lake liming, etc.

4.1 SOURCE EMISSION STRATEGIES

4.1.1 *Policy Implication*

It is listed under source emission strategies. The first step in acid rain control is to spread awareness among the people rather to enhancing any financial support to use advanced technology (Abbasi et al., 2013) or implications of the policies like restriction on using high sulphur coal, setting a limit on sulphur emission. It even turns out to be an effective strategy when local and central government work together towards the implementation of a policy which holds ecological importance and is in nation's best interests (Hao et al., 2007). The government can also sign the agreement with the industrialists to generate their interest in these national policies that helps in controlling acid rain as it is not easy to control acid rain.

4.1.2 Fuel Switching

Fuel switching is one of the easiest methods to reduce emission from the coal (with high sulphur) combustion activities. The use of low sulphur coal or reducing the use of coal or a step towards renewable energy sources (wind energy, tidal energy, hydrothermal and geothermal energy) can be a better option to reduce toxic gases responsible for the acid rain (Sivaramanan, 2015). In vehicles, we can switch from petrol or diesel to CNG or even better renewable energy options.

4.1.3 Advance Technology

There are several methods by which we can control acid rain by spending at cheap rates than the available technology but these are at underdeveloped or at developing stage, for example, Limb Injected Multistage Burner (LIMB). It is a method in which sulphur dioxide and nitrogen oxide can be reduced significantly by directly introducing the lime in the chamber which absorbs a considerable amount of these (Fay et al., 1983). There are also other methods which are just in Developing Stage which need to be financed. It comes under source emission strategies.

4.1.4 Scrubber

Scrubbers are the device that is used to control pollution by controlling the emission of acidic gases in the environment (Kerr, 1998; Smock, 1990). Positively charged Sulphur particles are attracted by the negatively charged plate in electrostatic precipitators. Instead of the negatively charged plate, we can also use chemical methods (Sivaramanan, 2015) like in "Flue gas desulphurization" it involves bringing post-combustion gas in contact with an aqueous solution of lime. The Sulphur dioxide reacts with this aqueous solution and other alkaline additives in it to form gypsum (calcium sulphate) this method is also known as a wet-scrubber method. Dry scrubbers method includes Limb injected multistage burner (LIMB) (Fay et al., 1983). It comes under source emission strategies.

4.1.5 Pre Combustion Cleaning of Fuels

Coal can be washed before utilization. It involves physical washing by water which can reduce sulphur from about 30% to 20%. It is a very effective method as there will be less emission of Sulphur dioxide after coal utilization. We can also opt for coal that has low Sulphur content however, this low Sulphur coal is not that much famous because it has low calorific content (Fay et al., 1983).

4.1.6 Models

We can also establish different models to ascertain a relation between the source of emission and the region of deposition. Such approach will further help the government to make policies, which will be also helpful in redistribution of emission sources. It will also be helpful to get the idea about the cost assessment between the damage caused by the source and cost it will take to recover the damage. There are different models for that like box-model and atmospheric models which depict the ongoing scenario and the complications associated with it (Fay et al., 1983). These models also tell us about the point of source and point of damage, so that we can sum up the damage caused and make policies accordingly.

4.2 RECEPTOR RECOVERY STRATEGIES

Receptor recovery strategies are for the recovery of the sites affected like lakes, streams and forests etc. Soil liming can be done to reduce the acidity of the soil in an effort to make the soil suitable for the crop cultivation or for the plant growth. We can also grow species that are suitable for the acidic environment and are of economic importance. Although liming is very expensive and not affordable to all, it is also not a permanent solution as it can also kill species that live in acidic soil by turning the soil too basic (Fay et al., 1983).

4.2.1 Liming

It comes under receptor recovery strategies. Lime is added to the water to reduce its acidity. Calcium present in the lime acts as sustenance for the primary production in an aquatic system. Lime is also helpful in reducing the toxicity of heavy metals and it also helps in the regeneration of the locked nutrients in the water bodies (Sivaramanan, 2015). But liming is not a permanent solution (Singh and Agarwal, 2007) and it is not recommended as it increases the turbidity and cloudiness in water (Sivaramanan, 2015). There is a wide application of liming in lakes, streams, running water and forest soils.

(a) Liming lake & Streams: Adding lime directly to the surface of lakes provides a cheap and clear-cut method for raising pH and acid-neutralizing capacity (ANC) of lakes. It was reported that lakes appear to recover faster than streams (Gerson et al., 2016). Acidified streams have different liming challenges than lakes. However, fewer data are available on trends in stream chemistry than lake chemistry, but the limited data suggests that chemical recovery in streams may be weaker than in lakes. Moreover, stream water chemistry is temporally changeable than lake water chemistry, and more prone to intermittent acidification during high flows.

(b) Liming forest soils: Liming in the forest soil is used to recover depleted Ca level due to soil acidification. The terrestrial liming is done through helicopters or with spreaders pulled by tractors or skidders (Long et al., 1997). Liming in forest soil is also helpful to prevent the mobilization of toxic Al forms in soils and help to restore both terrestrial and aquatic ecosystems. Liming could also be used to balance ecosystem nutrient relationships. Liming also helps in the re-establishment of biogeochemical linking between terrestrial and aquatic ecosystems.

Conclusion

Acid rain is one of the global issues with several adverse impacts on the environment. Oxides of nitrogen and sulphur dioxide are major gasses behind the formation of acids in the atmosphere responsible for acid rain. Emissions from industries are major sources for sulphur dioxide whereas several fossil fuel combustion activities and vehicular emissions are the major cause for emission of oxides of nitrogen in the atmosphere. As a result of these gasses acid rain happens after the formation of nitric acid and sulphuric acid. Acid rain causes several environmental problems such as the impact on the forest, crop, building, material, soil/water acidification including health-related issues (respiratory disorder, irritation in eyes and skin infections). To reduce such type of global problems several strategies have been adopted to reduce the acid rain and its impact on the environment. The effect of acid rain can be lowered by spreading awareness among the people and by the implementation of policies. Using advanced technology that is cost-efficient and reliable may also decrease acid deposition. The government can make some more strict policies regarding the emission of sulphur dioxide and nitrogen oxide from the transports and industries.

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A RESTORATION OF DEGRADED WETLANDS

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Abstract

Wetlands are one of the most productive ecosystems since they support a variety of floral and faunic biodiversity. Several types of wetlands such as marshes, swamps, water-lagoons, bogs and mangroves are home to some of the richest, diverse and fragile natural resources. Due to various threats, most of freshwater marshes and lakes have been lost in the past decades. The major concern includes urbanization, anthropogenic activities,deforestation, pollution, salinization, aquaculture and climate changes. Due to this ecological imbalance, the wetlands of India are also under continuous threat, thereby declining the ecological and economical functions provided. The mentioned threats have altered the local ecosystem services and its equilibrium, variation in floral phenology, increased competition from the invasive species and low lying and coastal cities due to sea level rise. Wetlands provide a wide range of ecological services like recharging of ground water, recycling nutrients, habitat for wildlife, recreational values, carbon stores, and mitigation of floods. Because of their diverse importance in maintaining the equilibrium of ecosystems, management and restoration of techniques should be deployed to retrieve the degraded wetlands.

Key words: Exotic species, Climate change, Wetlands, Restoration strategies, Threats

1. Introduction:

Wetlands are the transitional areas between terrestrial and aquatic ecosystems, occupying 4% of the world area (Prigent, 2001). According to Ramsar Convention, they are of different forms such as marshes, bogs and swamps, estuaries, lakes, rivers as natural water bodies and man-made ecosystems includes ponds, irrigated fields, sacred groves and canals (Ramsar Secretariat, 2013). In India, wetlands are distributed in different geographical regions and are well connected directly or indirectly with the large river system. India's wetlands are generally differentiated into eight categories, depending on their regional presence (SAC, 2011; Figure 1). These are: 1. The reservoirs of Deccan Plateau in the south, together with the lagoons and other wetlands of the southwest coast; 2. Vast saline expanses of Rajasthan, Gujarat and the Gulf of Kutch; 3. Freshwater lakes and reservoirs from Gujarat eastwards through Rajasthan and Madhya Pradesh; 4. Delta wetlands and lagoons of India's east coast (Chilka Lake); 5. Freshwater marshes of the Gangetic Plain and the flood plains of the Brahmaputra; 6. Marshes and swamps in the hills of northeast India and the

Himalayan foothills; 7. Lakes and rivers of the mountain region of Kashmir and Ladakh and 8. Mangroves and other wetlands of the Andaman and Nicobar Islands.

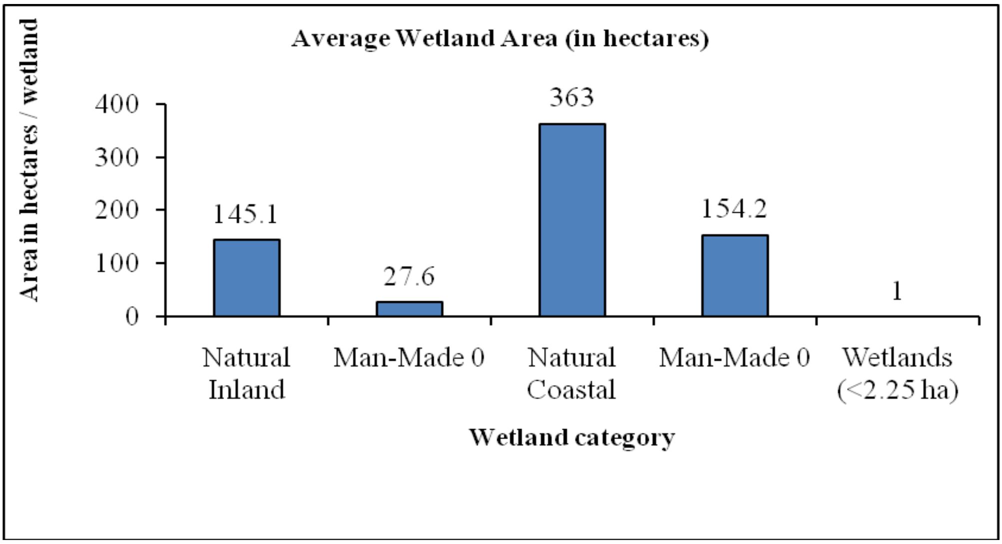

Figure 1: Average area under different wetlands, India (Source: SAC, 2011)

Wetlands are of immense importance as they provide a lot of ecological services such as home for at least one third of all threatened and endangered species (ten Brink et al., 2012; Singh et al., 2006), improve water quality, decrease the potential of eutrophication, maintain stream flows and importantly sequester carbon of approximately 10-14% (Mitsch and Gosselink, 2000). In India, around 18-19% of total geographical area is covered by wetlands of which 70% is under rice cultivations (Ministry of Environment and Forest – MoEF, 1990). They help check floods, prevent coastal erosion and mitigate the effects of natural disaster like cyclones and tidal waves. By acting as natural filters, wetlands are responsible for removing heavy metals, range of pollutants, harmful microbes from sewage and industries.Wetlands are effective in storing rainwater and are the primary source of recharging ground water aquifers; providegoods and services to lakhs of people, food and shelter for mammals. Most significant contribution of wetlands is accounted in terms of socio-economic values like constant water supply, livestock grazing, agricultural, energy and wildlife resources.

In the past decade, due to rapid urbanization, industrialization, population growth and people ignorance, wetlands of India are under tremendous and continuous stress (Central Pollution Control Board, 2008). As a result, ecosystems are threatened and degraded, thereby declining the valuable ecosystem services they perform especially groundwater recharge, nutrient cycling and biodiversity maintenance (Turner et al., 2000). Due to unplanned agricultural and urban development, industries construction, resource extraction wetlands have been drained and transformed. Construction of large number of reservoirs, canals to transport water to lower arid regions for irrigation has greatly affected wetland areas. Further, removal of vegetation in the catchment leads to soil erosion and siltation (Verma, 2002). Introduction of exotic plant varieties and unrestricted dumping of sewage and toxic chemicals from industries has polluted many freshwater wetlands. Increasing demand for shrimps and fisheries has provided economic incentives to convert wetlands into aquaculture and pisiculture ponds. Finally, increased air temperature, shifts in precipitation, increased frequency of storms, droughts and floods, increased atmospheric carbon dioxide concentration and sea level rise has also affected wetlands in majority (Bassi et al., 2014). Thus, the most important areas of '**wetlands**' are now considered as '**wastelands**' (Verma, 2002).

The present review highlights: 1. the value of wetlands towards mankind; 2. the various types of human activities which threaten the biodiversity of wetlands or stresses to which the wetlands are exposed to and 3. focuses on the management and restoration techniques that can be deployed to retrieve the degraded wetlands.

2. Threats to the wetland's ecosystems

Wetlands are the most threatened habitats of the world, causing adverse effects on the key functions of ecosystem services (Zedler and Kercher, 2005). The fast expanding human population, large scale changes in land use, burgeoning development projects and improper use of watersheds have all caused a considerable decline of wetland resources of the country. Some of these factors which led to these significant alterations in India's wetland ecosystems have been discussed.

2.1 IMPACT OF CLIMATE CHANGE ON WETLANDS

In the Indian subcontinent, global climate change is causing elevation in temperature and greenhouses gases. This has become one of the major concerns for the degradation of wetlands and disappearance of Gangetic plains (UNESCO, 2007; Bates et al., 2008). Among all the terrestrial ecosystems, wetlands are greatest source of carbon contributors to the environment due to the dissolution of high amount of carbon dioxide in air and water reservoirs aggravating the problems of eutrophication and algal blooms (Gopal et al., 2010). Also, in metropolitan cities like Delhi and Kolkata certain man-made wetlands like Baolis, lakes and marshes have been degraded extensively by increasing population, urbanization, sewage water drainage, pollutant contamination and invasion of exotic species has seriously disturbed the ecological services of wetlands ecosystem. Extensive eastern Indian coastline (mangrove forest) serves as the sink for carbon and is known to sequester tons of carbon per hectare (Kathiresan and Thakur, 2008); affecting the fish distribution and forest destruction. Limited analysis of climate change in inland natural wetlands of arid and semi-arid regions showed alterations in hydrological regimes due to changes in precipitation, run-off, temperature and evapo-transpiration (Patel et al., 2009).

A little less has been investigated on man-made wetland ecosystems and their utilization in carbon sequestration emphasizing more research requirement to manage wetlands as carbon sinks and their potential role in climate change mitigation strategies. According to Blankespoor et al., 2012, India will lose about 84% of coastal wetlands and 13% of saline wetlands due to climate change alterations. Consequently, there will be a loss of huge species diversity that rely on wetland ecosystems.

2.2 INTRODUCTION OF EXOTIC SPECIES

Invasive or Alien species are such species which are introduced outside their natural habitat where they survive and reproduce. In recent decade, it is observed that introduction of such species has devastated the wetland ecosystems extensively and have emerged as a great threat for the existing natural aquatic diversity and economy of the region. Invasive species threaten ecosystem processes by suppressing the biodiversity, cause local extinctions, alter wildlife habitat and affect livelihood of human wellbeing. Several such biological species have been recorded like *Eichornia crassipes*, *Salvinia molesta* and *Pistia stratioies* (plants); *Oreochomis niloticus, Clarias gariepinus* and *Cyprinus carpio* (animals) (Sandilyan et al., 2012). Impact of invasion of such species in India has resulted in altered aquatic (fish) ecology, change in water quality, water assimilation, extinction of natural flora due to reduction of food availability and enhanced competition. Thereby, fish trade has been affected the most and outbreak of diseases due to new invasive species encroaching in water systems has led to huge economic losses (Sandilyan, 2016; CBD, 2002). *Lantana* and *Prosopis juliflora* sp. have been introduced in India from western society in 19^{th} century, the plant has established itself in almost all parts of India occupying both arid and semi-arid regions. Consequently, the agricultural lands have been transformed into grazing areas and forced local people to search for new livelihood opportunities.

2.3 URBANIZATION AND LAND USE CHANGES

Rapid increase in population growth rate has put a tremendous pressure on wetland areas for meeting the demand of people. The increase in area for both agricultural and non-agricultural usage by the increasing population was at the cost of conversion of floodplain areas (Zhao et al., 2006).Urbanization exerts considerable influences on the function and structure of wetlands, mainly through modifying the hydrological and sedimentation regimes, and the dynamics of chemical pollutants, nutrients and chemical pollutants. Impact of urbanization is similarly alarming on natural water bodies in the cities. A study found that out of 629 water bodies identified in the National Capital Territory (NCT) of Delhi, as many as 232 cannot be recharged on account of large-scale encroachments (Khandekar, 2011). Similarly, between 1973 and 2007, Greater Bengaluru Region lost 66 wetlands with a water spread area of around 1100 ha due to urban slump (Ramachandra and Kumar, 2008). Further, poor management of water bodies, lack of concrete conservation plans, rising pollution, and rapid increase in localized demands for water are pushing these precious eco-balancers to extinction (Indian National Trust for Art and Cultural Heritage, 1998).

2.4 AGRICULTURAL, MUNICIPAL AND INDUSTRIAL POLLUTION

As a consequence of intensification of agricultural activities over the past four decades, consumption of fertilizers in India has increased tremendously. As per estimates, 10-15% of the nutrients added to the soils through fertilizers ultimately find their way to the surface water system (Indian Institute of Technology, 2011). High nutrient content resulted in high algal growth, leading to eutrophication of surface water bodies. Runoff from agricultural fields is the main source of non-point pollution for the Indian rivers flowing through Indo-Gangetic plains (Jain et al., 2007). Water from lakes that experience algal blooms is more costly to purify for drinking or other industrial uses. Eutrophication can reduce or eliminate fish populations (Verhoeven et al., 2006) and can also result in loss of many of the cultural services provided by lakes. Along with runoff from agricultural fields, untreated wastewater also contributes considerably to pollution of water bodies. Actual sewage treatment will be further low due to inadequacy of the sewage collection system and non-functional treatment plants. Thus, there is a huge gap in creation and treatment of wastewater in

Indian urban centres and most of sewage is discharged without treatment in the natural water bodies such as streams and rivers (Central Pollution Control Board, 2009).

3. Strategies for the conservation of wetlands

Wetlands conservation in India is indirectly influenced by an array of policy and legislative measures (Bassi et al., 2014). Major policies include - The Indian Forest Act, 1927, The Wildlife Protection Act, 1972, Coastal Regulation Zone Notification, 1991, Biological Diversity Act, 2001, National Biodiversity Action Plan, 2008 and Instrumental Act of Ramsar Convention on Wetlands and the Conservation of Biodiversity (Prasad et al., 2002). The main objectives of all the policies were the conservation of wetlands to prevent their future degradation.

A few strategies that the government can take is to forbid the conversion of water areas, demolish existing structures that pose threat to the effective functioning of the wetlands, remove any kind of mining sites from the area, measure the pollution levels to help monitor the sustenance of the damaged flora and fauna, to regularly update their strategies in order to maintain optimum conditions, increase awareness and make fisheries, plant cultures, research areas to effectively manage the sewage, waste and help in easy development of the wetland.

As a signatory to Ramsar Convention on Wetlands and recognizing the importance of protecting such water bodies, the Government of India recognized two sites, i.e. Chilika lake (Orissa) and Keoladeo National Park(Rajasthan), as Ramsar Wetlands of International Importance in 1981(MoEF, 2012). Thereafter in 1985-1986, National Wetland Conservation Programme (NWCP) was launched in close collaboration with concerned State Governments. Initially, only designated Ramsar Sites were identified for conservation and management under the Programme (MoEF, 2007). A number of measures were taken to seize further degradation and shrinkage of the identified water bodies due to encroachment, siltation, weed infestation, agricultural run-off carrying pesticides and fertilizers, catchment erosion and wastewater discharge. Later in 1993, National Lake Conservation Plan (NLCP) was carved out of NWCP to focus on lakes particularly those located in urban and semi-urban areas which are subjected to anthropogenic pressures. Over the years, number of designated Ramsar Sites have increased to 26 (Ramsar Convention on Wetlands, 2012), number of rivers under NRCP has increased to 39 and number of wetlands covered by the NWCP and NLCP has increased to 115 and 61 respectively (MoEF, 2012). However, these initiatives proved to be too little considering the extent of ecologically sensitive wetland ecosystems in the country and the fact that only a selected few wetland were taken up for conservation and management purpose (Dandekar et al., 2011).

Local people can also play a vital role in helping the conservation of the wetlands. They can practice sustainable cyclical farming, i.e. plants to animals, and animals to plants. Piscicultures and other edible faunas can be cultivated in there, and their waste can be utilized to form manures and bio-fertilisers for farming, while the plant waste can be utilized as food source for fishes and friendly bacteria. This will not only generate occupations, but will also lead to discovery of the medicinal properties that are hidden in those areas.

4. Restoration of wetlands

In the population rich countries with limited land resources, agricultural natural resource security is of utmost importance. Further, because the crop yields and productivity of the 'favoured agricultural regions' have reduced, it is essential that the degraded wastelands are rehabilitated and rejuvenated so that such lands are rendered cultivable and may become effective in supporting food crop production, agroforestry and forestry-based land-use systems. Further, global environmental change and variability are forcing irreparable damage to the arable lands adjoining degraded lands, water and biodiversity resources. These would have serious consequences on food production and food security in the coming years. This study on the degraded and wastelands of India in a way contains the first approximation of the harmonized results of the inter-institutional effort. Several points of immediate application are as follows –

a. Planning for land conservation should be prioritized based on the severity of the degradation problems arising owing to water and wind erosions and anthropogenic activities. Afforestation activities like agroforestry, silviculture and social forestry should be adopted to protect agricultural lands from further deterioration. Afforestation of degraded wastelands should be given priority.

b. As conservation and land rehabilitation measures are practised on a scarce level and are highly expensive, thus land reclamation should be prioritized.

c. In the areas where complex problems co-exist (water, wind and soil erosion simultaneously), research-based projects should be re-designed in a manner for bringing the best practices (such as cultivation of bio-fuel producing plants, fuel crops) of wasteland use.

d. The district-level data produced on degraded wastelands should be effectively used to prioritize areas for reclamation, water harvesting, etc. through different rural employment generation schemes at the local level. State- and district-level authorities should be trained to utilize information to operationally develop and implement activities at the state and district levels for rural development.

The outcomes of this study, would provide impetus in improving health of land resources through the adoption of recommended practices. This way an appreciable area of degraded lands can be brought under cultivation through reclamation processes in different problematic soils, which, in turn, will enhance production and productivity of various commodities, and safeguard further deterioration of lands. The acute problem of water shortage in the country, particularly in the rainfed areas, can be appreciably mitigated by employing special package of practices on the land parcels having problems related to land degradation. The output of the harmonized area statistics and maps of the degraded wastelands can be utilized in programmes related to land development under different schemes run by Government of India to uplift rural communities. This will also enhance livelihood security by generating additional financial resources and reducing food insecurity of the rural people by providing suitable land-based jobs, and the study may also help the National and State Planning Commissions/ departments to assign high priority areas identified as degraded wastelands, where public investments would yield benefits for the welfare of the people of the country and also for the security of the food and environment in the future.

5. Conclusion

Wetlands are ecologically important ecosystems that inhabit wide range of flora and fauna, provides multiple-use water services, carbon sequestration, pollution abatement, flood control and are biodiversity hotspots. Understanding the root causes of wetlands degradation, little attention has been paid by signatories towards conservation of wetlands. As a result, many wetlands are subjected to degradation. India is signatory to Ramsar Convention on wetlands but still no significant progress has been made on the conservation and wise utilization of wetlands; because only few selected wetland areas have gained financial and technical assistance and others continue to be in neglected state.

Thus, more research emphasis and better conservation strategies should be formulated for the effective conservation of such economically useful ecosystems. New guidelines should be developed for post-quarantine follow-ups, awareness should be spread among all policy makers, researchers, public people on the introduction of alien species into the wild and promoting research and strengthening the data base on invasive species. Other strategies such as survey and mapping by remote sensing technique, Catchment area treatment, re-establishment of pre-disturbed aquatic ecosystems, ecological landscaping, water management, awareness among general public and masses should be dealt along with to restore the degraded wetlands.

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PLANT GROWTH PROMOTING RHIZOBACTERIA (PGPR): AN APPROACH FOR SUSTAINABLE AGRICULTURE

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Abstract

India being a developing country with large population size, it is quite difficult to ensure food security for all with traditional agricultural practices. In order to ensure food security for everyone, production of crops was enhanced by excessive use of chemical fertilizers. Due to this, demand of chemical fertilizers increased day by day resulting in deterioration of soil microflora and destructive impact on environmental health was witnessed. Soil is considered as a source of nutrition for the crops. To get rid of hazardous outcomes of chemical fertilizers, biological inoculum could be an alternative and sustainable approach for environment friendly agricultural practices. Bacteria found in association with plant roots and improve plant growth by improving solubilization of different minerals like phosphorus, potassium and zinc, termed as plant growth promoting rhizobacteria (PGPRs). Recently PGPR fascinates agriculturists towards their crop promoting abilities by various direct or indirect mechanisms which help in improvisation of plant growth and its productivity by enhancing nitrogen fixation, phosphate solubilization, and synthesis of various phyto-hormones. Furthermore, PGPRs produce HCN which directly suppress the growth of phyto-pathogens, and could increase bio-availability of iron by producing siderophores, Due to these aptitudes PGPRs emerge as a promising tool for eco-friendly and sustainable agriculture practices. As PGPRs exhibit robust bio-control activity it might also be used as alternate to pesticides. Due to these facts PGPRs are considered as an effective tool for the growth and enhancement of the yields of agricultural crop that is performed as an environment friendly manner.

Key words: PGPR, Phosphate Solubilization, Siderophore, Bio-Control and Phosphate Solubilizing Bacteria (PSB)

1. Introduction

Soil is habitat of various micro-organisms like bacteria, algae, fungi, actinomycetes, spirochetes. It is thought to be main source for the cultivation of crops. In traditional agricultural practices soil is main nutritional source for the cultivation and harvesting of plants. As the world wide human population is increasing day by day and United Nation estimated in its report that world human population will reach the number of approximate 9 billion by 2050 (Wood, 2001). To fulfill the nutritional need of fastest growing population is too challenging as we have limited agricultural land available for agricultural practices. Keeping this fact in mind farmers use excess quantity of chemical fertilizers which ultimately results in higher increase in crop yield during last few decades, but this strategy also have some negative aspects. It will be very big challenge towards our society to feed large size population with limited agricultural land without affecting our environment. In this context reports of Alexandratos and Bruinsma (2012); Kumar et al. (2017a) highlighted the fact that demand of food will increase continuously as the population grows continuously and it creates a gap between supply and demand of food. The report claimed that demand of food will be increased up-to 70% by 2050 (FAO, 2009). Report of Altieri, (2004) emphasized that the importance of sustainable practices can fill the gap between food supply and production. For this purpose dynamic nature of soil and health is of prime importance (Paustian et al., 2016) it is not only required for the crop production but also required for the maintaining climatic health for next generations (Ahmad et al., 2016; Zahedi, 2016; Kumar et al., 2017b). In the present situation, sustainable agricultural practices could not be achieved without use of bacterial inoculums (Vaxevanidou et al., 2015). Use of rhizospheric micro-organism could be an alternative solution to overcome this concern. Plant Growth Promoting Rhizobacteria (PGPRs) are the group of bacteria which reside in rhizospheric zone and improve health of plant and soil as well. This term was first defined by Kloepper and Schroth (1978) to describe soil bacteria that colonize the rhizosphere of plants, growing in, on or around plant tissues that stimulate plant growth by several mechanisms. Kloepper et al. (2004); Haas and Defago, (2005) enlisted various mechanisms of PGPRs *viz.* nutrient cycling and uptake of nutrients, inhibition of plant pathogens, induction of resistance in plant host, direct stimulation of plant growth, bio-fixation of atmospheric nitrogen and bio-solubilization of insoluble nutrients such as phosphorus, potassium and some micro-nutrients. The use of PGPR for sustainable and environment friendly agriculture has increased globally during the last few years (Gupta et al., 2015; Gouda et al., 2018). In past years, PGPRs gain attention of scientific community as it become a potent alternate of synthetic fertilizers due to some of its mechanisms such as soil structure formation, decomposition of organic matter, employment of essential elements, solubilization of mineral nutrients, synthesizing numerous plant growth regulators, degrading organic pollutants, root growth induction, crucial for soil fertility, bio-control of soil and seed borne plant pathogens and in promoting changes in vegetation (Sivasakthi et al., 2014). Moreover, PGPRs not only have the potential to replace chemical fertilizers but also reduce the adverse impact on economic, climatic health, fertilizer cost and also promote sustainable agriculture as well as fertility of soil (Maheshwari et al., 2012). Several studies also claimed that PGPRs have potential to detoxify environment by killing pollutants such as heavy metals and pesticides. An ideal PGPR should exhibit following characteristics:

A) High rhizosphere competence

B) High competitive saprophytic ability

C) Enhanced plant growth

D) Ease of mass multiplication

E) Broad spectrum of action

F) Excellent and reliable control

G) Safe to environment

H) Compatible with other rhizobacteria

I) Should tolerate desiccation, heat, oxidizing agent and UV radiations (Jeyarajan and Nakkeeran 2000).

2. Plant Growth Promoting Rhizobacteria (PGPRs)

On the basis of their degree of association with plant roots Kizhakedathil and Devi (2018) categorized PGPRs into two broad categories: (1) extra-cellular Plant Growth Promoting Rhizobacteria (ePGPR) and (2) intra-cellular Plant Growth Promoting Rhizobacteria (iPGPR). The ePGPRs are generally inhabitant of the rhizosphere as well as on the rhizoplane where it enhances the plant growth by producing signals which increase the mobilization of nutrients inside the soil, while iPGPRs mainly inhabit inside the specialized nodular structures of root cells and are confined inside these structures. Different bacterial genera categorized under ePGPR and iPGPR are enlisted below:

Table 1: Classification of different groups of bacteria under various categories

S. No.	Class of PGPR	Bacterial genera	References
1.	e-PGPR	*Actinobacter sp., Aeromonas, Agrobacterium, Arthrobacter, Alcaligenes sp., Azotobacter, Azospirillum, Bacillus, Burkholderia, Caulobacter, Chromobacterium, Enterobacter, Erwinia, Flavobacterium, Micrococcous, Phyllobacterium sp. Pseudomonas* and *Serratia*	Gray and Smith, (2005); Bhattacharyya and Jha, (2012)
2.	i-PGPR	*Allorhizobium, Bradyrhizobium, Mesorhizobium, Rhizobium, Sinorhizobium* and *Frankia Sp*.	Verma et al., (2010)
3.	Actinomycetes	*Micromonospora sp. Streptomyces sp., Streptosporangium sp.* and *Thermobifida sp.,*	Gomes et al., (2000); Merzaeva and Shirokikh (2006); Sousa et al., (2008)

3. Role of Plant Growth Promoting Rhizobacteria in sustainable agricultural methods

Plant Growth Promoting Rhizobacteria have strong potential to induce growth in plants and it is a well known phenomenon among the scientific community now days due to its certain traits (Prasad et al., 2019). In the rhizospheric zone PGPR synthesize different secondary metabolites which promote the plant growth (Kloepper and Schroth 1981). There are several bacterial strains available which were previously used in agricultural practices like *Bacillus* (Borriss, 2011), *Pseudomonas* (Santoyo et al., 2012; Sivasakthi et al., 2014), *Actinobacteria* (Shivlata and Satyanarayana, 2017), *Lactobacillus* (Lamont et al., 2017) *Glomus* and many others. Report of Pachauri et al. (2014) claimed that climate change is the driving force behind reduction in crop production. Climate change is behind loss of agricultural land due to rising sea levels, soil erosion, salinization and desertification. Change in climatic condition affect the crop yield and it is a big challenge to maintain crop yield in adverse climatic conditions. The phyto-microbiome plays a censorious role in the survival of the holobiont, particularly for plants growing in extreme climatic conditions. Certain plants that have their habitat in hypersaline coastal surroundings or geothermal soils rely on endophytic fungi for survival (Rodriguez and Redman 2008). The microbiome of plants native to extreme environments may be rich sources of stress-ameliorating microbes. Plant growth promoting rhizobacteria (PGPR) have direct and indirect mechanisms. Direct mechanism include induction of plant growth by increasing supply of essential minerals such as N, P and K, synthesizing phyto-hormones, whereas indirect mechanism include inhibition of phyto-pathogens. Phosphate Solubilizing Bacteria (PSB) are bacteria which helps in solubilization of phosphate. This is an important trait that can be achieved by PGPR. Almost 95-99% of phosphorus in soil is present in insoluble, immobilized or precipitated form, therefore, it is difficult for plants to absorb it. PGPRs help in solubilization of inorganic phosphate into their simpler form so that plant can enhance its growth by absorbing phosphate. In this order these soil bacteria release different types of organic acids (Sharma et al., 2013; Zheng et al., 2018). These PGPRs have very important role in inducing plant growth by inducing different mechanisms some of them are: Mineral solubilization (Nitrogen, Phosphate, Potassium, Zinc, Iron etc.), phyto-hormone synthesis (Auxin, Gibberellin) etc.

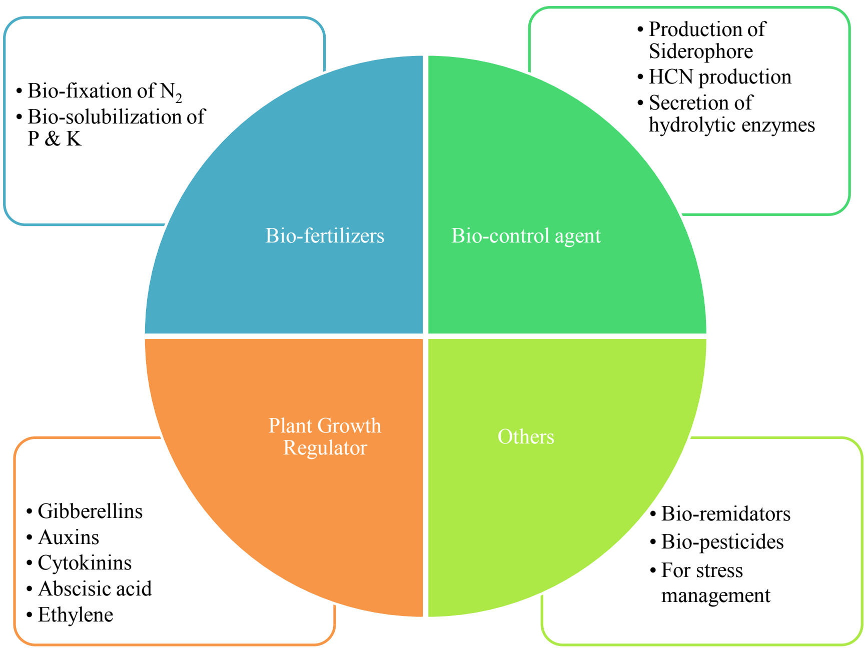

Fig. 1: Role of Plant Growth Promoting Rhizobacteria in agriculture, PGPRs exhibit diverse role in agriculture

4. Different traits of Plant Growth Promoting Rhizobacteria (PGPRs) promoting crop yield

4.1 NITROGEN FIXATION

Nitrogen is very important and essential for the growth and productivity of plants. Although nitrogen is most abundant gas in atmosphere, plants cannot uptake it because of its gaseous form. Till date no scientific reports are available in which uptake of atmospheric nitrogen by plants is reported. As plant species are unable to fix atmospheric nitrogen. The biological nitrogen fixation is limited to bacteria that possess an enzymatic complex (nitrogenase) which catalyzes the reduction of atmospheric nitrogen into ammonia (Weyens et al., 2010; Dahal, 2016). PGPRs could fix atmospheric nitrogen by two ways one is symbiotic and other one is non-symbiotic. Symbiotic nitrogen fixation is a mutualistic relationship between a microbe and the plant. The microbe first enters the root and later on forms nodules in which nitrogen fixation occurs. Similarly, non symbiotic nitrogen fixing bacteria takes place by various diazotrophs, which belongs to free living categories, and this can stimulate growth of non-legume plants like rice and radish. Both free living rhizospheric bacteria (e.g. *Azospirillum, Azotobacter, Achromobacter, Clostridium, Alcaligenes, Acetobacter, Arthrobacter, Bacillus, Azomonas, Beijerinckia, Corynebacterium, Derxia, Enterobacter, Klebsiella, Herbaspirillum, Pseudomonas, Rhodospirillum, Rhodopseudomonas* and *Xanthobacter*) (Tilak et al., 2005; Latt et al., 2018) as well as and symbiotic rhizospheric bacteria (*Rhizobium, Allorhizobium, Azorhizobium, Bradyrhizobium, Mesorhizobium* and *Sinorhizobium*) comes under nitrogen fixing prokaryotes.

At molecular level, *nif* genes are responsible for nitrogen fixation which are present in both symbiotic and free living systems (Reed et al., 2011). Nitrogenase (*nif*) genes include structural genes, involved in activation of the Fe protein, iron molybdenum co-factor bio-synthesis, electron donation and regulatory genes required for the synthesis and function of the enzyme.

4.2 PHOSPHATE SOLUBILIZATION

Phosphate, most important micro-nutrient after nitrogen have essential and key role in growth of plants, also have vital role in major metabolic processes like: photosynthesis, energy transfer, signal transduction, macromolecular biosynthesis and respiration (Khan et al., 2010). Phosphate is available in sufficient amount in organic and inorganic forms but unavailable for plants because it is in insoluble, immobilized and precipitated form (Pandey and Maheshwari, 2007). Investigation of Bhattacharyya and Jha (2012) claimed that plants could uptake phosphate only in two forms one is the monobasic (H_2PO_4) and the second one is dibasic (HPO_4^{2-}) form. Mechanism for phosphate solubilization by PGPR comprises (1) release of complex or mineral dissolving compounds e.g. organic acid anions, protons, phosphate mineralization and (2) the release of phosphate during substrate degradation (biological phosphate mineralization) (Sharma et al., 2013). There are various bacterial genera involved in phosphate solubilization some of them are: *Arthrobacter, Bacillus, Beijerinckia, Burkholderia, Enterobacter, Microbacterium, Pseudomonas, Erwinia, Rhizobium, Mesorhizobium, Flavobacterium, Rhodococcus* and *Serratia* (Parmar and Sindhu., 2013; Oteino et al., 2015; Tensingh and Lega, 2018). However, there are various scientific reports available which strongly recommends beneficial outputs of phosphate solubilizing bacteria while used alone or in combinatorial settings with other rhizospheric microbes (Zaidi et al., 2009).

4.3. SYNTHESIS OF PHYTO-HORMONES

Rhizospheric microbes are able to produce various growth regulating substances which govern development of plants also. PGPRs have the potential to synthesizing phyto-hormones like auxins, cytokinins, gibberellins and ethylene which could affect cell proliferation in the root architecture by overproduction of lateral roots and root hairs with a subsequent increase of nutrient and water uptake (Arora et al., 2013).

4.3.1. Role of Indole Acetic Acid (IAA) in Plant Growth And Development

Among all the phyto-hormones Indole Acetic Acid (IAA) is most common and most studied natural phyto-hormone found in plants (Miransari and Smith 2014). Most of rhizobacteria have the potential to synthesize indole acetic acid (IAA) colonized the seed or root surfaces is proposed to act in conjunction with endogenous IAA in plant to stimulate cell proliferation and enhance the host's uptake of minerals and nutrients from the soil (Vessey, 2003). IAA showed significant impact on cell division, extension, and differentiation; stimulates seed and tuber germination; stimulates the rate of xylem and root development; controls processes of vegetative growth; initiates lateral and adventitious root formation; mediates responses to light, gravity and florescence; affects photosynthesis, pigment formation, biosynthesis of various metabolites and resistance to stressful conditions (Spaepen et al., 2011). Root exudates contain tryptophan as most abundant amino-acid and identifies as the precursor molecule for synthesis of IAA in bacterial community (Etesami et al., 2009). This biosynthesis takes place via indole-3-pyruvic acid and indole-3-acetic aldehyde, the most common mechanism in the various sp. of microbial cultures like *Rhizobium*, *Agrobacterium*, *Pseudomonas*, *Enterobacter, Klebsiella,* and *Bradyrhizobium* (Shilev, 2013). Some free living PGPR strains such as *Alkaligenes faecalis, Enterobacter cloacae, Acetobacter dizotrophicous* and strains of *Azospirillum, Xanthomonas,* and *Pseudomonas sp.* reported with low level IAA release which helps in advancement of root development. However, phytohormones produced by microbes are more efficient due to the threshold stuck between inhibitory and stimulatory levels of produced hormones is low, while hormones released by microbial culture are more effectual due to their continuous slow release. These hormones have various functions and have big impact in the enlargement & expansion of plant as they also act as a signaling molecule (Fahad et al., 2015).

Numerous scientific reports confirmed the involvement of rhizobacteria in hormone synthesis. Reports of Omer et al. (2004) and Gupta et al. (2015) confirm the auxin production by PGPRs and also some reports confirm implication in plant microbes (Ahemad and Kibret 2014; Afzal et al., 2015). When plants have sufficient amount of IAA, effect of bacterial IAA may be of three type *i.e.* Neutral, Positive or Negative (Spaepen and Vanderleyden 2011). Auxin producing PGPRs that produce auxin have been shown to arouse transcriptional modification in hormone, defense-related and cell wall related genes (Spaepen et al., 2014) induce longer roots (Hong et al., 1991) enhancement of root biomass and reduction of stomatal size as well as density (Llorente et al., 2016) and stimulate auxin response genes that augment growth of plant (Ruzzi and Aroca 2015). Report of Kumar et al. (2015) explained that PGPRs also synthesize other phyto-hormones such as cytokinins and gibberellins but the role of hormones synthesized by bacteria and the mechanisms of their synthesis is still unclear (Garcia de Salamone et al., 2001; Kang et al., 2009).

4.4 BIO-CONTROL POTENTIAL OF PGPR

Biological control, which explain the decrease in the density of an inoculum or activity of disease production of a pathogen in its latent stage by one or few organisms accomplished logically or through manipulating the environment.

The four main mechanisms involved in the bio-control are: (i) the biological agent (antagonist), may resist the growth of other organism, (ii) antagonist may secrete metabolites (antibiotics) harmful to the pathogens (Antibiosis) e.g. Phenazine 1-carboxylic acid production (PCA) production by *P. fluorescens* plays a vital role in suppressing all the disease caused by foreign pathogen in wheat plant (iii) antagonist may compete with the pathogens for nutrients or space and in this way it suppresses the growth of the foreign pathogen (Competition) e.g. Pyroverdins which is a fluorescence iron chelator siderophore produced by *P. fluorescens* and (iv) may cause death of the parasite due to degradation of pathogens cell wall by secreting hydrolytic enzymes e.g. *Trichoderma viridae*. Recently, Fluorescent *Pseudomonads* strongly put its candidature for bio-control agent because of its ability to colonize the surfaces and internal tissues of roots and stems (endo and exorhizosphere) at high densities and production of anti-fungal secondary metabolites (Teja et al., 2019). Report of Feklistova and Maksimova (2008) enlisted more than 100 antibiotics and antibiotics like compounds from more than 20 *Pseudomonas sp*. Some well-known antibiotics are phenazine-1-carboxylic acid (PCA), phenazine-1-carboxamide (PCN), 2,4-diacetyl phloroglucinol, pyocyanin, 2-acetamidophenol, pyrrolinitrin, pyoluteorin, viscosinamide and tesin (Liu et al., 2007). Several bio-control strains are also known which can suppress the activity or growth of more than one pathogen. *Pseudomonas putida* produces phenazine and DAPG to suppress the growth of disease-causing pathogens in wheat plant (Pal and Gardener 2006). Some bacterial strains like *P. ceparcia, P. fluorescence, B. polymyxa* and *B. subtilis* used as bio-control agents against *Fusarium* wilt of melon (Hamed et al., 2009).

Conclusion

Over dependency on chemical fertilizers, herbicides, pesticides is not an advisable option as there is huge gap between crop production and supply of food and also subject to global concern. To overcome this issue, there is need to create awareness among all farmers about alternative approach for sustainable agriculture which not only have potential of bio-fertilizers but should be cost-effective. Use of Plant Growth Promoting Rhizobacteria (PGPRs) could be a promising and effective strategy as it is eco-friendly also. Plant growth promoting rhizobacteria not only enhance nutrient uptake ability of plants but also induce the synthesis of phyto-hormones and also secrete certain compounds which have potential to inhibit the growth of unwanted pathogens which can affect the growth of plant and ultimately affect crop yield. PGPR which have potential to induce plant growth factors and also lessen diseases in crops, would be an eco-friendly alternative. There are many studies on nitrogen and phosphate solubilization are going on, but there is need to explore research on potassium solubilization also as it is third major essential macro-nutrient for the growth of plants. It will help in exploration of various plant promoting aspects in PGPRs. These could be an excellent economical agricultural approach/model. As a general conclusion, we can say that many benefits have been reached with the application of bio-fertilizers in agriculture but many more opportunities need to be explored for the future sustainable agricultural developments. There is a huge need to commercialize and exploit the use of rhizospheric micro-flora *i.e.* PGPRs in a controlled manner and also flourish it's use as a key regulator in agricultural practices.

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BIOCHAR: A NOVEL APPROACH FOR WATER AND SOIL REMEDIATION

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Abstract

Biochar is a stable carbon-rich by-product synthesized through pyrolysis/carbonization of plant and animal based biomasses. Rising importance in the advantageous application of biochar has opened up multidisciplinary areas for science and engineering. The prospective biochar applications comprise carbon sequestration, soil fertility enhancement, pollution remediation, and farming by-product/waste recycling. The key parameters controlling its properties are temperature, rate of heating and the biomass used for its production. This review focuses on recent applications of biochars, produced from biomass pyrolysis (slow and fast), in water and wastewater treatment as well as its effects on soil fertility. Depending on the type of biochar used, heavy metal can be removed by different mechanisms such as complexation, physical sorption, precipitation and electrostatic interactions. Biochar for different biomass sources are used for removal of different contaminations (organic or inorganic) from a polluted water reserve. Biochar in the soil mixtures contributes to the physical nature of the system, affecting the depth, texture, structure, porosity and consistency which in turn affect the plant growth positively. Its applications are attracting significant attention as they offer cost-effective, feasible and environmentally sustainable solutions. Due to various potential uses of biochar, researchers believe that biochar will significantly gain more attention in the near future.

Key words: Pyrolysis, sequestration, remediation, complexation, sorption

1. Introduction

Biochar (*a form of ecological charcoal*) has been called "The Third Green Revolution" as it will allow the families of millions of urban and peri-urban dwellers to improve their daily food utilization by cultivating highly prolific vegetable gardens on tiny plots of land. Biochar is a carbon-rich organic material, obtained by the thermochemical conversion of biomass in an oxygen-limited environment (Masís-Meléndez et al., 2020). Biochar can be used as a product itself or as a component within blended produce, with a range of applications such as a means for soil improvement, enhanced resource use effectiveness, remediation and/or fortification against particular environmental contamination, and as a possibility for greenhouse gas (GHG) alleviation.

Biochar and activated carbon, both pyrogenic carbonaceous materials (PCM), are important products for environmental technology and intensively studied for a multitude of purposes. A strict distinction between these materials is not always possible, and also a generally accepted terminology is lacking. PCM is defined as "all materials that were produced by thermochemical conversion and contain some organic carbon" (Figure 1). (Lehmann and Joseph, 2015)

Char is a material that results from incomplete combustion of natural or anthropogenic origin and is sometimes used synonymously for natural *pyrogenic organic matter* (PyOM).

Black carbon may be of anthropogenic (combustion of fossil fuels—soot) or natural (vegetation fires) origin and is dispersed in the environment across the atmosphere, water bodies, soils and sediments.

Charcoal is defined as carbonized wood used mainly as fuel or as a reductant in industry, e.g., to reduce oxidized iron ores in iron and steel production.

Activated charcoal is defined as "any form of carbon capable of adsorption. (Hagemann et al., 2018).

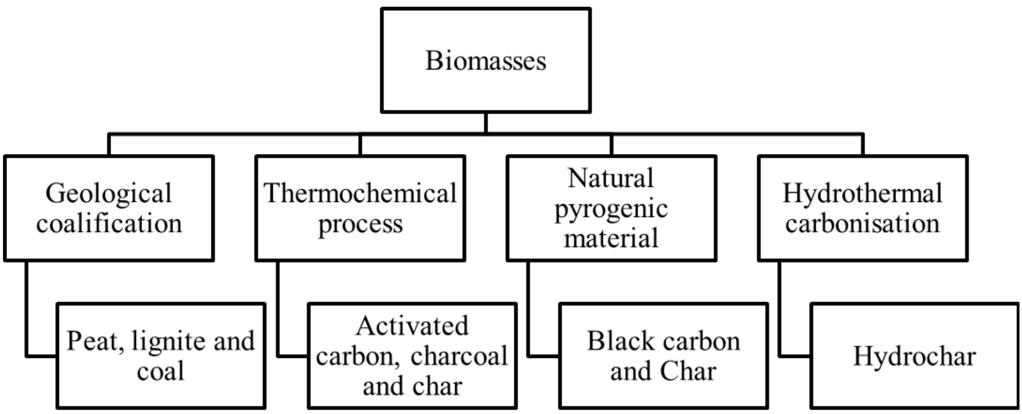

Figure 1. Production of various PCM through different processes

2. Production and properties of biochar

Biochar is produced by thermal decomposition of biomass in an oxygen- limited environment by a process called *pyrolysis*. Although, the properties of biochar are dependent upon the type of feedstock used and the process applied to yield biochar, but generally biochar is black, highly porous, and finely grained, with light weight and large surface area (Rawat et al., 2019). As compared to high- temperature pyrolysis low- temperature pyrolysis produces higher yield and enriched volatile matter composition. The slow pyrolysis is the most effective method for biochar production with a typical biochar yield of 35.0% from dry biomass weight (Figure 2). (Tomczyk et al., 2020).

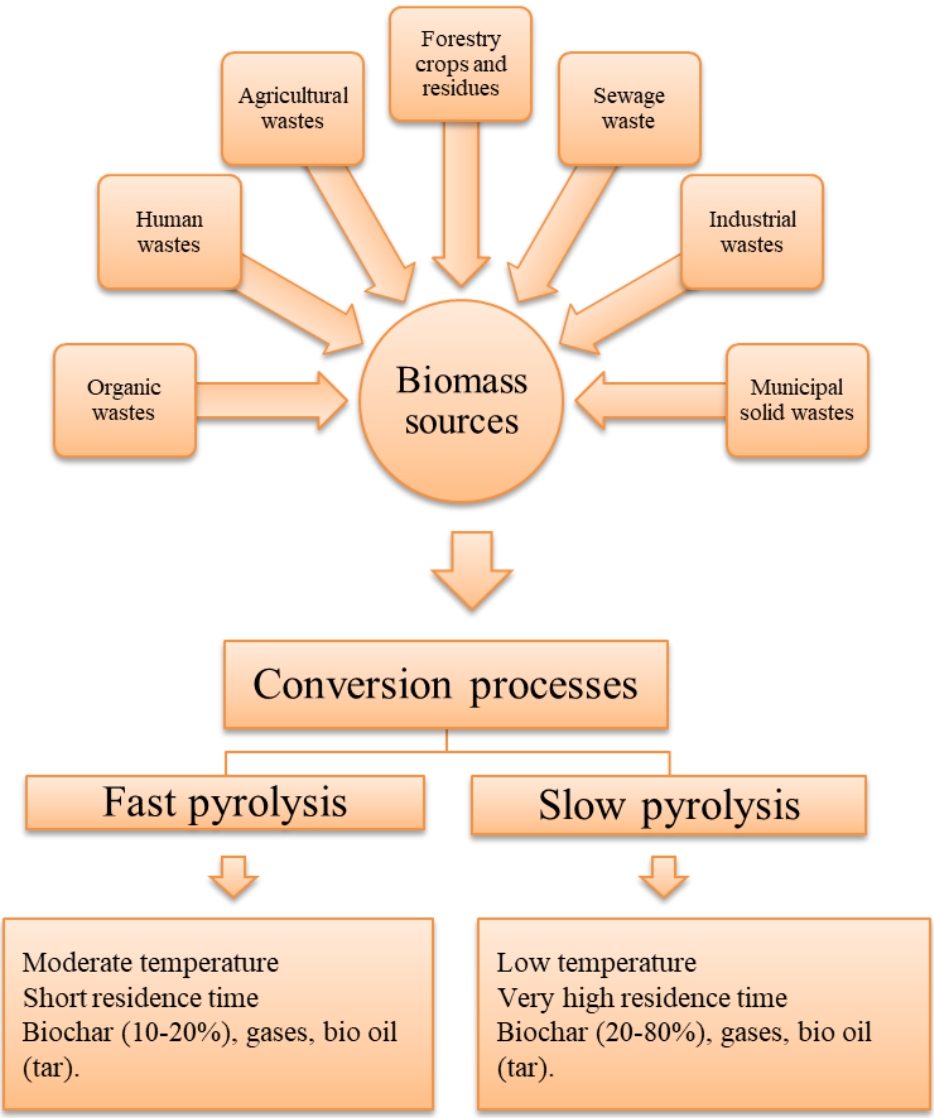

Figure 2.Biochar production from different biomasses (Rawat et al., 2019)

The properties of Biochar contribute to its function as a tool for managing the environment. The properties of biochar include (Figure 3):

1. *Stability*- The half-life of biochar is around 1,000 years, making it a stable compound. This property also contributes to carbon sequestration as biochar adds an inert carbon source in the soil.

2. *Surface Area*- Biochar has a very high specific surface area (SSA) of several hundred m^2g^{-1} to thousands m^2g^{-1} which usually tends to increase with increasing pyrolysis temperature. Biochars produced from animal litter and solid waste feedstocks exhibit lower surface areas compared to biochars produced from crop residue and wood biomass, even at higher pyrolysis temperatures (Ahmad et al., 2014)

3. *Cost- Effective*- Most of the biochar are prepared from waste materials hence, are inexpensive and thus may not require regeneration after being used as adsorbent.

Figure 3. Properties of biochar

4. pH- Almost all the biochars are usually alkaline, which is common for biochars prepared with dry- pyrolysis technology. It reduces soil acidity by increasing the pH (also called the liming effect) and helps the soil to retain nutrients and fertilizers. The pH of the biochar increases with increase in temperature and it's because high pyrolysis temperature increases the per cent of alkaline cations (Wang et al., 2015).

5. *Hydrophobicity*- Low-temperature biochars are strongly hydrophobic, which affects the water uptake by biochar, therefore affecting the water holding capacity of the biochar. Soil water retention capacity increases with an increase in organic carbon.

6. *Bulk Density*- Biochars have a bulk density of about 0.06- 0.7 g/cm^3. Low bulk density biochars are useful in amending compacted soils, thus helping in water management, aeration and increased root growth.

7. *Cation Exchange Property*- Biochar has the greater capacity to absorb cations per unit carbon as compared to soil organic matters because of its greater surface area and charge density. The extent of this cation exchange capacity (CEC) effectively increases at higher pH.

8. *Soluble and Mineralisable Carbon*- Biochars have water-soluble and mineralizable compounds, which act as food for microbes and stimulate seeds and plants for growth. Due to its high organic carbon content, biochar has the potential to serve as a soil conditioner to improve the physicochemical and biological properties of soils. It improves soil fertility by adding nutrients to the soil (such as K, some amount of P and many micronutrients) or retaining nutrients from other sources, including nutrients from the soil itself.

3. Biochar as a water remediating agent

Worldwide, nearly 600 million people lack access to clean drinking water especially in developing countries like India and Africa. Achieving the Sustainable Development Goal number 6 on ensuring availability and sustainable management of water and sanitation till the year 2030 is a major challenge. This calls for the identification of 'quick-win' water treatment methods, and their rapid translation into practical and economical solutions.

Using biochar is one such method which fulfils the criteria best for

- Low-cost capital and operating costs
- Ideal for adaptation to both, individual households, small and sparsely distributed households, and concentrated populations
- Require low technical skills to operate and maintain
- Function without electricity, which has narrow uptake of other reasonable solutions (e.g., electro-coagulation, reverse osmosis)
- Removed both microbial pathogens and the three alarming inorganic killers (arsenic, fluoride and uranium)
- Produce co-benefits contributing to addressing the simultaneous developmental issues including clean energy condition, food security and environmental quality.

Conventional affordable methods such as boiling, solar disinfection, slow sand filtration and ceramic filtration fail to meet these criteria in several respects (fail to remove dissolved toxic inorganic: fluoride, nitrate, uranium and arsenic; and organic contaminants: pesticides, pharmaceutical products). Similarly, membrane technology, chlorination and nano-technology relying on imported devices/reagents with high technical requirements are at best bridging solutions.

4. Application of biochar in water remediation

Depending upon the type of water contaminant and its source, different feedstock of biochar is used. The following flowchart (Figure 4) explains the division of biochar applications for water remediation.

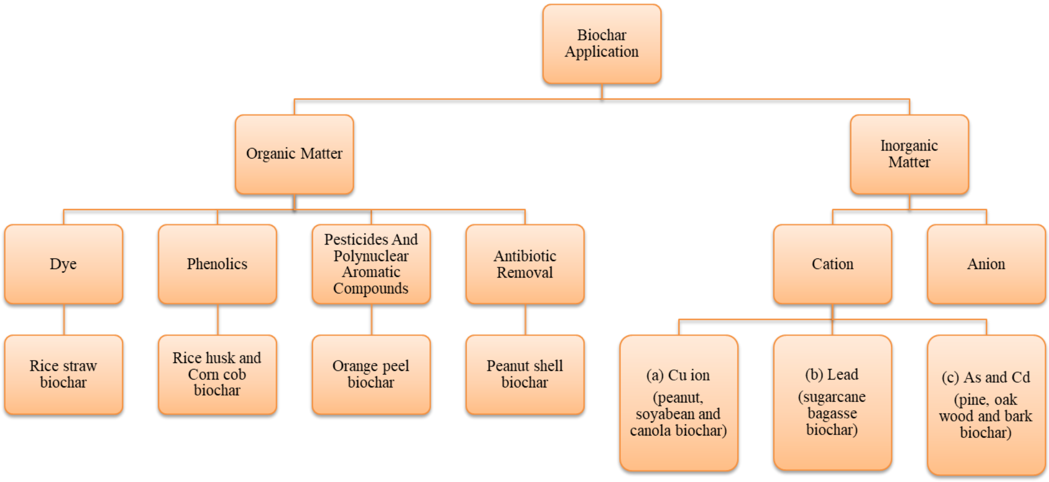

Figure 4. Detailed flow chart explaining applications of biochar

4.1. REMEDIATION FOR ORGANICS

Coloured dye generated from dye or textile industries contain toxic compounds acids, bases and dissolved solids, imparts visible colour which is stable to light oxidizing agents and resists aerobic digestion. Rhodamine B dye and Reactive brilliant Blue dye were removed by using biochar and activated carbon. It was found that due to the higher surface area and larger micropores in biochar than activated carbon the absorption of the dye was more in biochar. Adsorption via acid–base interaction and hydrogen bonding between phenol and the functional groups, extensive P–P interactions were proposed to explain the process (Liu et al., 2011). Naphthalene adsorption was controlled by surface coverage and partition whereas 1-naphthnol adsorption was controlled by the partition, surface coverage, and surface interactions (Mohan et al., 2014).

4.2. REMEDIATION FOR INORGANIC

Biochar has high sorption capacity for metallic contaminants because (Inyang, et al., 2016) of their surface heterogeneity. It has a high surface area with well-distributed pore network including, micropores (50nm), mesopores (2- 50nm), and macropores (>50nm). This high surface area and pore volumes have a high affinity for metals because metallic ions can be physically sorbed onto the char surface and retained within the pores. Negatively charged surfaces can adsorb positively charged metals through electrostatic attractions (Dong et al., 2011). Specific ligands and functional groups on biochars can also interact with various metals to form complexes or precipitates of their solid mineral phases (Figure 5).

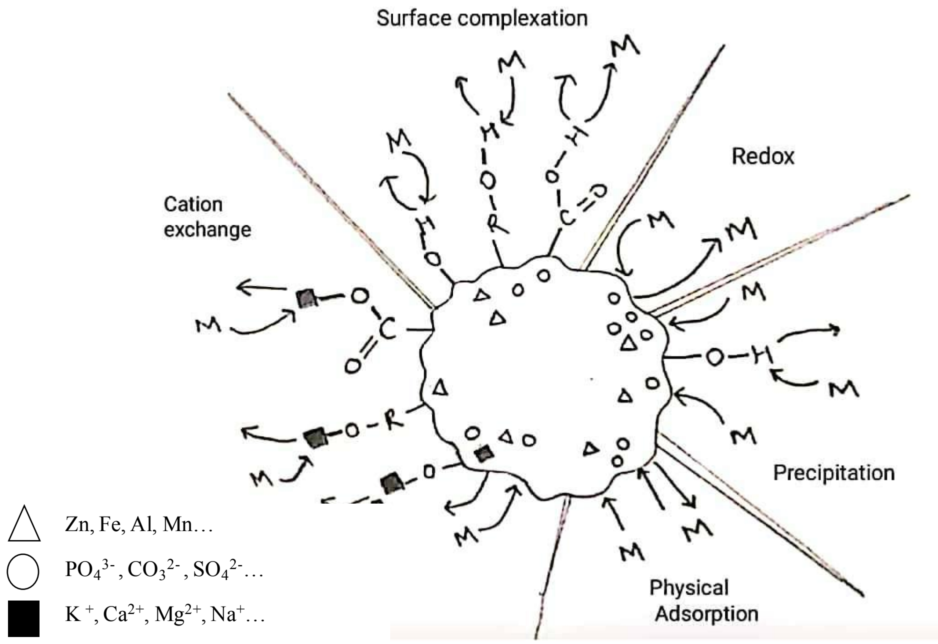

Figure 5 : The removal mechanism of heavy metals by biochars (reproduced from Li et al., 2017)

4.3. EFFECT OF BIOCHARS ON SOIL HEALTH

Research on Terra Preta soils in Amazonia has revealed the effects of biochar on the functionality of soils. This has also increased the quest amongst many researchers and farmers worldwide to pay attention to its hidden secrets (Ahmad et al., 2014). Biochar is known to affect the soil in the following ways:

(a) Significant increases in seed germination, plant growth, and crop yields have been reported in the soils amended with biochars. Biochar stimulates the activity of a variety of agriculturally important soil microorganisms thus enhancing crop yields.

(b) The porous structure of biochar, its high internal surface area and its ability to adsorb soluble organic matter, gases and inorganic nutrients provide a highly suitable habitat for microbes to colonize, grow and reproduce.

(c) The pore size disparity observed across biochar particles from different feedstocks and pyrolysis conditions, such that the micro-flora could colonize and be protected from grazing, especially in the minor pores.

(d) The high porosity of biochar also allows it to retain more moisture. In addition to water, a variety of gases, including carbon dioxide and oxygen, are dissolved in pore water which occupies the air-filled pore space or chemisorbed onto biochar surfaces.

(e) Adding biochar to soil, whether acidic or alkaline, leads to significant changes in the soil community composition by changing the overall ratio of bacteria to fungi, as well as the predominance of different genera within these populations.

(f) The presence of biochar in soil enhances the adsorption of DOC, inorganic nutrients, various gases, as well as potentially toxic compounds, such as pesticides, heavy metals and toxic secondary metabolites, all of which can influence the abundance, diversity and activity of soil organisms.

(g) For free-living diazotrophs, the fine pores of biochar create a habitat where reduced oxygen tensions are likely. The low nitrogen content of most biochars and the exchange of ammonium ions between the biochar surface and soil solution modifies nitrogen availability to plant roots and stimulates nodulation and nitrogen fixation in legumes and actinorhizal plants.

(h) Biochar particles act as a microhabitat for AM fungi and enable them to survive, and may also provide protection from predator grazing competition. Facilitative interactions could be altered in the presence of biochar or as a consequence of effects on physio-chemical soil properties.

(i) Biochar may prove a most efficient inoculant delivery system and may also improve outcomes of bioremediation efforts by increased sorption of organic pollutants onto biochar impregnated with bacteria selected for their capacity to degrade the target pollutants.

(j) Biochar has been used as a carrier substrate for both rhizobia and AM fungi over the past 20+ years with excellent accomplishment.

(k) Serves as a habitat for extra- radial hyphae that sporulated in micropores due to lower antagonism from saprophytes and therefore can serve as an inoculum for AM fungi.

(l) Biochar pores possibly will act as a refuge site or micro-habitat for colonizing microbes, where they are secluded from being grazed upon by their natural predators or where microbes are less aggressive in the soil environment.

4.4. IMPLEMENTATION IN INDIA

In India, UZH (University of Zurich) in collaboration with GKVK (Gandhi Krishi Vigyana Kendra) College of Agriculture and the Indian Institute of Science (IISc), Bengaluru has been working on Biochar for over 12 years. Biogeochemist Samuel Abiven’s team’s field trial is ongoing in the town of Mandya, Karnataka. The current availability of biomass in India (2010-2011) is estimated at about 500 million metric tons/year. Studies sponsored by the Ministry of New and Renewable Energy; Govt. of India have estimated surplus biomass availability at about 120–150 million metric tons/annum. Biochar having high pH value can be a good remedy for acidic soil amelioration. North-East India has the potentiality of producing 37 million tons of agricultural waste biomass. If only 1% of this biomass is converted to biochar, about74 thousand tons of carbon can be sequestered annually. Out of this, if 1% of the process of producing biochar is carried out through modern equipments, about 1300 and 900 tons of bio-oil and biogas can be produced, respectively which is equivalent to 31 terra joules of energy.

Furthermore, charcoal is inefficiently produced in the earth-mound kiln releasing a considerable amount of methane emissions. Therefore, the establishments of the commercialization chain of highly-efficient biochar-making cookstoves, diffusion of improved small-scale kilns, pyrolysis of agricultural residues that are burnt otherwise, offer an opportunity to enhance the living conditions of rural families, counteract deforestation, defend biodiversity, augment crop production, improve agricultural waste management and eradicate carbon from the atmosphere as a carbon-negative strategy.

5. Conclusions and future recommendation

This review provides an overview of definitions of biochar and the distinction of biochar, activated carbon and other pyrogenic forms. Biochar has the potential to remediate soil and water contaminated with various organic/inorganic contaminants. Studies have demonstrated the biochar capability to serve as a green environmental sorbent. However, one type of biochar may not be appropriate for all contaminant’s removal. A number of variables are involved in determining the exact role of biochar for environmental management. Pyrolysis condition and feedstock type are the main factors influencing biochars sorption behaviour. Converting waste biomass into biochar will also promise an effective solution for the safe and beneficial disposal of a number of materials. The complex nature of soil systems compared to aquatic systems has limited biochar applications to the soil. Biochar reveals the potential to contribute to resolving economic, public health and environmental problems that are widespread and need to be overcome. Biochar research mostly focuses on the pyrolysis process, its applications and characteristics. In addition, biochar production technologies offer completely new business area and opportunities. However, the field is lacking economic and market- based research, and there is limited activity or capacity anywhere in the world for the technological evaluation of biochar production. Biochar market is emerging gradually and there is a strong need for further research, which will increase both the knowledge in the field and the rate of adoption while decreasing the uncertainties.

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BIOREMEDIATION OF HEAVY METALS: A STEP TOWARDS ENVIRONMENTAL SUSTAINABILITY

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Abstract

Environmental pollution is a serious issue faced by the present world. Due to lack of waste management, industrial effluents are directly disposed into rivers. Among all pollutants, heavy metals are amongst dangerous ones because of their adverse effects on mankind. Water pollution by heavy metals has become a global issue that needs considerable attention to combat its harmful effects. Since industrialization, human intervention has been increasingly affecting our environment. The common heavy metals that have been identified in polluted water include arsenic, lead, mercury, chromium and cadmium. Persistence and biomagnification of these metals in nature present a significant threat to public health and safety. The danger of heavy metal pollutants in water lies in two categories. Firstly, heavy metals can persist in natural ecosystems for an extended period. Secondly, they can accumulate in successive levels of biological chain, thereby causing cardiovascular, central nervous system, renal, endocrinological, reproductive, neurological, developmental and immunological disorders. Removal of heavy metal contaminants from wastewater using microorganisms like algae, fungi or bacteria has a great potential. The process of abatement of heavy metals with the help of bioremediators like algae is known as phycoremediation. It is a clean-green technology which is an easy, safe and economical solution. In this chapter, adverse effects of the heavy metals on human health and remediation of heavy metals with the help of microalgae have been discussed in detail.

Keywords: Bioremediation, Heavy Metals, Mechanism, Phycoremediation, Health Hazards, Abiotic and Biotic factors.

1. Introduction

Rapid industrialization, as well as urbanization, leads to the increased rate of consumption of heavy metals and subsequently their accumulation into the ecosystems. Keeping its economic importance aside, it has been proved as major agent causing a detrimental effect on the environment and human health (Hansda et al., 2014). Sources of heavy metal are both natural and anthropogenic. Naturally, they enter the ecosystem through minerals weathering, volcanic eruption, etc. Anthropogenic activities such as waste effluent of industries like tanneries, batteries, dyes, electroplating, smelting, mining, fertilizers, fungicidal sprays, metal plating, painting, car radiator manufacturing, etc. (Wuana and Okieimen, 2011). These industries release their waste into rivers without proper treatment which is hazardous to humans as they use this water for drinking, for agricultural purposes. (Gupta et al., 2018). Industries release heavy metals like lead, arsenic, mercury, cadmium, chromium, copper, nickel. Out of these arsenic, mercury, cadmium, and lead are the most hazardous (Padil and Rao, 2011). Heavy metals are non-biodegradable in nature. In India due to lack of treatment plants, effluents are directly released into the water bodies which is creating environmental havoc and posing deleterious effect on human health. They cause acute and chronic intoxications affecting the central nervous system, renal, endocrinological, reproductive, neurological, developmental and immunological systems, premature birth and reduced birth weights (Jomova and Valko, 2011).

Heavy metals are natural materials that are present on earth's crust and soil. They have a relatively high density as compared to water (Lombi et al., 2001). Earlier, it was considered that heavy metals can’t be fully removed from environment and only converted into the less-toxic form. There are some heavy metals which are important in biological reaction which are known as micronutrients or trace elements like copper, lead, selenium, iron, etc. (WHO, 1996).

For the abatement of heavy metals from environment, various traditional, as well as novel approaches have been devised and applied. Traditional approaches like chemical precipitation, redox reactions, solvent extraction, ion exchange and reverse osmosis are used. However, these techniques are ineffective and expensive. They don’t show the complete abatement of heavy metals (Padil and Rao, 2011). To overcome this, biological methods have been tested to be more efficient, economical, effective and sustainable than conventional methods. Removal of heavy metals by using bio-remediators like algae, fungi, etc. is known as bioremediation. This chapter covers different types of heavy metals and their detrimental effects on the environment and human health. The bioremediation mechanisms that include biosorption and bioaccumulation have been discussed. Also, the parameters that affect the abatement process efficacy, as well as the recent development in phycoremediation, have been presented.

2. Heavy Metals and Toxicity

Heavy metals affect the biochemical pathways of cellular organelles like mitochondria, endoplasmic reticulum, and nucleus, etc. (Aryal and Liakopoulou-kyriakides, 2015). Five highly toxic heavy metals are: arsenic, cadmium, chromium, lead and mercury as they accumulate in their stable oxidation state. Then, they react with biological system and make the stable toxins which can’t be easily separated (Kulshreshtha et al., 2014). According to the United States Environmental Protection Agency (USEPA, 2002), these are systematic toxic compounds which lead to multi-organ dysfunction.

2.1. ARSENIC

It is a trace element. It finds its application in formulations of several pesticides and medicines. It is present in our diet naturally and doesn’t have any hazardous effect when taking less than 5 µg/dL (Bräuner et al., 2014). Arsenic regulatory limit (EPA) for drinking water is 0.01ppm (Dixit et al., 2015). In nature, it is found in 3 allotropic forms which are black, metallic grey &

yellow. It occurs in organic as well as inorganic form. The latter form is very harmful as compared to the former one. When arsenic is present with hydrocarbons, it is known as organic arsenic. On the other hand, when it is present with oxygen, chlorine or sulphur, it is known as inorganic arsenic. Generally, it is seen that most of the acute heavy metal diseases are caused due to this heavy metal. These diseases are observed in children as well as in adults (Flora, 2012). It is not identified in food products as it is odorless and colorless. Due to this, it is considered to be the most toxic and risky heavy metal because it can't be diagnosed. Thakur stated its deleterious effects, some of them are as follows; keratosis, leuco-melanosis, hemolysis, skin cancer, etc. (Parmar and Thakur, 2013). It also affects the bioenergetics of microorganisms like in oxidative phosphorylation.. Many respiratory diseases that are caused due to arsenic are listed by Mazumder and Dasgupta (2011) which are lung cancer, liver fibrosis, gastroenteritis, etc. Microalgae used for the remediation of arsenic is *Cladophora* species (Jasrotia et al., 2014).

Table 1: Microalgae used for the abatement of arsenic

Microalgae strain	**Removal efficiency (%)**	**Mechanism**	**Reference**
Cladophora sp.	100	Biosorption	(Jasrotia et al., 2014)
Eichhornia crassipes, Spirodela polyrhiza, Lemna minor	0.04	Detoxification	(Singh et al., 2016)

2.2. CADMIUM

It has properties like high ductility, malleability and shining which are the main reasons that they are frequently used in many industries. Industries like alloys, batteries, etc. widely used this heavy metal (Llewellyn, 1994). In most of the cases it is seen that oxidation number of Cd is +2. Cadmium shows its toxicity through lungs, skin, and intestines in human beings. This heavy metal is exposed through cigarettes, contaminated land by cadmium, metal industries and mining (Paschal et al., 2000). It is present in many food products like grains, leafy vegetables, seeds, etc. (Satarug et al., 2003). Mostly they get accumulated inside the kidneys and liver. It is carcinogenic, which mainly causes prostate and renal cancer (Dixit et al., 2015). It causes diseases like itai-itai, osteomalacia, and osteoporosis (Baba et al., 2013). Its toxicity is measured in blood and urine (Jarup 1998). Its limit is 5.00 ppm according to EPA (Dixit et al., 2015). The microalgal strain used to remove cadmium are *Dunaliela, Amphora coffeaeformis, Nannochloropsis salina, Scenedesmus quadricauda, Chitosan algal biomass* and *Cladophora fracta* (Sayed et al., 2019).

Table 2: Microalgae used for the remediation of cadmium

Microalgae strain	**Removal efficiency (%)**	**Mechanism**	**Reference**
Cladophora fracta	78	Biosorption	(Bulgariu and Bulgariu, 2016)
Chlorella minutissima	74	Adsorption	(Yang et al., 2015)
Chitosan algal biomass	37	Adsorbent	(Sargin et al., 2016)
Dunaliela	74-95	Biosorption	(Anastopoulos and Kyzas, 2015)
Osmundea pinnatifida	75	Biosorption	(Anastopoulos and Kyzas, 2015)

2.3. CHROMIUM

It is the seventeenth most abundant element (Bhalerao and Sharma, 2015). They are present in the environment through sources like industrial effluent of leather, dyes, metal processing, pigment, stainless steel welding, weathering of the rocks which have chromium, etc. (Khatri and Tyagi, 2015). Chromium is present in the environment in three forms mainly which are Cr(0) the most stable one, Cr(III), and Cr(VI) (Bhalerao and Sharma, 2015). Hexavalent form is the most toxic form of chromium which occurs in chromate, dichromate and chromium trioxide. Workers who work in these industries are at high risk of adapting diseases. Its detrimental effects are mostly due to the inhalation or through skin (Costa, 1997) . It's toxicity is seen in multiple ways like asthma, renal damage, cancer, etc. (WHO 1996). It is carcinogenic (Pellerin and Booker, 2000). It's toxicity results in gastrointestinal, respiratory, cardiovascular, neurological, renal disorders, etc. (Pellerin and Booker, 2000). In animals, chromium is an important essential micronutrient as it is necessary for the protein, fat or glucose metabolism. EPA regulatory limit for chromium is 0.10 ppm (Dixit et al., 2015). Most prominent microalgal strain used to biotransform the chromium are *Chlorella miniate, Scenedesmus quadricauda and Nannochloropsis salina* (Torres et al., 2017; Anastopoulos and Kyzas, 2015).

Table 3: Microalgal strains used for the chromium removal

Microalgae strain	**Removal Efficiency (%)**	**Mechanism**	**References**
Spirulina maxima	77	Biosorption	(Singh et al., 2016)
Chitosan algal biomass	68	Adsorbent	(Sargin, Arslan, and Kaya, 2016)
Chlorella miniata	85	Biosorption	(Anastopoulos and Kyzas, 2015)
Ulva lactuca	60-86	Biosorption	(Anastopoulos and Kyzas, 2015)

2.4. LEAD

Lead is a naturally occurring bluish-grey metal present in small amounts on the earth's crust. It is highly ductile, malleable, soft, and has low melting point. Due to these physicochemical properties, it is widely used in industries like paint, plastics, automobiles, etc. (Branvall et al., 1999). Naturally lead is present in environment due to the activities like mining, combustion of fossils etc. Industries like batteries, metal, devise to shield x-ray deposit Pb (lead) into the ecosystem (Guberman, 2017). This heavy metal is exposed to humans through inhalation of dust particles or lead contaminated food (Guberman, 2017). EPA limit for lead is 15.00 ppm (Dixit et al., 2015). Lead mainly affects children (Kumar and Clark, 2009). It has a detrimental effect on kidney, bone, nervous, reproductive, cardiovascular system, etc. Maximum amount of lead accumulation occurs in kidney, then liver, heart or brain. If it is deposited in high amount, it can give fatal results such as paralysis, delirium, convulsions. Early symptoms are head-ache, irritation, restlessness, loss of memory (ATSDR 2019). If a pregnant lady is exposed to lead, it can be transferred to the fetus (Ong et al., 1985). Acute deposition leads to kidney, brain and gastrointestinal diseases. Whereas chronic exposure has fatal effects (ATSDR 2019). *Cystoseira stricta, Sargassu myriocystum, Chlorella sp., Anabaena oryzae, Cyanosarcina fontana, Nannochloropsis salina,* etc. are the algal strains used for the bioremediation of lead (Sayed et al., 2019).

Table 4: Microalgal strains used for the lead removal are mentioned below:

Microalgae strain	**Removal efficiency (%)**	**Mechanism**	**Reference**
Cystoseira stricta	10	Biosorption	(Iddou et al., 2011)
Sargassu myriocystum	87	Biosorption	(Anastopoulos and Kyzas, 2015)

2.5. MERCURY

Naturally mercury gets accumulated into the environment through volcanic activities. It is found in organic (most hazardous), inorganic and vapor state (elemental form) (Clarkson et al., 2003). It is used in industries like paints, cosmetics, batteries, electrical industries, etc. In pharmaceuticals, it is used in thermometers, barometer, dental amalgams, nuclear reactor, etc. (Patrick 2002). Exposure to mercury can occur in many ways, it can be accidental, agricultural or through food which is contaminated by mercury (Dopp et al., 2004). All states of mercury are toxic. Organic and elemental forms are more toxic as they can easily bypass the placental barrier and blood-brain barrier. Thus, gets deposited inside kidney (Patrick, 2002) and brain (Clarkson et al., 2003). It affects the body in different ways such as memory loss, hair loss, loss of vision and many autoimmune diseases (Dixit et al., 2015). It has detrimental effects on Central Nervous System (CNS) as it is a neurotoxin, not only this, it affects the muscle, speech, hearing, lungs, severe changes in tissues, etc. (Bhan and Sarkar, 2005). According to the United States Environmental Protection Agency (USEPA), limit for mercury in drinking water is 2 ppm (Dixit et al., 2015). Microalgal strains used for the abatement of mercury are *Ulva lactuca, Jania rubens, and Sphaerococcus coronopifolius* (Anastopoulos and Kyzas, 2015).

Table 5. Microalgae used in the removal of mercury

Microalgae strain	**Removal Efficiency (%)**	**Mechanism**	**Reference**
Ulva lactuca	60-86	Biosorption	(Anastopoulos and Kyzas, 2015)
Jania rubens	54-71	Biosorption	(Anastopoulos and Kyzas, 2015)
Sphaerococcus coronopifolius	70-90	Biosorption	(Anastopoulos and Kyzas, 2015)

3. Phycoremediation Mechanism for Heavy Metals

Phycoremediation is a green-clean technique in which remediation of pollutants is carried out with the help of algae. Algae are found in fresh as well as marine water. It is an economical process. By treating the waste, one can get a dual product that is treated water and biomass. This biomass can be further used to produce biofuels, bioplastic, and several other platform chemicals etc. Mechanism showed by the algae for abatement of heavy metal is biosorption and bioaccumulation. For the remediation process live as well as dead biomass can be used (Monteiro et al., 2012). Biosorption and Bioaccumulation differ in their metabolic requirements.

3.1. BIOSORPTION

It is a physical and chemical process in which abatement of hazardous compounds is carried out with the help of various mechanisms such as adsorption, absorption, ion exchange, complexation, and precipitation. Heavy metals are remediated with the help of algae by forming ionic as well as covalent bonds (Zeraatkar et al., 2016).

They can abate organic or inorganic pollutants. Biosorption occurs due to the presence of different functional groups such as thiol, hydroxyl, carboxylic or phosphate. These groups are present on the membrane surface. Due to which algae are considered to be the potential candidate for remediation. These groups impart a negative charge on the algae surface (Sayed et al., 2019). Metals which are not stable (mobile), can't be bioaccumulated so, biosorption is the only mechanism for abatement of such pollutants (Aksu, 2005).

Biosorption is an energy-dependent as well as energy-independent process. There are two types of biosorbents used (living and non-living biomass). The former one is energy-dependent whereas the latter one shows energy-independent mechanism. According to the scientists, remediation using dead biomass is an economical process. As it doesn't require any energy or food for its maintenance (Vijayaraghavan and Yun, 2008). Biosorption is the dominant process in bioremediators as compared to the bioaccumulation (Furey et al., 2017). Different mechanisms responsible for the biosorption are as follows:

3.1.1. Adsorption

It is a process in which pollutants adhered to the surface of remediator due to the presence of various functional groups. It is an energy-independent process.

3.1.2. Absorption

In this, pollutant is transported into the cell. It comprises of two steps:

- Adsorption of the pollutant.
- Transportation of the pollutant into the cell. (It is an energy-dependent process) (Fulekar and Singh 2010).

3.1.3. Precipitation

In this, algae secretes some compounds in the defense which favors the precipitation reaction (Fulekar and Singh 2010).

3.1.4. *Surface Complexation*

Heavy metals react with the functional groups which are present on the algal surface and form a complex. Remediators secrete organic acids in the defense which helps in the formation of the metallo-organic complexes (Srivastava and Goyal, 2010)

3.1.5. *Ion Exchange*

As discussed above, functional groups (counter ions) are present on the surface, which help in exchange of the bivalent metal ions (Srivastava and Goyal, 2010).

3.2. BIOACCUMULATION

Bioaccumulation is the process in which toxins are accumulated into the living cells. It is an energy dependent process. These toxins when accumulated, they inhibit various cell processes, which result in the inhibition of their growth (Mantzorou et al., 2018). In this process first, adsorption of the pollutant occurs, it then enters through the outer membrane and gets deposited inside the cell or various organelles such as vacuoles (Perales-vela et al., 2006). Due to the bioaccumulation, bioremediators release various chemicals under such stressed conditions, which favor precipitation and decrease the toxicity of the pollutants (Juang and Chang, 2016). It is a sustainable technology. Phycoremediation depends mainly upon biosorption and bioaccumulation. Although biosorption is dominant over bioaccumulation but there are pollutants like dyes, pesticides and many heavy metals (lead, arsenic) which are remediated by using bioaccumulation process only (Gadd, 1992).

4. Factors Affecting Heavy Metal Remediation

There are many abiotic and biotic factors which affect the heavy metal abatement process as well as growth of the biomass. However, algae have its own defense mechanism against toxins that influence the remediation process but many other factors affect the process. These factors are discussed below:

4.1. ABIOTIC FACTORS

4.1.1. pH

The remediation process is mostly influenced by the pH. Algae have functional groups on their surface which are negative, so to maintain that charge on the surface of algae, it requires acidic pH. It affects the solubility of metals in wastewater. It is seen that at higher p^H remediation process slows down. Thus, for quick abatement, it is important to determine the optimum pH. Hargraves and Whitton stated that 3.5 to 4 is optimum pH for the *Hormidium* species (Hargreaves and Whitton, 1976). Extreme pH hinders the remediation process as it affects the binding of a ligand to the cell surface (Volesky, 2001). Cesium biosorption is optimum at pH 4 (Jalali-rad et al., 2004). If pH is highly acidic, it can be controlled by pumping CO_2 in the media (Zeraatkar et al., 2016).

4.1.2. Ionic Strength

It is stated by Dwivedi that increase in ionic strength decreases the remediation process (Dwivedi, 2012). The presences of monovalent cations increase the ionic strength. This, in turn, reduces the abatement capacity of algae (Mehta and Gaur, 2005).

4.1.3. Temperature

Temperature affects the growth of algae and the remediation process (Chairat and Bremner, 2016). John (1988) observed that chemical reactions are also affected by temperature. Khan studied that increase in temperature, will increase the remediation process of heavy metals (Khan et al., 2012). It's explanation is given by Bayes et al., (2012) that it leads to the increase in number of active sites; reducing the diffusion boundary thickness; which in turn reduces the mass transfer resistance. Temperature has overall less effect as compared to pH (Lau et al., 2010).

4.1.4. Hardness and Salinity

It is observed that hardness and metal toxicity have an inverse relationship. It is seen in the case of cadmium, copper, mercury and zinc (Wang, 1987**.** Wilde and Benemann stated that salinity and remediation are inversely proportional (Wilde and Benemann, 1993). It is observed that for every metal, the salinity has a different effect like for cadmium it is observed that 2.5% is optimum and 20% for copper (Rebhun and Amotz, 1986). Several studies are seen which state that remediation is fast when salinity increases (Wang, 1987).

4.1.5. Effect of Counter Ions

Ions present in the medium influence the growth rate of algae and the remediation rate. Qiwie stated that *Aphanocapsa* remediation rate for cadmium increases with an increase in the concentration of nitrate ion (Qiwei et al., 2016).

4.1.6. Phytohormones

Due to the presence of these phytohormones, algae respond in stress conditions. These phytohormones (auxins, cytokinin, gibberellin, etc.) are responsible for the defense action (Asgher et al., 2016).

4.2. BIOTIC FACTORS:

4.2.1. *Species:*

Different species have different remediation effect due to the presence of different functional groups on algae. Due to the difference in species, same genus of algae may have different heavy metal remediation efficiency (González et al., 2011).

4.2.2. Tolerance Capacity

Arunakumara stated that heavy metals affect the oxidative balance of algae (Arunakumara and Xuecheng 2008). Its tolerance depends upon its defense action against the oxidative damage (Hu et al., 2001).

4.2.3. Biomass Concentration

It is seen that with the increase in biomass concentration, remediation of heavy metal increases. This happens because the number of active sites available for heavy metals increases (Monteiro et al., 2012). Beside this, it is stated by Esposito that growth above threshold level may have a negative effect on remediation process as their will be a reduction in the metal binding per unit cell (Esposito et al., 2001).

4.2.4. *Size of Microalgae*

The size and age of bioremediators are considered to be an important parameter for remediation. Hein stated that small algae show higher growth as their photosynthetic rates are higher, thus show fast remediation (Hein et al., 1995). Khoshmanesh et al., (1997) reported that small algae have a large surface to volume ratio, so show better remediation.

5. Recent Developments

Development in the field of bioremediation is rapidly increasing like the use of nanoparticles, immobilized biomass, non-living biomass or transgenic microbes tasked with specific remediation purpose. The application of these have been carried out by various scientists in the sequestration of heavy metals from the environment. These are very effective techniques but more studies should be carried out for the complete remediation of heavy metals.

5.1. NANOPARTICLE

When the size of any particle is reduced from bulk to nanoscale (10^{-9}), there is a change in its physical, chemical, mechanical, optical properties, etc. This occurs because of the high surface to volume ratio. Use of these nanoparticles in remediation enhances the rate of abatement. Remediation increases due to the high surface to volume ratio because the number of active sites available for heavy metals increases (Fulekar and Singh, 2010). Superparamagnetic iron oxide nanoparticles (i.e. SPION) used for the remediation of heavy metals showed increased heavy metal removal from the targeted system (Mody et al., 2010). Many advancements have been made during recent years to transform the heavy metals by using nanoparticles but more research is needed to carried out in the future for the complete transformation of the heavy metals.

5.2. DEAD BIOMASS

Remediation using non-living biomass is one of the best approaches. It does not require nutrient media, so provides an economic advantage as compared to living biomass based remediation mechanisms. Also, metal toxicity has no effect on it. This method is very cost-effective. One can use leftover dead biomass of industries for the remediation process. No energy is required for the maintenance of cell as it is a metabolically independent process (Monteiro et al., 2012)

5.3. TRANSGENICS

To enhance the remediation process, scientists uses the transgenic technology. Many genes are altered using this technique to develop an economical method of remediation. Main aim is to decontaminate the metals from wastewater or land quickly. Metal binding activity is increased by 5 fold by using this technique in the study exercised by Rajamani et al., (2007). This technique is very effective but there is more need to explore for the complete remediation of metals.

5.4. IMMOBILIZED ALGAE

Immobilization is carried out in bioremediation, as it is a cost-effective process. One can re-use the biomass. It includes the adsorption, entrapment, encapsulation and covalent binding. It is an efficient technique but still, more has to be discovered in the field of bioremediation (Hameed and Ebrahim 2007)

6. Conclusion

Industries like tanneries, batteries, dyes, electroplating, etc. release their untreated effluent into rivers. Their effluent consists of heavy metals like arsenic, lead, mercury, cadmium, chromium, etc. Industrial effluent containing these heavy metals has detrimental effects not only towards aquatic life but towards the human as well as to the environment. So, to overcome this problem, modern remediation techniques are carried out which are economical and show complete removal of heavy metals from the targeted environment. Algae show two mechanisms biosorption and bioaccumulation for the remediation of heavy metals. Biosorption is more advantageous over bioaccumulation. Bioremediation can be carried out by using dead as well as living algal biomass. There are many abiotic and biotic factors that affect process efficacy. Biotic factors like species, tolerance capacity, biomass concentration, and size of microalgae affects the process whereas abiotic factors like pH, temperature, counter ions, salinity, hardness, ionic strength and role of phytohormones have been studied. In the end, recent developments like transgenic, nanoparticles, immobilization and non-living biomass are discussed to improve the remediation process. It is suggested to move towards the clean-green technology sustainably by combining the treatment of wastewater by using algae and then the biomass produced can be used to make products like biodiesel, biohydrogen, bioplastics, etc. By using this approach, dual advantage in terms of cost-effective removal of heavy metals from effluents as well as feedstocks for extraction of several products can be achieved.

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BIOREMEDIATION AS A TOOL FOR THE TREATMENT OF EXPLOSIVE CONTAMINATED ENVIRONMENT

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Abstract

The nitro aromatic compound 2,4,6-trinitrotoluene (TNT) is highly explosive and is produced on a massive scale for use in military and industrial applications. Through many years of production and use of this explosive, large quantity of toxic waste has been generated, which has resulted in extensive contamination of soil and water. TNT is a xenobiotic compound, as it is recalcitrant in nature and not normally found in the environment. High concentration of TNT in environment poses serious threat to human health due to its toxic nature. Therefore, it is essential to treat this chemical before entry into the environment. The various physical and chemical methods for the remediation of TNT contaminated sites are expensive and has negative effect on the environment. Phytoremediation and microbial remediation hold a potential for treating TNT in an environmentally sound manner.

1. Introduction

Our environment is composed of atmosphere, earth, water and space and the life on earth depends on air, water and soil. But we are deteriorating our environment with activities including industrialization, construction and transportation. Although these activities are desirable for human development and welfare, they also leads to generation and release of objectionable materials into the environment thus turning it into unsuitable and thereby disturbing our ecosystem. Defense activities are unavoidable for the security of the nation. Whilst often overlooked as a cause of environmental degradation, these activities are also significant contributors of environmental pollution. Military activities related to manufacturing of explosives and their usage in related processes viz, loading, assembly, packing, firing and training leads to contamination by these explosives and their by-products. Awareness of harmful effects of explosives has increased in the recent past. The physical and chemical methods used for the treatment of explosives are expensive and sometimes results in the formation of toxic byproducts. On the other hand, biotreatment is highly efficient, environment friendly, cost effective way of removing the explosives from the environment using plants and microbes.

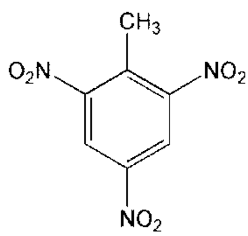
1.1 EXPLOSIVES

Explosives are the chemicals which produce large amount of energy on initiation. Shock waves which are produced on initiation are due to expanded gases, which exert high pressure and cause destruction. Explosives contain oxygen and nitrogen mixtures, which lead to the formation of the gaseous products typically carbon dioxide, carbon monoxide, oxygen, nitrogen and water vapour. The heat and expanding gases released in an explosion can incinerate and smash nearby objects. Mass production of these explosives in the last century during the World Wars led to extensive contamination of soil and water, which need remediation.

1.2 NITROAROMATICS

Nitroaromatics are stable compounds, which contain an aromatic ring and one or, more nitro groups. TNT is a nitroaromatic explosive with three nitro groups; produced by sequential nitration of toluene, resulting in the formation of mono-, di- and tri-nitrotoluene (Lewis et al., 2004).

Table 1.1: Chemical and physical properties of TNT

CHARACTERISTIC	**INFORMATION**	**REFERENCE**
IUPAC Name	2-Methyl-1,3,5-trinitrotoluene	HSDB, 2012
Molecular formula	$C_7H_5N_3O_6$	Budavari et al., 1989
Structure of TNT		Hawley, 1987
Molecular weight	227.13 g/mol	Budavari et al., 1989
Color	Yellow	Budavari et al., 1989
Solubility in Water at 20˚ C	130 mg/L	HSDB, 2012
Boiling point	240˚ C (explodes)	HSDB, 2012
Melting point	80˚ C	Budavari et al., 1989
Specific gravity	1.654	HSDB, 2012
Vapour pressure at 20˚C (mm Hg)	1.99×10^{-4}	HSDB, 2012

TNT was first synthesized by the German chemist Joseph Wilbrand in 1863; however, it was not used as an explosive until 1891.The various physical and chemical properties of TNT are given in Table 1.1. The π electrons of its benzene ring are drawn away by the resonance of electron withdrawing nitro groups resulting in an electron deficient, highly stable ring structure (Qasim et al., 2007). The nitro groups also contribute a strong oxidizing power, which makes TNT highly toxic to living organisms. This toxicity, combined with its widespread use and recalcitrance to degradation make TNT a priority target for remediation.

TNT manufacturing began in United States in 1916 and was produced in enormous quantity for use in military amunitions during World War I and World War II. Process of TNT manufacturing often generates significant quantities of explosive-contaminated waste-waters. Waste produced during TNT manufacture contains the by-products 2,6-dinitrotoluene and 2,4-dinitrotoluene (2,6-DNT and 2,4-DNT). The contaminated waste-water from the manufacturing plants pollutes the surrounding soil, surface water and ground water.

1.3 TOXICITY OF TNT

TNT toxicity is long lasting, sites that are inactive since World war II still exhibits TNT contamination of more than 1,000 mg/Kg. TNT manufacturing operation during World War I caused toxicity of TNT to humans that was documented in the 20th century with more than 17,000 cases of TNT poisoning (ATSDR 1995; Bodeau 1993). TNT is also inhibitory to plant growth (Pennington et al., 1995). Liver necrosis and aplastic anemia can be significant health effects due to inhalation of dust and ingestion of TNT particulates (ATSDR 1995, HSDB 2012). TNT has been classified as class C carcinogen i.e. possible human carcinogen. The aqueous wastes, known as red water which is produced during TNT manufacture contained up to 30 nitro aromatics besides TNT (Urbanski, 1985). Toluene is the precursor reagent used for manufacturing explosives and can itself present a soil and water contamination risk. The drains may also contain explosive residues which can be a source of ground water contamination (Bulloch et al., 2001) Nitric and sulphuric acids used in TNT manufacturing processes are likely to be retained in the soil rendering it acidic. TNT is classified as an environmental hazard because of it toxic and explosive nature. Effects of TNT on human health are reported to include liver damage and anemia in workers engaged in large scale manufacturing. TNT has been shown to cause liver, blood, immune system and reproductive damage in animals (EPA 2005).

1.4 TREATMENT METHODS OF TNT

Conventional treatment technologies based on physical and chemical methods (Table 1.2) for treating the explosives contaminated waste water and soil require further follow-up process as they merely transfer the contaminant from one phase to another. There is an urgent need to develop sustainable technologies which can minimize the environmental foot prints of a clean-up process. Techniques using the abilities of living organisms to treat hazardous contaminants present in the environment emerge as a sustainable alternative to conventional waste management strategies.

1.5 BIOREMEDIATION

Bioremediation is the use of microorganism and plants to break down or degrade toxic chemical compounds that have accumulated in the environment. Hence the catalytic abilities of living organisms are exploited to increase the rate or extent of pollutant destruction. Bioremediation can be of two types i.e. Phytoremediation and Microbial remediation

Table 1.2: Various treatment methods of TNT

TECHNIQUES	ADVANTAGES	LIMITATIONS
PHYSICAL METHODS:		
Granular activated carbon Open burning/ Open detonation/ Incineration	Can be used for ground water as well as for waste water	Carbon generation and air emissions
CHEMICAL METHODS:		
Alkaline hydrolysis AOP	Can be used for treatment of waste water	Cost is high
BIOLOGICAL METHODS:		
Phyto remediation Microbial remediation	Can be used for waste water and soil, ecofriendly, sustainable	Relatively slow

1.5.1 Phytoremediation

Phytoremediation is defined as use of green plants to cleanup contaminants from soil and water. The term “Phyto” comes from Greek word for plants, and “remediation” comes from Latin word “remedium” which means restoring balance. Phytoremediation mainly targets heavy metals, metalloids, petroleum hydrocarbons, pesticides, explosives, chlorinated solvents, and industrial by-products. Techniques of Phytoremediation includes: phytoextraction, phytostabilization, phytotransformation, phytostimulation, phytovolatization and rhizofiltration.

1.5.2 Microbial Remediation

Microbial remediation or Bioremediation is the use of microorganism to degrade or transform recalcitrant molecules to less or non-toxic compounds. According to Philip et al., (2000) microbial remediation is defined as “cleanup of pollution from soil, ground water, surface water and air, using biological, usually microbiological processes”.

Microorganisms are very important in microbial remediation process because of their extraordinary metabolic diversity. Various other factors also play a major role in the complex process including:

- Ambient environmental conditions
- Composition of the microbial community
- Nature and amount of pollutant present

The use of specific bacteria to bioremediate can be a much eco-friendlier method compared to physico-chemical methods. By selecting the native bacterial species capable of degrading the contaminant of interest, characterized, and by providing optimal conditions, the biodegradation is accomplished. The organisms themselves or the enzymes produced by them can be used for bioremediation.

2. Literature review on microbial treatment of tnt in waste-water and soil

Microorganisms have been used for decades to treat recalcitrant environmental contaminants. The potential advantages of these biological treatment include low cost, ease of operation and public acceptance (Rodgers and Bunce, 2001). Exploiting the abilities of adapted microbial community for treating waste contaminants is an effective approach than using pure cultures for bioremediation. The importance of promoting the growth of naturally occurring microbial consortia to degrade contaminants is better than selecting or engineering specific strains as the latter usually lack survivability in the field. Therefore, Bio augmentation is considered as a potential bioremediation technique wherein a consortium of micro-organisms with specific degradative properties are added to the contaminated environment to enhance degradation (Kuiper et al., 2004).

A native microbial consortium isolated from a high molecular weight poly aromatic hydro-carbon contaminated coke industry site was found to have potential for degrading pyrene, fluroanthene and benzo [a] pyrene (Sun et al., 2010). Microbial consortium consisting of adapted microbial species from a soil site which was polluted with 1,2,4-tri chloro benzene (TCB) for more than 25 years was found to degrade TCB (Wang et al., 2007). Studies on degradation evaluation of two widely used pesticide chemicals viz., atrazine and alachlor by selective microbial consortia from an actual contaminated site revealed that the degradation of alachlor depends on the initial degradation of atrazine and the half-life of atrazine and alachlor degradation were found to be 7.5 and 11 days respectively. Five strains were identified in the pesticide contaminated samples by fatty acids methyl ester (FAME) analysis and were found to have similarity indexes above 70% (Chirnside et al., 2007).

The transformation and degradation of TNT by microorganisms has also been well researched and documented (Lewis et al., 1996; Won et al., 1974; Kalderis et al., 2011). In an endeavor to harness the astonishing abilities of adapted native microflora which has developed the inherent abilities to live in contaminated environmental media, an attempt has been made to isolate and characterize them from the contaminated soil and water environment of a TNT manufacturing facility. Site characterization with respect to extent and type of explosive contamination of the selected TNT manufacturing facility was also carried out as it is essential to conduct a thorough site characterization of the environment before taking up any waste treatment/on-site remediation technology.

Utilization of natural microbial agents to transform TNT into innocuous compounds is considered as more economical and innovative treatment option. Biodegradation of TNT contaminated waste-water has been evaluated both in free culture and in immobilized state. In a study by Claus et al., (2007), free cells of a bacterial isolate *Routella terrigena* strain HB originating from a contaminated former explosive production site, were found to remove TNT completely from contaminated waters (10 and 100 mg/l) under optimum aerobic conditions within 7 days of incubation. Immobilized micro-organisms were found to degrade TNT effectively

(97.5%) in aqueous solution (Wang et al., 2010). Ullah et al., (2010) reported the biodegradation of TNT from water by immobilized B*acillus sp*. Bacteria isolated from the red effluent introduced on charcoal and polystyrene in free as well as in immobilized form. Immobilized cells were found to show 96% of TNT reduction.

Montgomery et al., (2013) compared the incorporation and mineralization of TNT by natural assemblages from a small estuary and stated that one fate of aromatic organic carbon metabolized by bacteria is incorporation into bacterial macromolecules another fate is mineralization to CO_2 and respired for energy. Biodegradation of TNT in soil was reported by a variety of native and nonnative microbes. For instance, native free bacterial cell cultures such as *Delftia tsuruhatensis* (Hooda et al., 2013), *Psedomonas aeruginosa* (Oh et al., 2003) were reported to cause biotransformation of TNT in soil. A soil slurry and soil column reactors were compared for their efficiency in degrading TNT contaminated soil. Percent reduction in TNT was found to be 50 and 60 in a duration of 15 days and 60 days respectively for soil column and soil slurry reactor respectively (Park et al., 2003).

Anaerobic degradation of TNT was studied in a soil slurry reactor under sulfate and nitrate reducing conditions using enrichment cultures developed from a TNT contaminated soil from the Louisiana Army Ammunition Plant (LAAP) in Minden, USA. Sulfate reducing conditions were found to have better degradation efficiency than nitrate reducing conditions. The metabolic analysis showed complete mineralization of TNT with acetic acid, CO_2 and ammonia as end products (Boopathy et al., 2014).

3. Conclusion

Due to various defense activities and explosive manufacturing facility, TNT contamination in soil and water is a widespread problem, which requires the development of green technology at an urgent basis. Physical and chemical methods of treatment used (Granular activated Carbon, Incineration, Alkaline hydrolysis, AOP etc.) so far have been expensive and also caused environmental problems by transferring explosives from one phase to other. To overcome this contamination problem the need of the hour is to evolve green technology. Green techniques like phytoremediation and microbial remediation are emerging as a technology to overcome the problem of TNT contamination in soil and water.

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PHYTOREMEDIATION: A METHOD TO REMEDIATE SOIL HEAVY METALS USING PLANTS

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Abstract

Heavy metals accumulate in the water bodies and soil as a result of human activities like mining and industrial processes. This accumulation poses a threat to the environment and human life, especially once the heavy metals enter the food chain; they cause serious harm due to biomagnifications. The traditional chemical and physical methods used to remediate the heavy metals are tedious and require time and efforts. Hence, the focus has shifted on the use of biological methods such as phytoremediation. It's a natural, ecofriendly, affordable, and effective procedure in which plants remediate the soil by lowering the concentration of metals in water and soil. However, conventional phytoremediation techniques have certain disadvantages which make them unsustainable on an industrial scale. Therefore, effective ways to use phytoremediation should be found to decrease the rising heavy metal concentration in the soil. Using these advancements on a wider scale can cause successful elimination of metals from soil. This review discusses an overview of different techniques of phytoremediation and the different methods that enhance phytoremediation for better soil treatment.

1. Introduction

The term "heavy metal" refers to the elements with high atomic mass and high densities. Cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), mercury (Hg) and zinc (Zn) are some examples of heavy metals. These elements can be toxic at a high concentration, causing various problems in the ecosystem. Due to their non-biodegradable nature, they easily accumulate in living beings through the method of biomagnification, showing dangerous effects at higher levels on the food chain. Other hazardous effects of heavy metals are inhibition of growth of plants and disruption of the soil's microflora (Roy et al., 2005). Therefore, there is a requirement of an efficient method which can resolve this problem.

Table 1: Heavy metals sources

Heavy Metals	Atomic Mass (in u)	Atomic Density (in g/cm^3)	Sources	Negative Impacts
Arsenic	74.9216	5.727	Wood preservatives, pesticides.	"Pins and Needles" in hands and feet, encephalopathy, bloody and watery diarrhea, detrimental to oxidative phosphorylation and ATP synthesis in cells
Cadmium	112.411	8.69	Paints, pigments, electroplating, phosphate fertilizers, plastic stabilizers, cadmium containing plastic incineration	Disrupts metabolism of Ca, carcinogenic, mutagenic, induces anemia and hypercalciuria
Chromium	51.9961	7.19	Steel industries, tanneries, fly ash	Digestive issues, rashes, organ damage in kidney and liver, lung cancer, alteration of genetic material
Copper	63.546	8.92	Pesticides, fertilizers, sewage sludge	Hair and skin discoloration, irritation of upper respiratory tract, nausea, flu symptoms
Mercury	200.59	13.534	Medical Waste, byproduct of silver and gold mining, coal combustion	Mitochondrial activity interference, disruption of membrane lipids in plants. Induces insomnia, drowsiness, tremors, carcinogenic in humans
Nickel	58.6934	8.908	Automobile batteries, kitchen appliances, steel alloys, surgical instruments, industrial waste	Multiple organ damage, carcinogenic, hormonal issues, eventual infertility, cause cardiovascular and musculoskeletal defects in newborns.
Lead	207.2	11.34	Aerial emissions from lead petrol, herbicides, insecticides, battery manufacture.	Chlorosis, reduced seed germination, growth retardation, oxidative stress and abnormal morphology in plants. Memory loss, coordination problems, retardation, and foot drop palsy in humans.

2. Phytoremediation: A Green Alternative to Remediate Heavy Metals

Phytoremediation uses plants and related microbes to lower the harmful effects of potential pollutants in soil (Greipsson, 2011). The term "phytoremediation" comprises of two words: "*phyto"* (Greek, meaning "plants") and "*remedium"* (Latin, meaning "removal or correction of an evil"). This technique effectively remediates any heavy metals, organic compounds and metalloids present inside soil. Phytoremediation is comparatively a new technique and it is an environment-friendly, economical approach which uses solar energy to remediate heavy metals unlike the other chemical and physical remediation techniques such as soil washing, adsorption, soil incineration, membrane filtration, ion exchange, biosorption etc. (Ali et al., 2013). The idea about phytoremediation (as phytoextraction) was first given by Chaney in 1983. It's a clean and green technique in which plants take up the pollutants from wastewater or soil without causing damage to the top soil. They conserve the practical use of top soil and make the soil more fertile by providing organic matter in the soil (Mench et al., 2009). Phytoremediation can be performed easily in a large field area whereas the other remediation techniques cannot be practically performed in such a space and are also expensive (Garbisu and Alkorta, 2003).

Heavy metals are taken up by the plants according to the bioavailability of metals and various other plant nutrients in soil. This bioavailability depends on various factors like weather, the plant species, structure of root, root zone and other biological, chemical and physical characteristics of soil (Yadav et al., 2018). Concentration gradient of different non-essential and essential elements present in soil contributes to the difference in their uptake by the plants, since only a few selective ions enter inside plants via diffusion (Peralta-Videa et al., 2009). Roots of plants are involved in the adsorption of cationic forms since pectin, glycoproteins and cellulose, main components of a plant's cell walls, have ion-exchanging capacity and can exchange specific metallic ions (Arif et al., 2016). Different heavy metals enter inside the plants via special and highly specific transporters present inside them. These include: Copper transporter (CTR) family, Natural Resistance-Associated Macrophage Protein (NRAMP) family and Zinc Iron Protein (ZIP) family. The NRAMP family is accountable for the movement of Cadmium, Copper, Iron, Nickel and Zinc in the roots (Krämer et al., 2007; Nevo and Nelson, 2006). The ZIP family is accountable for the accumulation of heavy metals such as manganese (Mn), iron (Fe) and zinc (Zn) inside the plants (Guerinot et al., 2000). The CTR family specifically accumulates copper, nickel, cobalt and various other metals (Li et al., 2013; Chakravarty et al., 2017). Metals concentrate inside the root tissues, i.e. phytoimmobilization. Another way heavy metal accumulate is by moving towards the shoots (translocation) via apoplastic and /or symplastic pathways where they are deposited inside the vacuoles.

According to an economic perspective, phytoremediation is important due to the following reasons:

1. Phytoextraction of metals like gold, nickel, have high market value.
2. Immobilization of heavy metals inside soil, so they are less harmful to the environment.
3. Enhancement of soil quality so that plants of higher market value can be grown on that land.

Plants follow different methods to make the environment free of heavy metals. They are divided into six different techniques discussed in the section below (Fig 1.).

3. Phytoremediation Techniques

3.1. PHYTOEXTRACTION

Phytoextraction is a process wherein heavy metals inside soil or waste water enter inside plant roots and move towards the harvestable biomass i.e. shoots, where they accumulate (Rafati et al., 2011). This technique is also referred to as phytoaccumulation. The movement (translocation) of metals to shoots via the roots is necessary since it is difficult to harvest the root biomass. Several plants can hyperaccumulate metals i.e. when heavy metals such as chromium, copper, nickel and zinc and some radionuclides have concentration greater than 0.1% dry weight (DW) inside the plant tissue (in case of cadmium, it's 0.01%) (Susarla et al., 2002). Limit of hyperaccumulation for manganese and iron is more than 1% DW. While performing hyperaccumulation, some plants can remove a significant amount of metals available in the soil. The most efficient technique to make the polluted soils free of metalloids or heavy metals is phytoextraction. Its effectiveness can further be enhanced by raising the heavy metal bioavailability inside the soil, by varying the properties of soil and by expanding the sink capability of the particular plant species (Sarwar et al., 2017). Phytoextraction can also permanently remediate heavy metals by harvesting and detaching the shoots, after plants achieve optimum growth and they accumulate maximum amount of metals (Jabeen et al., 2009). It's the major remediation technique, and involves five important steps:

a) Movement of metals in water samples and soil

b) Metal ions enter inside plant roots (uptake)

c) Metal ions move towards the shoot (aerial plant parts)

d) Accumulation (aggregation) of heavy metals in the tissues of plants

e) Tolerance/resistance mechanism of these heavy metals

The tolerance mechanism of plants involves the biosynthesis of :- Metallothioneins (Sharma et al., 2016); Ferritins (Ding et al., 2018); Phytochelatins (Emamverdian et al., 2015) and highly reactive antioxidative enzymes like glutathione S-transferase, ascorbate peroxidase, superoxide dismutase, glutathione reductase, proline and catalase (Bauddh et al., 2015; Bauddh et al., 2012; Ni et al., 2013 ; Shanmugaraj et al., 2013).These techniques improve resistance of the plants and increase the deposition of such metals inside the plants even at high concentration level (Abdelsalam et al., 2019).

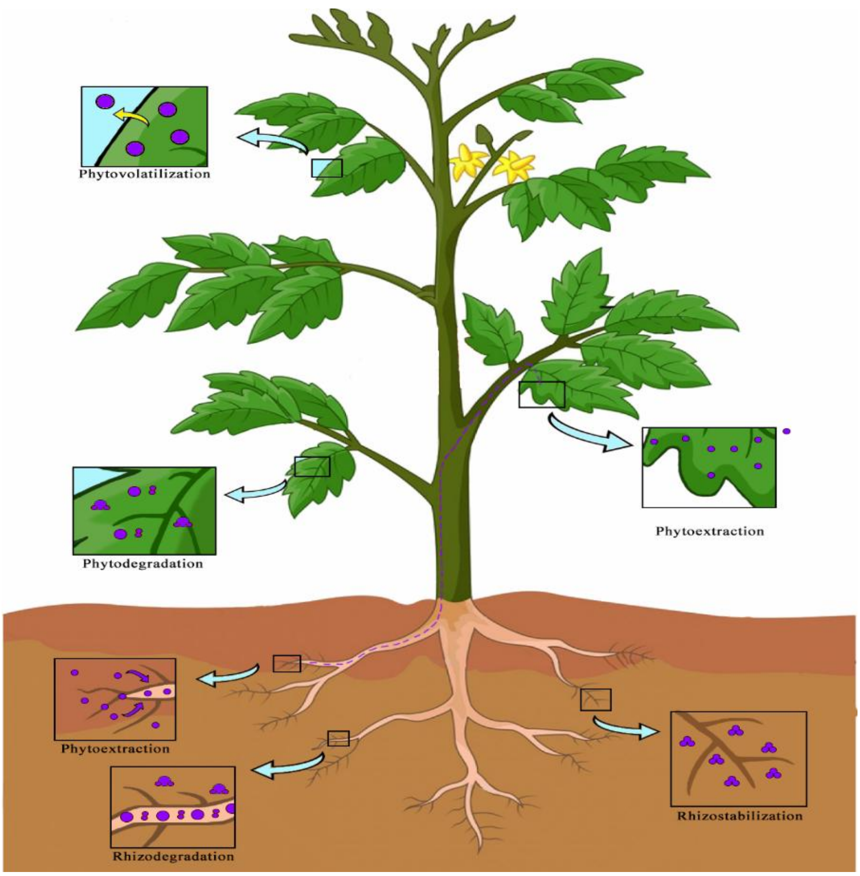

Figure 1: Different types of phytoremediation techniques

3.2. PHYTOSTABILIZATION

The technique by which the bioavailability and movement of heavy metals inside soil decreases is known as phytostabilization. It does not let heavy metals seep into groundwater or enter the food chain. Heavy metals get immobilized by roots of plants inside soil by different mechanisms including complexation, metal sorption via roots, reduction of valency of metals inside rhizosphere or precipitation (Yoon et al., 2006; Wuana and Okieimen, 2011; Ghosh and Singh, 2005). Therefore, this technique is also called phytoimmobilization. Metals having different valences have different levels of toxicity. Plants release unique redox enzymes which efficiently convert toxic metals to non-toxic form and hence reduce the harmful effects caused by the metals. This technique minimizes amount of metals present in the atmosphere. However, it is comparatively less effective since these metals are immobilized in soil and just their mobility is restricted. It's an effective technique for inactivation of potentially harmful pollutants.

3.3. PHYTOVOLATILIZATION

In the phytovolatilization method, heavy metals enter into plants (uptake) from soil and convert into a non-toxic volatile (elemental) form. After this, the volatile form is released in the air (Cristaldi et al., 2017). In this technique, pollutants are absorbed through roots and move via xylem vessels and undergo certain metabolic changes by which they get converted into the less harmful form and are released into atmosphere via the leaves (aerial plant parts) through transpiration. Metals also diffuse through the non-aerial parts like stem before reaching the shoots and leaves. Only some metals like Selenium (Se), Mercury (Hg) and Arsenic (As) which have high volatility in comparison to other metals (Van Oosten and Maggio, 2015) can be removed by phytovolatilization. However, phytovolatilization is a questionable technique since metals can pollute the air and be resettled in the soil after a period.

3.4. PHYTODEGRADATION

Phytodegradation is a process by which the pollutants are accumulated and degraded in plant tissues through various metabolic pathways using plant enzymes and this technique is independent of rhizospheric microorganisms (Ali et al., 2013; Susarla et al., 2002 ; Vishnoi and Srivastava, 2008). However, this technique cannot breakdown heavy metals since they are non-biodegradable. Various plant enzymes used for phytoremediation are:

a) Peroxidases – for the breakdown of phenolic compounds.

b) Dehalogenase – for the conversion of chlorinated compounds.

c) Nitroreductase – for the transformation of nitrogen containing compounds and explosives.

d) Phosphatase- for the breakdown of organophosphate pesticides.

e) Nitrilase – for conversion of cyanate aromatic compounds.

Research has been conducted on the phytodegradation of several organic pollutants in soil such as synthetic insecticides, herbicides, chlorinated compounds and other inorganic pollutants.

Transgenic plants are being tested for degradation of specific organic contaminants (Yadav et al., 2018).

3.5. RHIZOFILTRATION

Rhizofiltration is a subset of phytofiltration technique which is based on the elimination of heavy metal from polluted water samples. The remediation of heavy metals occur by the roots via either adsorption or absorption (Jeevanantham et al., 2019). Other techniques of phytofiltration involve blastofiltration (removal by seedlings) or caulofiltration (removal by excised plant shoots). Precipitation and sequestration of these metals occur simultaneously when they absorb into or adsorb onto the roots.

An ideal plant that is used for rhizofiltration should have the following characteristics:-

1) It should have roots that grow quickly and should produce a large amount of biomass (root)
2) It tolerates high target metal concentration
3) Easy to handle , readily available and inexpensive plant
4) It shows growth when submerged in water
5) It doesn't give rise to secondary waste products which require disposal.

Rhizofiltration is an efficient and cost-effective technique to remediate wastewater and ground water having low metal concentration (Lee, 2013). Rhizofiltration is mainly used to remediate radionuclide polluted water containing Strontium (Sr), Caesium (Cs) and Uranium (U) (Yadav et al., 2018).

3.6. RHIZODEGRADATION

Rhizodegradation is a process through which organic contaminants inside rhizosphere are broken down (Mukhopadhyay and Maiti, 2010). Rhizosphere is the area of soil (about 1 mm) near the plant roots. The rhizosphere contains various soil microbes. The major reason for the degeneration of contaminants is the rapid growth and high activity of microorganisms. Plants can trigger about 10-100 folds greater microbial activity in rhizosphere by releasing exudates through roots of plants including carbohydrates, flavonoids, amino acids etc. These exudates serve as nitrogen and carbon sources which promote the multiplication of rhizospheric microorganisms. Rhizospheric microbes also produce several chelating agents like biosurfactants, siderophores, acids such as oxalic, gluconic and citric acid, which are important for mobility and conversion of these metals (Rajkumar et al., 2012). Plants also release various enzymes which can breakdown organic contaminants. The increased microbial activity and plant enzymes released into the rhizosphere cause an enhanced breakdown of rhizosphere pollutants. This technique cannot be utilized for heavy metals since they are non-biodegradable.

Table 2: Advantages and disadvantages of Phytoremediation (Jeevanantham et al., 2019)

Technique of Phytoremediation	Advantages	Disadvantages
1. Phytoextraction	• Reuse of pollutant can be done in some cases • This technique is more cost effective as compared to other techniques • There is a reduction in the waste material to be discarded by 95% • Heavy metals are completely removed from the soil	• Metals are taken up by the roots at a slow rate • Certain amount of metal gets concentrated inside roots of the plant
2.Phytostabilization	• Best suited for use when immobilization of heavy metals is necessary for saving soil and ground water • Transfer of risky biomass or materials is not essential	• Use of soil revisions or broad treatment • Checking is obligatory • Heavy metals and other contaminants are not removed from the soil
3. Phtovolatilization	• Heavy metal gets conveted into a non-toxic form (eg mercury)	• Heavy metals released in the air can come back to the soil and water bodies via precipitation
4. Phytodegradation	• Eco-friendly and cost-effective technique	• Productivity is higher after more than one season • Ground water should be 10 feet inside of ground and soil should be 3 feet outside and inside of the surface • The degraded materials are permanently removed when the plants are taken up by animals and microbes • This technique cannot be used for heavy metals
5. Rhizofiltration	• The translocation of pollutants to the shoots does not occur • Both oceanic and earthy plants can be used for both ex situ and in situ applications	• Collection and transfer of plants takes place • pH needs to be changed regularly • The growth of plants should be done in a nursery prior to application
6. Rhizodegradation	• Mineralization of the pollutants can occur at the end • More significant for in situ applications • Set up and maintenance cost is low	• The movement of roots is restricted because of soil's physical structure • Broad Root zone advancement is needed which is time consuming • Cannot be applied to heavy metals since they are non-biodegradable

4. Potential Usage of Plants for Phytoremediation

4.1. AQUATIC PLANTS

World Health Organization (WHO) has set the global standard for drinking water to have arsenic (As). However, the groundwater table in the Indian subcontinent, among other regions, has arsenic concentration much higher than the standardized level. Phytoremediation can efficiently tackle the increased concentration of heavy metals in water, with the help of several emergent aquatic plants. These species have been both studied and tested for their potential in decontaminating the water containing arsenic and to identify whether they could be natural As accumulators. *Hydrilla verticillata* was one such aquatic plant that held potential for remediation (Srivastava et al., 2011). Robinson et al., (2006) studied over twenty-eight different species collected from Taupo River, New Zealand, for their potential. *Myriophyllum propinaquum, Ceratophyllum demersum, Lemna gibba* (Mkandawire and Dudel, 2005), and *Elodea canadensis* are all aquatic plants that have shown potential as hyperaccumulators of As. In particular, aquatic macrophytes, when used in succession, do greater heavy metal removal than these plants independently. In an investigation, *Ceratophyllum, Lemna* and *Hydrilla* were tested to remove As and it was found that these plants were able to remove arsenic from water samples (Poonam et al., 2017). The study reported that the plants removed as much as 27% of the arsenic present in the sample. In another study, Srivastava et al., (2014) took samples of five different aquatic plants and planted them in several combinations for 30 days. In this time period, pairs were tested to remediate 4 L of arsenic solution (2500 ug L21). The results yielded that the combination of *Ceratophyllum* and *Lemna* remediated maximum amount of As from the solution in 30 days compared to the other plant combination pairs. Scientists also noted that the plants used in pairs remediate the soil better than single plant samples. There is ample evidence to suggest that aquatic plants hold great potential as potent hyperaccumulators to remediate soil and wastewater.

4.2. TERRESTRIAL PLANTS

Terrestrial plants have great application in metal uptake, soil remediation and can greatly improve the efficiency of translocation of metals. As excellent hyperaccumulators, terrestrial plants exhibit a great capacity for tolerating the high toxicity of these metals. There are two unique ways by which the uptake of heavy metals occurs: Active and Passive. Passive uptake is the uptake through apoplast whilst active uptake is the uptake through symplast (Zhao et al., 2010). Translocation occurs after the uptake; the heavy metals travel throughout the other parts of the plant from the roots. Multiple potential accumulators have been identified through various studies conducted. *Pteris vittata* is a famous example, with the capacity to accumulate up to 20 mg of heavy metal within its system (Ma et al., 2001).

5. Techniques to Enhance Phytoremediation

5.1. CHELATING AGENTS ASSISTED PHYTOREMEDIATION

Chelating agents, specifically Ethylene diamine tetraacetic Acid (EDTA), have been immensely researched and thus have shown great potential in enhancing a plant species' uptake of heavy metal (Bareen 2012). The efficacy of a plant's ability to perform phytoremediation is influenced by factors such as the presence of heavy metals, and how easily the plants can access these pollutants. If these factors are low, chelating agents can increase the heavy metal's absorption and solubility capabilities, thereby enhancing the plant's intake capacity.

When EDTA is introduced, it enters the soil solution and forms a complex with metals present, making it easier for the plant to absorb (Lasat et al., 2002). Studies by Lesage et al., report that the usage of EDTA can increase the heavy metal concentration of the soil by 5 mg/kg (Lesage et al., 2005). Once it enters the plant, EDTA is transported through the plant through its apoplastic pathway. By changing the heavy metal's route in the plant from symplastic to apoplastic, it makes the transport process easier and faster (Nowack et al., 2006).

There are some noted negative effects in using EDTA to enhance a plant's phytoremediation capability. The increased accumulation of heavy metals might leak into the water table. The chelating agents also interfere in the translocation of heavy metals through the plant network. (Munn et al., 2008). Therefore, it is vital that the optimum concentration of chelating agents is used as an enhancement.

5.2. MICROBE ASSISTED PHYTOREMEDIATION

Phytoremediation assisted by endophytic microorganisms is considered a novel strategy in removing the metal content from a site (Shukla and Srivastava, 2017). The assistance from the microbial interactions with the plants can enhance rhizospheric metal uptake, which amplifies the plant's metal sequestration property. They can also help by affecting the ion exchange potential, chelation and redox balance. The microbes can assist or even take over the biostimulation, bioaccumulation and biotransformation process of the plants. *Lysinibacillus* and *P. vittata* are two such species that can tolerate concentrations of arsenic up to 1136 mg L21 for As31, and can also accumulate 5.65 mg L21 of As31 (Singh et al., 2015). Therefore, microbial assisted phytoremediation is an effective advancement that helps in amplifying and increasing the speed and efficacy of phytoremediation.

5.3. TRANSGENIC PLANTS FOR PHYTOREMEDIATION

Plants suitable for carrying out phytoremediation require certain essential characteristics such as: fast growth rate, rapidly growing roots and high root/shoot biomass. These plants should be easily harvestable and are able to store a high concentration of heavy metals within their systems (Rostami and Azhdarpoor, 2019). Hence, the development of transgenic plants through genetic engineering can be employed to develop plants with these desired characteristics. Transgenic plants have an over-expression of certain genes that govern the plant's uptake, movement, storage, tolerance and detoxification abilities of xenobiotics, pollutants and heavy metals. (Aken, 2008). Desirable genes from animals, microorganisms or plants are introduced to the plant by using vector-mediated methods such as *Agrobacterium tumefaciens* (bacterium) or vector-less methods (direct gene transfer) such as gene gun or microinjection to develop transgenic plants (Seth, 2012). The main target of developing transgenic plants is the enhancement of the tolerance, translocation and accumulation processes that occur in the shoot portion of the plant (Clemens et al., 2002). Two crops that were developed specifically for remediation are *Arabidopsis thaliana* and *Nicotiana tabaccum*. *Arabidopsis thaliana* over-expresses the mercuric ion reductase gene, which increases its mercury (Hg) tolerance. *Nicotiana tabaccum* has a gene whose expression leads to yeast metallothionein production for Cadmium (Cd) tolerance (Sarwar et al., 2017).

5.4. BIOCHAR ASSISTED PHYTOREMEDIATION

Biochar is a product rich in carbon, synthesized by the pyrolysis (thermal degradation) of organic matter such as plants, manure and sludge (Paz-Ferreiro et al., 2014). Older records show that charcoal, a common form of biochar, has been in use since prehistoric times. Biochar possesses unique physico-chemical properties which allows it to immobilize harmful heavy metals. These properties can effectively enhance phytoremediation. Its properties include its alkaline nature, ash, having a greater surface area for absorption, and high amounts of carbon. Heavy metal-biochar complexes can be formed by physical adsorption or through an exchange of metal cations -such as potassium, calcium, magnesium, and sodium- with the cations of heavy metals such as cadmium and mercury. The given larger surface area also allows for more absorption to take place (Lu et al., 2012).

Because of biochar's inherent alkaline nature, the heavy metal precipitation in the biochar-added soil increases while their bioavailability decreases. pH of biochar is correlated with pyrolysis temperatures, i.e. if the pH is increasing then temperature is also increasing. This may directly result from the ash content also proportionately increasing in the biochar (Wu et al., 2012; Cantrell et al., 2012). After many studies, biochar has been reported to increase the yield of biomass by 10%, thereby enhancing the plant's growth (Jeffery et al., 2011; Liu et al., 2013). The enhancement in the biomass yield results from the high cation-exchange capacity (CEC), and the rise in alkalinity, moisture, and nutrient holding capability of biochar due to which significant changes occur in the recycling of nutrients and hence, the plants can receive a good amount of nutrients (Liu et al., 2013; Fellet et al., 2014; Ahmad et al., 2016). An additional feature of biochar to note includes controlling microorganisms present in a soil sample. Using biochar as a technique to enhance phytoremediation capabilities can support probiotic growth and decrease the growth of pathogenic microbes by releasing toxic compounds that can kill the pathogenic microbes (Elad et al., 2012). Overall, biochar has shown to have multiple advantages that can substantially raise the biomass yield and plant growth rate and can be used along with both non- accumulator and hyperaccumulator plants and also with chemicals like EDTA for effective remediation of harmful heavy metals (Sarwar et al., 2017).

6. Advantages

Phytoremediation has shown several advantages over known conventional physical remediation methods of heavy metals and other pollutants. These advantages include:

- This is a much more aesthetically pleasant method of remediation, also being eco-friendly method compared to any other.
- This is a cheaper alternative. According to research, the total cost of using phytoremediation is at least 50-80% of the cost of known methods. Even the engineering portion of it requires very little funding (Pulford and Watson, 2003), because it can be conducted both in situ and ex situ.

- The species of plants being used can also treat a broad range of other pollutants, including multiple organic contaminants.
- It causes minimal disruption to the habitat it takes place in.
- The recovered heavy metals can then be reused as valuable metals. It can be extracted by either microbial, chemical or thermal means (Cunningham and Ow, 1996).

7. Limitations of Phytoremediation

Although phytoremediation has multiple advantages over the conventional remediation techniques, it has some notable limitations. Plants that perform phytoremediation have low biomass yield; hence, multiple harvesting cycles are required to extract the pollutants. Phytoremediation is also a time-consuming process, effective only during the weather conditions the chosen plants grows in (seasonal) (Chintakovid et al., 2008). If edible crops are utilized for phytoremediation, the metals and other contaminants can accumulate inside them and can reach higher trophic levels via bio magnification. A hyperaccumulator plant can only remediate a particular metal, and the other metals remain unaffected (Xi et al., 2008). Although phytoremediation is classified as a green technique, it can cause some pollution and release harmful by-products if coupled with chelating agents which enhance phytoremediation (Nam et al., 2008). Moreover, disposing of the plant matter which have metal deposited inside them is a tedious task, potentially being an environmental threat since the metals extracted can be redeposited to the soil. Phytoremediation is effective, but it still cannot apply to all contaminants present in soil or waste water.

8. Conclusion and future perspectives

Heavy metals that enter the environment due to a rise in urbanization and other related processes such as industrialization and various human activities are major pollutants in the soil, air or water. These heavy metals are toxic in nature and might cause deleterious effects on the health of humans and animals. Phytoremediation has emerged as an effective technique to remediate heavy metals from soil and wastewater and can be used on an industrial scale. Comparatively, it has many advantages compared to the conventional physical and chemical remediation techniques known. Traditional techniques do have certain limitations. However, since phytoremediation is a relatively novel field, a lot of research is being done to enhance and fight these limitations, such as the use of transgenic plants, use of biochar and use of microbes. Hence, phytoremediation is a promising technology for the removal of heavy metals from the environment.

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EFFECTS OF SEAWEED LIQUID EXTRACT ON SEEDLINGS GROWTH AND PIGMENT CONTENT OF *Vigna radiata*

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Abstract

The development in synthetic fertilizers and pesticides helped countries to increase their crop yield. However, at the same time it has also raised many issues related with soil fertility and degradation of the local ecosystem. Hence, there is a need to look for alternatives which not only can increase production to fulfill world food demand but also help in maintaining soil fertility without any negative impact on local environment. Amongst various available organic fertilizers, seaweeds are considered as a potential alternative to mainstream synthetic fertilizers, as these are rich in macronutrients, micronutrients as well as growth regulators, which directly help in the improvement of growth and yield of crop plants. In the present study effects of seaweed's liquid extracts from *Gracilaria* species on the growth and pigment contents in seedlings of *Vigna radiata* were evaluated. The results indicate that the addition these extracts significantly enhanced growth and pigment contents during seed germination.

Keywords: *G. cylindrica, G. verrucosa, G. edulis, G. corticata, G. crassa, Vigna radiata*, Biochemical Parameters, Growth Parameters, Seaweed Liquid Extracts (SLE).

1. Introduction

India is an agriculturally rich country and a large portion of its GDP comes from the agriculture and allied sectors. However, India's overall production of food crops has been increased several folds after green revolution still feeding all the people is a biggest challenge against government and scientists. International Food Policy Research Institute (IFPRI) has reported that India has moved from 97th to 100th place in 2017 on global hunger parameter. In addition the existing agriculture practices and trends of using chemical fertilizer lead to serious conditions which not only increasing water, soil and air pollution but also it is severely affecting human health. In addition bio-magnification of chemical fertilizers and pesticides resulted in various new diseases such as cancer. Therefore, sustainable agriculture without inorganic fertilizers and toxic pesticides is a need of hour for developing countries like India (Prakash et al., 2018).

Natural organic fertilizers which are composed of farmyard manure and residues of animal or plant products may be a substitute of chemical fertilizers without compromising the overall crop yield. Seaweeds are important marine renewable resources. They are used as food, feed, fodder, fertilizer, agar, alginate, carrageenan and source of various fine chemicals. Seaweeds are superior to chemical fertilizer because it contains high level of organic matters, micro and macro elements, vitamins, fatty acids and growth regulators (Jayasinghe et al., 2016). Furthermore leftover of seaweeds based industry which is generally rich in nutrient content can also be used as soil conditioner. These fertilizers not only can be used as biostimulants, biofertilizers, bioregulators to improve plant yield but also seaweed based fertilizers can control the deficiency diseases (Chekli et al., 2017). Due to these advantages in recent years there are many reports on use of seaweed extracts to enhance the growth of vegetables, fruits, and other crops. Seaweed extracts can be applied directly to seeds or added to the soil or sprayed on crops at vegetative and flowering stages, can stimulate seed germination, growth and yield of various crops (Kumar and Sahoo, 2011). In addition to this better nutrient uptake, better plant growth, deep root development by improving lateral root formation, increased total volume and enhanced plant defense against pest and diseases were also reported by applying SLE (Kumar and Sahoo, 2011). However, not much literature is available on effect of SLE on *Vigna radiata.* Similarly there are also very few reports on making SLE from leftover of agar based industry. *Gracilaria* is one of the world's most cultivated and important marine seaweed. Its large scale cultivation has also been started in various states of South India. It contains beneficial content for human nutrition. Moreover, it has docosahexaenoic acid (DHA) and polyunsaturated fatty acid (PUFA) which reduces the possibility of cardiovascular disease. It is a good source of polysaccharides that influence antibacterial, antiviral, anticonvulsant, antioxidant and anti-inflammatory activities. However, the role of *Gracilaria* species as biofertilizers is also reported by many researchers still there is a great need to check its potential as fertilizers after extraction of agar. Thus the present study intends to examine the effect of SLE from five species of *Gracilaria* (*G. verrucosa, G. cylindrica, G. crassa, G. corticata* and *G. edulis*) after extraction of agar on growth and various pigment parameters during initial seedling development of *Vigna radiata*.

2. Material and methods

Field dried species of *Gracilaria* from Marine Biotechnology Laboratory were used for making extract. Seaweeds were washed thoroughly with tap water to remove any extraneous particle, sand particle, and epiphytes. Then the seaweeds were allowed to dry under the direct sunlight after removing excess water with the help of blotting paper.

2.1. PREPARATION OF SAMPLE

Agar and all other soluble compounds were extracted from five species of *Gracilaria* by mild boiling of 10 g of sun dried seaweed in 200 ml of water for 2 hours at ~80°C. This is one of the most popular traditional thermal agar extraction method. Agar was separated by filtering the biomass through muslin cloth. The remaining leftover pulp used to make SLE.

2.2. PREPARATION OF SEAWEED LIQUID EXTRACT

10g of leftover pulp boiled with water in the ratio of 1:20 until the water reduced to half to leach out bioactive compounds present in leftover of seaweeds. Then concentrated SLE were filtered through a double-layered muslin cloth. This SLE was stored at 4°C for further experiments.

2.3. PREPARATION OF *Vigna radiata* SEEDS

The seeds of uniform size, color and weight were selected manually. All the seeds were treated with 90% ethanol and then washed thoroughly with distilled water. The sterilized seeds were soaked in distilled water for 1-2 hours followed by 4-6 hours soaking in different SLE.

2.4. CULTURE OF SEED

10 pretreated seeds from each SLE were kept in petri plates with three layered Whatman filter paper no. 5 as surface medium. This Whatman filter paper were carefully washed and dried in microwaves to wash out all impurities and ensuring proper sterilization before use. 5 ml of respective SLE were also added in each petri plates. Petri plates were kept in the incubator (25 °C) for germination of seeds. Spraying of water was also done at regular intervals of time to ensure proper moisture to prevent seeds from dehydration.

2.5. MORPHOLOGICAL AND PIGMENTS ESTIMATION

All the estimations were done after 5 days of incubation of seeds. Total chlorophyll, chlorophyll a, chlorophyll b and carotenoid pigments content was estimated according to Hiscox and Israelstam method (1979).

3. Results & Discussion

Seaweeds are one of the richest sources of minerals and trace elements because the cell wall of seaweeds contains anionic carboxyl, sulfate and phosphate groups which act as binary sites for metal retention. In *Gracilaria* many bioactive compounds such as alkanes, ketones, fucoxanthin, phenols, steroids, polyphloroglucinol and bromophenol along with many growth regulators like aspartic acid, alanine, glutamic acid and glutamine has been reported (Rosemary et al., 2019).

In the present study maximum fresh weight (230±0.46 mg) and dry weight (85±0.29mg) was observed in seedlings treated with the SLE of *G. cylindrica*, while *G. corticata* showed minimum gain in fresh and dry weight (70±0.45 mg and 23±0.31 mg respectively). Hernández-Herrera (2013) also reported that fresh weight of seedlings in tomato can be enhanced by various kinds of seaweed's extracts. In the present study maximum seedling heights were observed in the SLE of *G. verrucosa* (14.53±0.15 cm) after 5 days. With these results it is evident that seeds treated with SLE from leftover of *G. verrucosa*, *G. cylindrica* showed better results in various morphological growth parameters. In the present study SLE from *G. cylindrica* improve total pigment content (26.05±0.54 mg/g), Chl. b content (17.58±0.16 mg/g) and carotenoids contents (5.6±0.92mg/g). However Chl. a were reported maximum in the SLE of *G. edulish* (6.19±2.88 mg/g). Increase in pigment concentration of seedlings were also reported by Thirumaran et al., (2009) in *Cyamopsis tetrogonolaba* and el-Sheekh and el-Saied (2000) in *Vicia faba*. Present study shows that the SLE of leftover after agar extraction from *Gracilaria* can increase growth, plant height, weight and various kind of pigment content which increase the overall production in *Vigna radiata* plant. However, different species of *Gracilaria* showed different kind of effects. Similarly, Rama Rao (1991) reported increased yield and improvement in the quality of *Zizyphus mauritiana* Lamk with foliar applications of SLE. Our findings are consistent with some earlier studies conducted on marigolds (Aldworth and van Staden, 1987; Russo et al., 1994). Similar results were also seen in *Cajanus cajan* (L.) Millsp. (Mohan et al., 1994) and *Vigna sinensis* L. (Sivasankari et al., 2006). Enhanced Chl. a and Chl. b pigments and glycine betaine content were also observed with all SLE treatments under water deficit by Mansori et al., (2015).

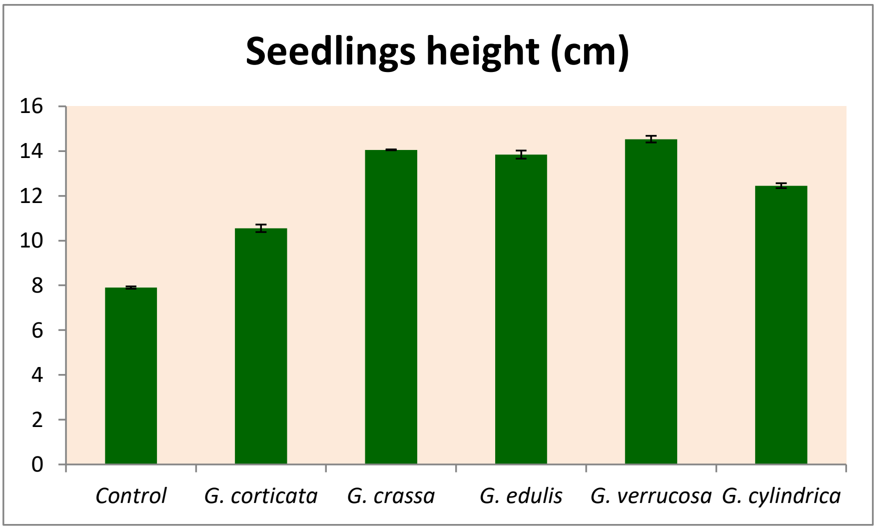

Fig. 1. Height of seedlings of *Vigna radiata* treated with SLE from different *Gracilaria* sps

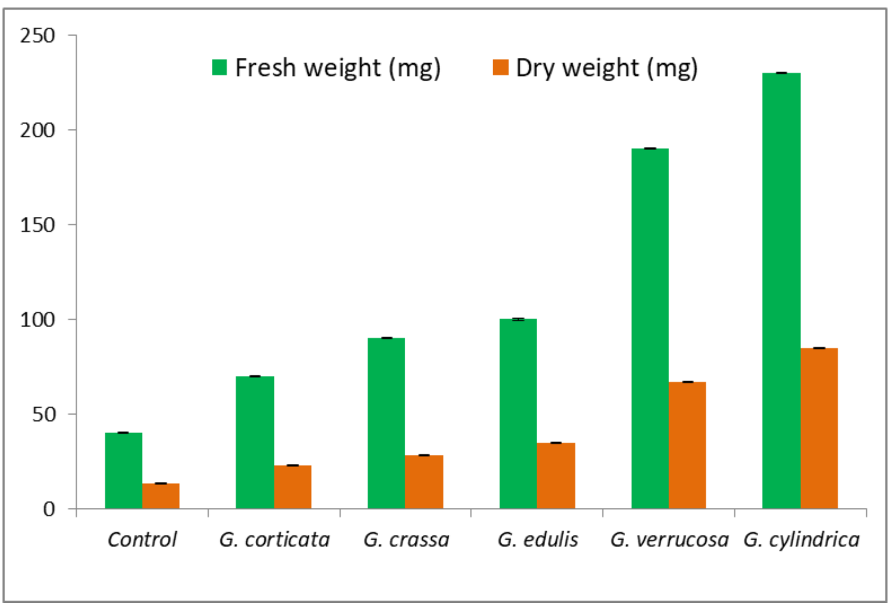

Fig. 2. Fresh and dry weight of seedlings of *Vigna radiata* treated with SLE from different *Gracilaria* sps

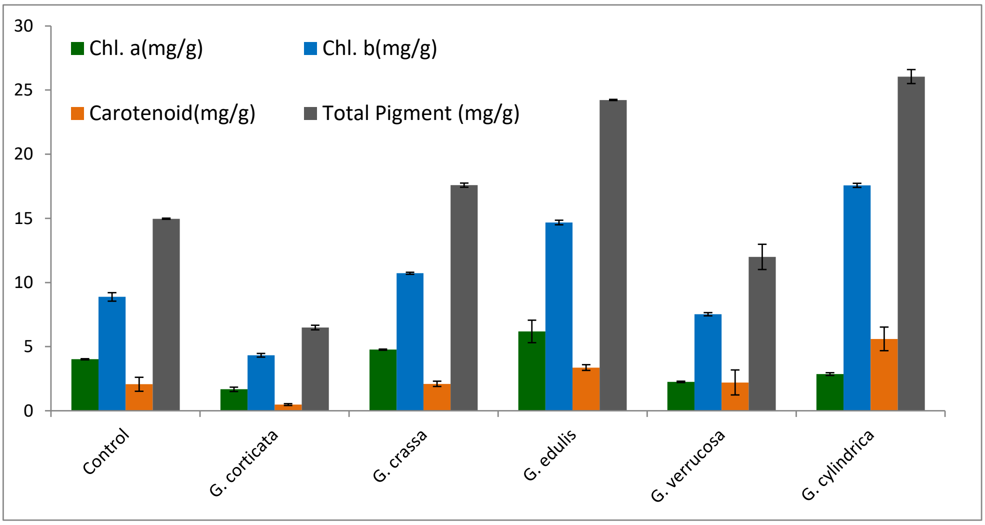

Fig. 3 Pigment content in seedlings of *Vigna radiata* treated with SLE from different *Gracilaria* sps

Liquid fertilizer based on SLE originally introduced in 1952 (Nabti et al., 2016). It is reported that SLE work effectively when it had been mixed with soil or composted with straw, or any other organic wastes (Craigie, 2011). Fertilizers obtained from seaweeds are biodegradable, non- toxic, non- polluting and not- hazardous to humans or animals. SLE solution is being used for the reclamation of saline soils and to overcome osmotic stress affecting plant growth (Nabti et al., 2016). Therefore, numbers of researches are presently focused on transforming algae into high-value biomass co-products in the form of extracts (Chekli et al., 2017). Thus, the Science Council of Canada (1992, p. 15) has said that "Sustainable Agriculture food systems are those that are economically viable, and meet society's needs for safe and nutritious food while conserving and enhancing natural resources and the quality of the environment for future generations" (Waltner-Toews, 1996). Increases in pigments content, resulted into improved photosynthetic rate which eventually increase the overall biomass production. Similar studies can also be performed after using seaweeds biomass for agar or bioactive compounds extraction followed by biofuel production and finally as soil conditioners. Although results of present study are very promising, further improvements and research in this field is required.

4. Conclusion

Present investigation revealed that seaweeds like *Gracilaria* can yield several products from the same biomass which makes them perfect candidates for the biorefinery concept. Present study proved that not only entire seaweeds but also leftover of seaweeds industries can be used as fertilizers. Using such leftover of seaweed would lead to the sustainable ecosystem, economy, and agriculture. Keeping all these observations in consideration it can be concluded that seaweeds biorefineries will start shining like a beacon of hope for the upcoming generations.

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IMPACT OF AGRO-BASED INDUSTRIAL EFFLUENT ON GROUND-WATER QUALITY

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Abstract

This chapter focuses on to study the impact of industrial waste on ground water quality collected from the adjoining areas of various agro-based industries of Aurangabad (Maharashtra) and Lucknow (Uttar Pradesh). Studies showed that the dominant anion is bicarbonate (HCO_3^-) and cations are calcium (Ca^{++}) and magnesium (Mg^{++}) in the ground water samples of Aurangabad and Lucknow. In general, ground water has low concentration of chloride (Cl^-) ion, but the results demonstrated that samples collected from the locations adjoining to industrial sites or with in the industrial sites such as Chikalthana and Jalna road of Aurangabad having excessive chloride (Cl^-) ion and sodium (Na^+) ion concentration. Which, is evidently, showing the impact of waste water of distillery and paper mill on ground water quality of these adjoining areas**.** Sodium adsorption ratio (SAR) varied from 1.19 to 5.31 with an average of 2.82 in groundwater of Aurangabad whereas, it ranged between 0.03 and 2.35 with average value of 0.86 in groundwater of Lucknow. Based on the Todd's classification, the water samples of the study areas fall in excellent category of irrigation.

1. Introduction

Groundwater quality is found to be deteriorated due to various anthropogenic activities such as landfill, industrial, agriculture etc. Untreated or partially treated wastewater contains a wide variety of inorganic, organic, and biological contaminants. Even treated wastewater, commonly referred to as effluent, may contain elevated concentrations of various chemicals including chloride, nitrate, hydrocarbons and metals (Zaporozec, 2004). Treated wastewater after treatment could be utilized in agricultural fields for the purpose of irrigation or as artificial recharge to raise the groundwater level. Leaking treatment facilities, the storage of wastewater in ponds and lagoons, and the discharge of untreated or partially treated wastewater on the land or into an open water course entails the risk of infiltration of contaminants there by contaminating the groundwater. Natural geochemical processes also considered as an important factor for determining the quality of ground water like rock-water interaction and evaporation (Ismail et al., 2015). Groundwater chemistry mainly assigned to their interaction with aquifer minerals or internal mixing among different groundwater flow-paths in the subsurface (Wallick and Toth, 1976; Toth, 1984; Schuh et al., 1997) showed that increased concentration of solutes in groundwater owing to spatially variable recharge which is, led by various micro topographic factors. In addition to this, the weathering of primary and secondary minerals is also responsible for contributing cations and silica in the aquifers (Freeze and Cherry, 1979; Jacks, 1973; Bartarya, 1993).

The analysis of groundwater quality is of prime importance in order to explore its hydrochemistry and suitability for drinking and irrigation purpose. This can be done by analyzing the major cations and anions of water samples. Many interrelated processes control the groundwater quality, these aspects are highly required for water quality control and water resource management. In recent past numerous studies have been carried out regarding groundwater quality and its chemistry in different parts of the world (Nagarajan et al., 2010; Wang et al., 2011; Zhang et al., 2012; Nagaraju et al., 2016; Adimalla et al., 2018; Kawo and Karuppannan, 2018; Jasrotia et al., 2018). The hydro geochemical processes help to get an insight into the contributions of rock-water interaction and industrial influences on groundwater quality (Maliva, 2020; Zaporozec, 2004). These geochemical processes are responsible for the seasonal and spatial variations in groundwater chemistry (Matthess, 1982; Kumar et al., 2006).

This chapter focuses on the study of the impact of industrial waste on the quality of ground water collected from the adjoining areas of the agro-based industries in Aurangabad and Lucknow. Multivariate analysis, such as factor analysis and cluster analysis were applied simply as a numerical method of discovering variables that are more important than other data for representing parameter variation or demonstrating hydro chemical processes. This technique helps to simplify and organize data set in order to make useful generalizations and insight.

According to the geographical formations, soil type and human activities, the major ionic species and their distribution in natural water varies a lot. Major ionic species (cations and anions) in all-natural aquifers that govern the water quality and represent the principle chemical constituents are listed below:

Table 1. Major cations and anions in natural water (Singh et al., 2014).

Cation	**Anions**
Calcium (Ca^{2+})	Bicarbonate (HCO_3^-)
Magnesium (Mg^{2+})	Carbonate (CO_3^{-2})
Sodium (Na^+)	Chloride (Cl^-)
Potassium (K^+)	Sulfate (SO_4^{2-})
Iron (Fe_2^+)	Nitrate (NO_3^-)
Manganese (Mn^{2+})	Phosphate (PO_4^{3-})

Table 2 Drinking water quality standards as recommended by WHO (1997)

Elements/radicals	**Guideline values (mg/l)**
Chloride	250
Sulfate	500
Nitrate	50
Fluoride	1.5
Iron	2
Manganese	0.5
Copper	2
Nickel	0.02
Lead	0.01
Zinc	3
Arsenic	0.01
Cadmium	0.003
Chromium	0.05
Mercury	0.001

Table 3: Drinking Water Characteristics (IS: 10500:1991) (BIS, 1991)

S.No.	**PARAMETER**	**Desirable limit (mg/l)**	**Permissible limit (mg/l)**
1	pH	6.5 – 8.5	No relaxation
2	Iron (Fe)	0.3	1.0
3	Chloride (Cl^-)	250	1000
4	Fluoride (F^-)	1.0	1.5
5	Calcium (Ca^{++})	75	200
6	Magnesium (Mg^{++})	30	100
7	Copper (Cu^{++})	0.05	1.5
8	Mangnese (Mn^{++})	0.1	0.3
9	Sulphate (SO_4^{--})	200	400
10	Nitrate (NO_3^-)	45	100
11	Cadmium (Cd)	0.01	No relaxation
12	Zinc (Zn)	5.0	15
13	Alkalanity	200	600
14	Dissolved solid	500	2000

Table 4 General Standards for Discharge of Environmental Pollutants (MOEF, 1993)

Parameter	Standards			
	Inland Surface water	**Public Sewers**	**Land of irrigation**	**Marine/Costal areas**
Suspended solids mg/1, max.	100	600	200	For process waste water 100* For cooling water effluent 10 per cent above total suspended mater of influent
Particle size of suspended solids	Shall pass 850 micron IS Sieve	--		Floatable solids, solids max. 3 mm Settleable solids. Max 856 microns
pH value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
Temperature	Shall not exceed 5°C above the receiving water temperature	--	--	Shall not exceed 5°C above the receiving water temperature
Total residual chlorine, mg/1 max	1.0	--	--	1.0
Ammonical nitrogen (as N), mg/l, max.	50	50	--	50
Total nitrogen (as N), mg/l, max.	100	--	--	100
Free ammonia (as NH_3), mg/l, max	5.0	--	--	5.0
Biochemical oxygen demand (3 days at 27°C), mg/l, max	30	350	100	100
Chemical oxygen demand, mg/l,max	250	-	-	250
Fluoride (F^-) mg/l	2.0	1.5	-	15
Nitrate Nitrogen	10 mg/l	_	_	20 mg/l

*The permissible limit of suspended solids should be 100 mg/l for the process water (i.e.Water that comes in contact with any raw material, product, by-product, or waste during any production or industrial process) discharging in marine or coastal area.

2. Material and Methods

2.1 PHYSICOCHEMICAL PARAMETERS

Ground water (hand pump) samples randomly collected from city areas which are away from industrial areas and purposely from adjoining areas of agro-based industries located in Lucknow, Uttar Pradesh (Fig 1) and Aurangabad, Maharashtra (Fig 2). Samples of ground water collected in polypropylene bottles were brought to the laboratory and stored in cold room at 4°C temperature in order to avoid any major biochemical alteration (APHA, 1995). For the cations and anions, the water samples were not fixed with acid and samples were analyzed as per (APHA, 1995). The bicarbonate (HCO_3^-), pH, electric conductivity (EC) parameters were analyzed with unfiltered water. All physico chemical parameters were analyzed as per methods given in (APHA, 1995), for dissolved organic carbon (DOC) samples were collected and stored in brown bottles to avoid sunlight exposure and measured as per Hach process.

2.2 MULTIVARIATE ANALYSIS

The data were prepared and processed in SPSS 11.0 and excel in window XP. Descriptive statistics, factor analysis and cluster analysis were processed in SPSS. Factor analysis was used to understand the correlation structure of collected data and identified most important factors contributing the data structure (Ashley and Lloyd, 1978). For factor analysis varimax rotation method was used to find association between parameters so that the number of measured variables can be reduced. After getting the correlation matrix and eigen values, factor loading was applied to measure the correlation between variables and factors. These variables were then rotated by varimax rotation technique to obtain new variability which is easy to interpret (Jolliffe and Cadima, 2016).

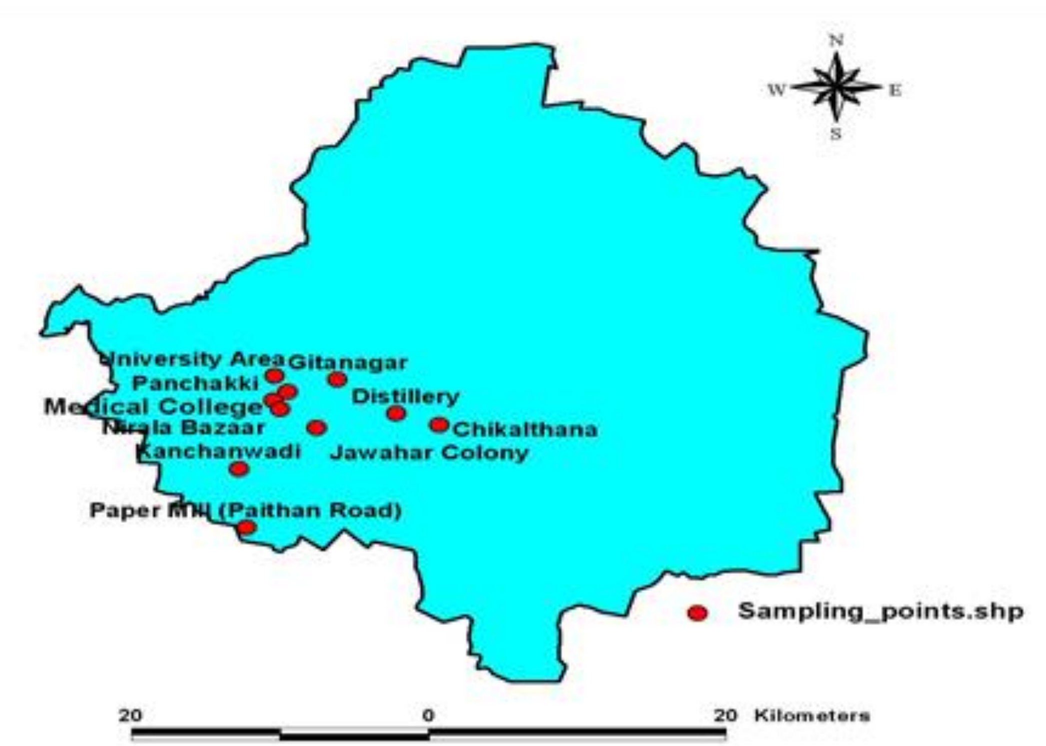

Fig 1. Map showing sampling locations in Aurangabad district of Maharashtra (image developed by using GIS software)

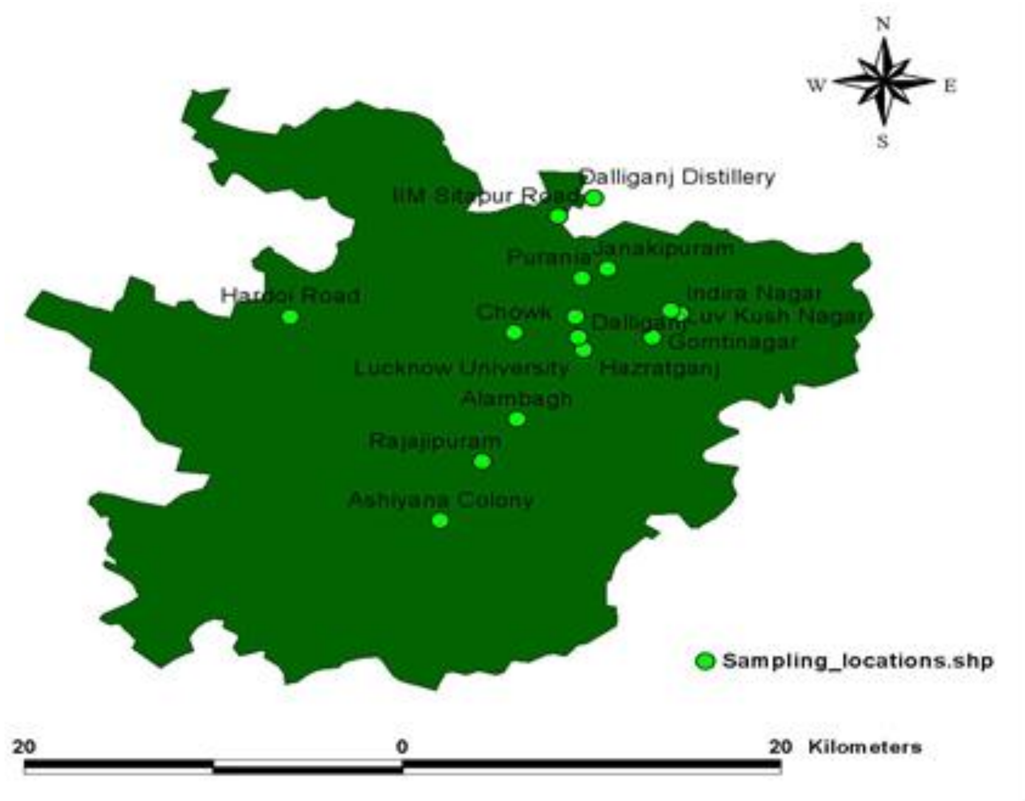

Fig 2. Map showing sampling locations in Lucknow district of Uttar Pradesh. (image developed by using GIS software)

3. Results

The results of various physicochemical parameters and their correlation matrices have been furnished in Table 5 and 6

Table 5. Various physico-chemical parameters in ground water samples of Aurangabad and Lucknow. All parameters in mg/l except EC (µs/cm) and pH.

Ground water samples	pH	EC	TDS	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+
Vishva Papermill Aurangabad	6.9	1895	1345	245	1.21	560.74	75.66	160.56	336.9
Kanchanwadi Aurangabad	7.4	708	340	278	1.03	187.94	46.86	60.75	146.2
Medical collage Aurangabad	7.2	753	448	275	2.74	30.89	18.75	233.25	112.7
Industrial area Aurangabad	7.6	1297	928	355	0.44	331.2	15.4	113.34	73.72
Niralabazar Aurangabad	7.6	734	380	365	0.87	150	37	154.8	145.7
Chikalthana Aurangabad	7	1015	689	230	0.32	198	48	356.89	159.6
Jyotinagar Aurangabad	7.3	755	462	245	1.03	185	28.9	135.76	125
Jubleepark Aurangabad	7.4	767	430	235	0.52	153.14	36.58	146.08	115.6
Rajabazar Aurangabad	7.3	799	495	265	1.03	85.04	30.78	98.9	104.8
Panchakki Aurangabad	7.3	823	565	275	2.45	118	6.67	195.5	125.6

Daliganj Lucknow	7	865	534	280	0.3	5.84	6.79	12.68	10.82
Distillery Lucknow	6.9	1095	711	270	1.03	38.07	58.9	127.95	99.45
Indiranagar Lucknow	6.9	687	409	265	1.04	22.18	29.97	43.5	1.4
Luv kushnagar Lucknow	6.8	650	334	260	1.39	18.64	13.85	19.44	1.96
Jankipuram Lucknow	7.4	1060	650	295	0.63	36.8	12.35	21.82	5.24
Hazaratganj Lucknow	7.3	986	539	280	0.57	25.96	15.45	10.67	30.8
Gomtinagar Lucknow	7.2	975	634	255	0.94	40.12	25.4	18.51	15.39
Puarania Lucknow	7.2	897	589	265	0.56	28.07	43.5	130.91	50.52
Alambagh Lucknow	7.4	785	368	285	0.12	32.09	20.02	51.73	65.5
Rajajipuram Lucknow	7.4	840	452	280	0.72	38.9	8.56	18.69	30.7
Chowk Lucknow	7.1	610	348	210	0.7	20.02	2.6	50.66	26.98
Hardoi road Lucknow	7.2	630	356	265	0.4	8	0	65.75	20.12
IIM Sitapur road Lucknow	7.5	680	388	279	0.16	33	0	36.29	32.69
University Lucknow	7.3	870	525	275	0.2	12.69	10.03	30.5	20.32
Ashiana Colony Lucknow	7.3	793	378	280	0.14	13.5	7.03	49.56	30.75
Mean	7.2	892	544	273	0.94	99.45	23.99	96	79.79
Minimum	6.7	610	334	210	0.12	5.84	0	10.67	1.4
Maximum	7.6	1895	1345	365	3.56	560.74	75.66	356.89	336.9

Ground water samples	**K^+**	**Mg^{++}**	**Ca^{++}**	**DOC**	**TZ+**	**TZ-**	**%**	**SAR**	**Water**
Vishva Papermill Aurangabad	1.96	95.6	145.6	3.5	29.94	24.44	10.12	5.31	Na-Cl
Kanchanwadi Aurangabad	1.44	50.15	79.09	3.2	14.53	11.93	9.83	3.15	Na-Cl
Medical collage Aurangabad	3.44	25.68	91.2	2.1	11.69	10.68	4.49	2.68	Na-SO_4
dustrial area Aurangabad	1.61	56.57	197.57	1.9	17.84	17.78	0.16	1.19	Ca-Cl
Niralabazar Aurangabad	2.55	40.7	118.5	1.5	15.72	14.08	5.5	2.93	Na-HCO_3
Chikalthana Aurangabad	4.98	26.46	207	1.8	19.62	17.57	5.45	2.77	Ca-SO4
Jyotinagar Aurangabad	1.09	42.5	118.79	1.3	14.95	12.58	8.61	2.5	Ca-Cl
Jubleepark Aurangabad	0.97	38.95	120.04	1.5	14.3	11.83	9.46	2.34	Ca-Cl
Rajabazar Aurangabad	1.09	18.58	94.59	1.6	10.86	8.85	10.18	2.57	Ca-HCO_3
Panchakki Aurangabad	3.2	24.28	115.35	2.2	13.33	12.16	4.62	2.77	Ca-HCO_3
Daliganj Lucknow	3.5	17.84	45.78	0.9	4.34	5.15	-8.6	0.34	Ca-HCO_3
Distillery Lucknow	1.89	13.78	112.9	0.6	11.17	9.17	9.82	2.35	Ca-HCO_3
Indiranagar Lucknow	5.34	29.05	102.75	0.5	7.76	6.41	9.48	0.03	Ca-HCO_3
Luv kushnagar Lucknow	2.97	21.03	90.59	0.56	6.44	5.49	8	0.05	Ca-HCO_3
Jankipuram Lucknow	3.8	16.87	80.96	1.6	5.78	6.56	-6.33	0.14	Ca-HCO_3
Hazaratganj Lucknow	1.03	12.45	45.64	1.5	4.69	5.66	-9.42	1.04	Ca-HCO_3
Gomtinagar Lucknow	1.98	16.71	60.9	10.5	5.16	6.16	-8.82	0.45	Ca-HCO_3
Puarania Lucknow	1.89	14.52	70.65	1.5	6.99	8.59	-	1.43	Ca-HCO_3
Alambagh Lucknow	1.98	10.1	61.69	1.25	5.82	6.98	-9.04	2.35	Na-HCO_3
Rajajipuram Lucknow	1.9	15.98	50.08	1.8	5.22	6.33	-9.64	0.96	Ca-HCO_3
Chowk Lucknow	2.4	12.9	74.87	1.65	4.55	5.14	-6.06	0.91	Ca-HCO_3

Hardoi road Lucknow	1.68	16.56	96.8	0.6	7.14	5.96	8.99	0.5	Ca-HCO_3
IIM Sitapur road Lucknow	1.23	18.35	66.78	0.6	6.32	6.27	0.42	0.91	Ca-HCO_3
University Lucknow	3.66	15.34	50.8	0.8	4.8	5.67	-8.38	0.64	Ca-HCO_3
Ashiana Colony Lucknow	3.08	20.52	62.35	0.9	6.24	6.12	0.97	0.86	Ca-HCO_3
Mean	2.26	26.71	93.79	1.84	10.44	9.69	1.44	1.74	
Minimum	0.09	10.1	45.64	0.5	4.34	5.14	-	0.03	
Maximum	5.34	95.6	207	10.5	29.94	24.44	10.18	5.31	

Table 6. Correlation matrix of ground water samples collected from Aurangabad and Lucknow

	pH	**EC**	**TDS**	**HCO_3^-**	**F^-**	**Cl^-**	**NO_3^-**	**SO_4^{2-}**	**Na^+**	**K^+**	**Mg^{++}**	**Ca^{++}**	**DOC**
pH	1												
EC	-0.20	1											
TDS	-0.25	0.98	1										
HCO_3^-	0.537	0.11	0.06	1									
F^-	-0.40	0.03	0.10	-0.08	1								
Cl^-	-0.04	0.74	0.75	0.06	0.17	1							
NO_3^-	-0.20	0.57	0.55	-0.09	0.00	0.58	1						
SO_4^{--}	-0.06	0.26	0.33	-0.09	0.26	0.44	0.50	1					
Na^+	-0.09	0.61	0.61	-0.05	0.31	0.84	0.73	0.66	1				
K^+	-0.14	-0.13	-0.10	-0.05	-0.16	-0.22	-0.06	0.14	-0.24	1			
Mg^{++}	0.02	0.62	0.62	0.11	0.09	0.92	0.58	0.33	0.77	-0.11	1		
Ca^{++}	-0.07	0.46	0.54	0.13	0.13	0.67	0.48	0.75	0.58	0.07	0.58	1	
DOC	-0.00	0.24	0.26	-0.12	0.16	0.19	0.17	-0.03	0.12	-0.12	0.14	-0.034	1

3.1 PHYSICOCHEMICAL PARAMETERS

3.1.1 pH

The pH value of most of the ground water collected from Lucknow and Aurangabad varied between 6.75 and 7.65 showed their neutral range. Only the ground water taken from the industrial premises were found slightly acidic in nature which may be due to excessive discharge of acidic waste water of paper mill and distillery.

3.1.2 EC and TDS

The values of electrical conductivity (EC) are very effective tool to evaluate the water quality. The EC values in water samples ranged between 610 µS/cm to 1895 µS/cm. Usually, the total dissolved solids (TDS) concentration is the sum of the cations (positively charged) and anions (negatively charged) in the water. TDS values owing to various sources gives us insight of general water quality which, varies from geogenic, domestic sewage, agricultural run-off, industrial wastewater, and various chemicals used during water treatment process (Andik and Eslami, 2015). In present study the TDS values varied between 334 mg/l to 1345 mg/l. The results showed the values of EC and TDS are within the permissible limits prescribed by WHO for most of the samples. Results indicated the higher values of EC and TDS for the samples of Aurangabad as compared to Lucknow which might be attributed to more industrial activities in Aurangabad district.

3.1.3 Calcium

Calcium is a major constituent responsible for water hardness and calcium concentration between 40 and 100 mg/l are generally considered as hard to very hard. In present study the calcium concentration in ground water samples varied from 41.69 mg/l to 207.00 mg/l. The minimum concentration was reported in ground water sample collected from the residential areas and the maximum concentration of calcium reported in the sample taken from the Chikalthana industrial area of Aurangabad where a distillery unit is present, as the distillery waste water are rich in calcium thus it may be one of the reasons for the higher values of calcium ions reported in sample taken from industrial areas.

3.1.4 Magnesium

Higher concentration of magnesium salts in water may have laxative effects. They may also responsible for the unpleasant taste of drinking water at concentrations above 500 mg/l. Magnesium is linked with hardness of water, and is undesirable in several industrial processes (Sengupta, 2013). However, Magnesium is also essential plant nutrient as well as soil conditioner (Assunçao et al., 2020). In the present analysis the magnesium values varied between 10.10 mg/l to 95.60 mg/l which are well with in the limits, from Table 5. It is clearly evident that the higher values were found in water samples which, have been collected from adjoining areas of industries.

3.1.5 Sodium and Potassium

Sodium salts are very soluble and remain in solution. Typical sodium concentrations in natural waters ranges between 5 and 50 mg/l (Hem, 1991). Here in the present work the sodium concentration ranges between 1.40 mg/l to 336.90 mg/l. Since sodium in waste water of paper industries is a major constituent, therefore the ground water of paper mill in Aurangabad showed higher concentration of sodium.

Potassium is usually present in lesser quantity than sodium in natural waters. Its concentration rarely goes beyond 10 mg/l in natural waters. Agricultural runoff may contribute to temporarily high concentrations of potassium from fertilizer as plants take up potassium and release it on decay. As far as domestic water supply is concerned, potassium is of less importance and it creates no harmful effects (Hem, 1991). The potassium concentration varied between 0.09 mg/l to 5.34 mg/l in ground water samples collected from the Aurangabad and Lucknow, which were well within the expected range.

3.1.6 Bicarbonate

Bicarbonate is the major anion present in natural water. It comes in water from the weathering of limestone, marble, chalk, calcite, dolomite and other minerals containing calcium and magnesium carbonate. The carbonate-bicarbonate system in natural water regulates the pH and the natural buffer system. In general, the concentration of bicarbonate in surface waters is less than 200 mg/l as $HCO3^-$. In groundwater, the bicarbonate concentration is significantly higher. In present study the HCO_3^- concentration in ground water samples were found to be varied between 210-365 mg/l which renders the water alkaline in nature.

3.1.7 Chloride

Cl^- occurs naturally in all-natural water bodies particularly where sedimentary bedrock layers of shale occurs. Cl^- is soluble in water and highly mobile with water through soil and rocks. Cl^- is more persistent in nature than nitrate as it is resistant to microorganisms to some extent, the concentration of chloride are usually low in natural water bodies but, exceptions occur where the streams receive inflows of high chloride ground water or industrial waste water (Hem, 1991) High content of Cl^- may give a salty taste to groundwater and can corrode pipes, pumps and plumbing fixtures. People who are not accustomed to high chlorine in drinking water are subjected to laxative effects (WHO, 1997). Concentration of chloride in the study area varied from 5.84 to 560 mg/l. The higher value was found in ground water from paper mill of Aurangabad which could be attributed to use of chlorine as bleaching agent in paper mills.

3.1.8 Sulfate

Sulfate (SO_4^{2-}) ions are naturally present in almost all types of water bodies, which is a major contributor to total hardness. SO_4^{2-} content more than 200 mg/l is objectionable for domestic purposes; beyond this limit, SO_4^{2-} causes gastro-intestinal irritation (WHO, 1997). Most of the water samples of all the cities (Aurangabad and Lucknow) had SO_4^{2-}contents within permissible limits, ranging from 10.67 to 356.89 mg/l. Higher values were observed in adjoining areas of industries (Table 5**).** This clearly shows the impact of industrial activities.

3.1.9 Fluoride

Fluorite (Caf_2) is a common fluoride mineral. Fluorite mineral has rather a low solubility and present in both igneous and sedimentary rocks. In present analysis the fluoride concentration in ground water samples was found to be varied between 0.12 mg/l to 3.56 mg/l. The fluoride concentration in ground water of Lucknow was well with in the limits prescribed by the BIS and WHO where as in few samples of Aurangabad the F^- concentration was found above the permissible limits. Since basaltic rocks are igneous rocks and the rocks rich in alkali metals are higher in fluoride contents (Rankama and Sahama, 1950) thus it could be one of the reasons of high F^- concentration in Aurangabad which is located in basaltic terrain.

3.1.10 Dissolved Organic Carbon

The dissolved organic carbon (DOC) in ground water comes from either surface organic matter or from kerogen, the fossilized organic matter present in the geologic material of the aquifer. In case of shallow ground water, the DOC is from surface waters. Dissolved organic carbon (DOC) in ground water ranges from 0.2 mg/l to 15 mg/l with a median concentration of 0.7 mg/l. the majority of all ground water have concentrations of DOC below 2 mg/l (Leenheer et al., 1974; Barcelona, 1984). In the present study the dissolved organic carbon (DOC) ranges between 0.50 mg/l to 3.50 mg/l. The Table 5 demonstrates that dissolved organic matter is more in ground water samples of the Aurangabad as compared to Lucknow because of more units of agro based industries in this belt.

3.2. COMPARISON BETWEEN PHYSICO-CHEMICAL PARAMETERS OF WASTE WATER AND GROUND WATER

The Table 7 showed that waste water from agro based industries are acidic in nature where as the average value of pH of ground water is almost neutral. The electrical conductivity and total dissolved solids of industrial waste water is much higher than the ground water. The Dissolved organic carbon (DOC), major anions like NO_3^-, Cl^-, SO_4^{2-} and cations Ca^{++}, Mg^{++}, Na^+ and K^+ were found in higher concentration in waste water as compared to ground water. The Table 7 also shows the impact of industrial waste water on the quality of ground water.

Table 7. Comparison between average values of waste water and ground water

Parameters	Average values of industrial waste water	Average values of ground water
pH	4.9	7.2
EC (µS/cm)	15176	893
TDS (mg/l)	8614	544
Cl^- (mg/l)	493.94	99.45
NO_3^- (mg/l)	42.97	23.99
SO_4^{2-} (mg/l)	7472.40	96
Na^+ (mg/l)	988.49	79.79
K^+ (mg/l)	3144.80	2.26
Mg^{++} (mg/l)	913	26.71
Ca^{++} (mg/l)	803	93.79
DOC (mg/l)	3186	1.84

3.3 MULTIVARIATE ANALYSIS

3.3.1 Principal Component Analysis

The Table 8 represents the initial eigen value, percent of variance and cumulative percent of total variance and cumulative percent of total variance of ground water data. From the table it was inferred that the first four components together account for 75.845% of the total variance in which the first component accounts for 42.118% of the total variance. The second component explains 13.621 %, the third component 11.21 % and fourth component exhibit 8.89 % of the total variance. Guidelines have been developed for determining the number of factors to be used and ignored. For interpreting the data, the method of Kaiser Criterion was followed which retains only those factors having eigen values greater than 1. Further interpretation was made on the basis of first four factors having an eigen value greater than 1. The extracted components explain nearly 75.84% of the variability in the original variables. The number of eigen values can be estimated from a scree plot demonstrated in Fig 3. As shown in this figure, the eigen value sharply decreased with in the first four components and then slowly stabilized for the remaining ones.

Factor 1: This factor has an Eigen value of 5.475 and accounts for 42.1% variance in the data. The variables are Na^+, Cl^-, TDS, EC, Ca^{++}, Mg and SO_4^{--}. The first factor is characterized by very high loadings of Cl^- and Na^+ and moderate to high loadings of TDS, Mg, EC, NO_3^-, Ca^{++} and SO_4^{--}. This factor reveals that the EC and TDS in the study area are mainly due to Na^+ and Cl^-, which can be attributed to pollution load due to industrial activities.

Factor 2: This factor has an Eigen value of 1.771 and accounts for 13.6% variance in the data. The variables are pH and HCO_3.

Factor 3: This factor has an Eigen value of 1.457 and accounts for 11.2% variance in the data. The variables are K^+ and SO_4^{--}.

Factor 4: This factor has an Eigen value of 1.157 and accounts for 8.9% variance in the data. The single variable is F. So, this factor can be attributed to natural geochemical process taking place in the area.

Table 8. Varimax Rotated component matrix, Eigen value, Percentage of Total Variance and Cumulative Percentage of Groundwater

Variable	Factor 1	Factor 2	Factor 3	Factor 4
Cl^-	0.928			
Na^+	0.903			
TDS	0.845			
Mg^{++}	0.844			
EC	0.823			
NO_3^-	0.763			
Ca^{++}	0.752			
SO_4^{--}	0.625		0.586	
pH		0.854		
HCO_3^-		0.784		
K^+			0.603	
F^-				0.669
Eigen value	5.475	1.771	1.457	1.157
Percentage of variance	42.1	13.6	11.2	8.9
Cumulative Percentage	42.1	55.7	67.0	75.9

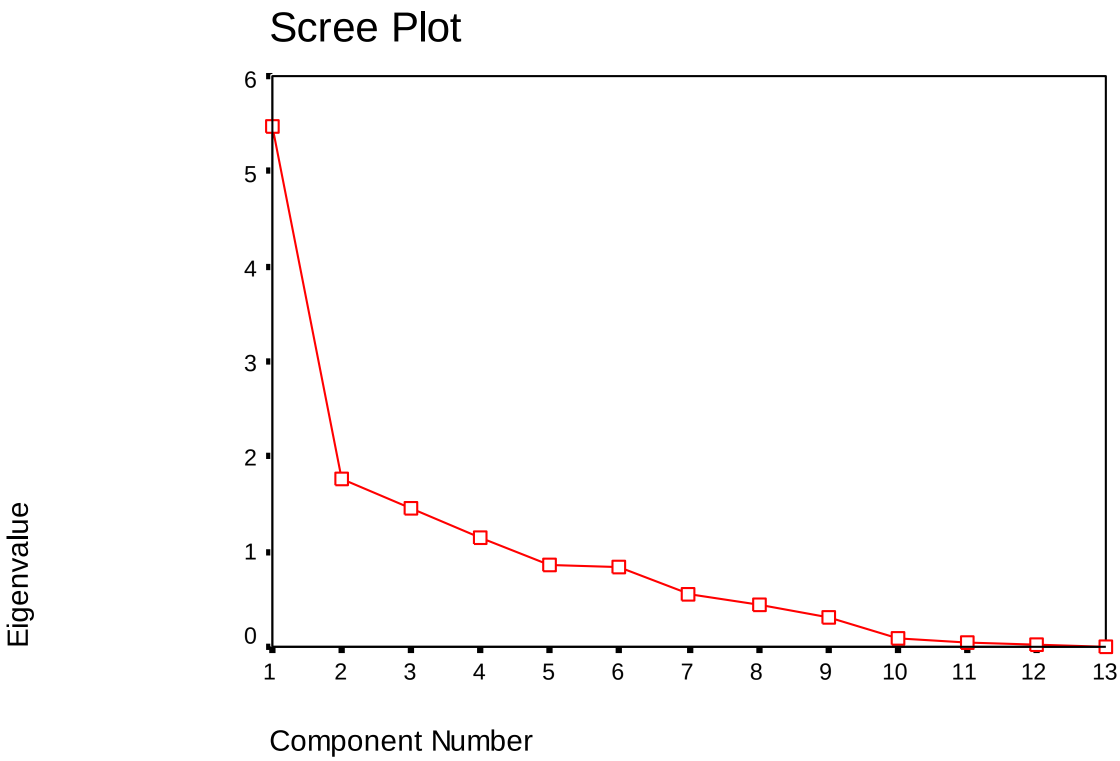

Fig 3. Scree plot of ground water

3.3.2 Cluster analysis

Another data reduction method is cluster analysis. In present study it was applied to classify variables with similar properties. Multivariate statistical method encompasses cluster analysis, factor analysis and principal component analysis, these statistical techniques have been successfully applied in various hydrochemistry studies for several years. In cluster analysis single linkage method was used. In this method the distance between the clusters was determined by the distance of the two closest objects (nearest neighbor) in the different clusters (Pathak et al., 2008).

The dendrogram of various parameters produced two major groupings (Fig 4). The dendrogram shows that the association between EC and TDS parameters is more significant. The first cluster group shows close association between HCO_3^- and Mg^{++}. Samples belonging to cluster 1 have high salinity, hardness, Ca^{++}, Mg^{++}, Na^+, K^+, Cl^-, DOC, SO_4^{--} and the Fig 4 shows that EC and TDS have grouped into cluster 2 and rest of the parameters form a separate cluster.

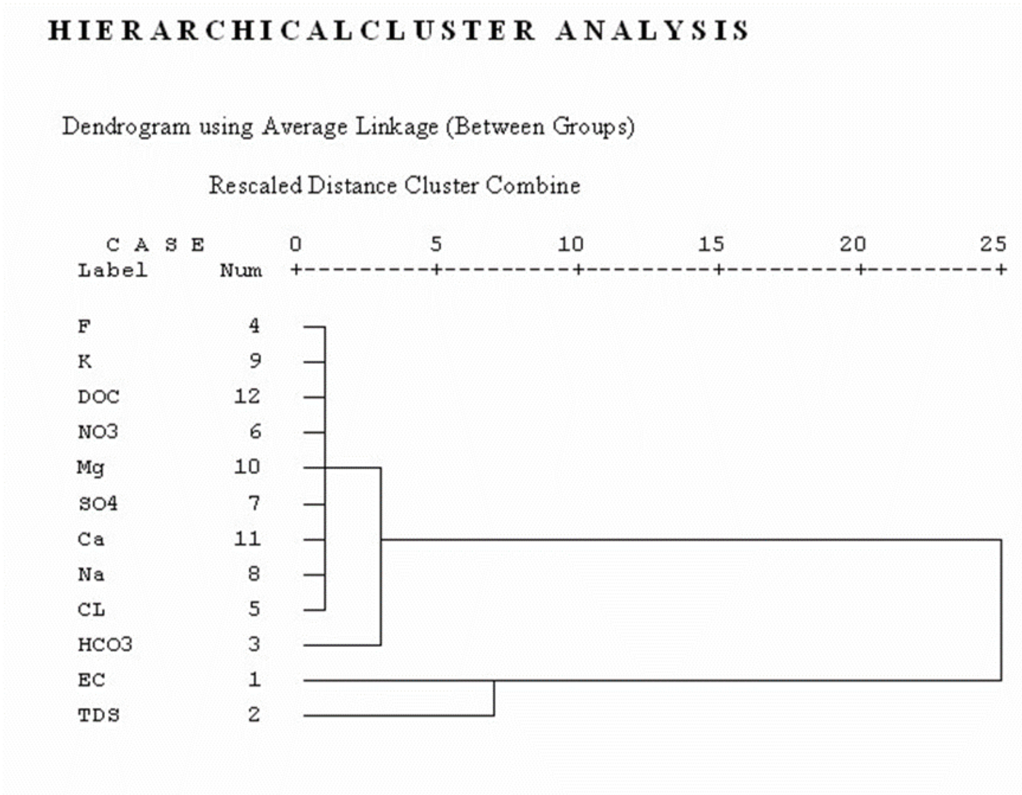

Fig 4. Dendrogram of 12 parameters of 27 cases

3.4 CHEMICAL CLASSIFICATION OF GROUND WATER

3.4.1 Sodium Adsorption Ratio

The Sodium Adsorption Ratio (SAR) is an important parameter for determination of suitability of irrigation water. It is an index of sodium/alkali hazard. This index quantifies the proportion of sodium (Na^+) to calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in a sample. The sodium adsorption ratio (SAR) values for each water sample were calculated by using following equation (Richard, 1954).

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

Where, the concentrations are reported in meq/l.

Sodium adsorption ratio varied from 1.19 to 5.31 with an average of 2.82 in the ground waters of Aurangabad whereas, it varied between 0.03 and 2.35 with mean value of 0.86 in Lucknow groundwater samples (Table 5).

As per Todd (1980), the irrigation water having SAR values less than 10 can be classified as 'excellent' and the water is considered as suitable for any crop. In the present study the suitability of groundwater samples of the investigated areas for irrigation purpose was judged and classified them into different categories on the basis of their Sodium Adsorption Ratio (SAR). SAR values exhibited that the ground water samples of the investigated areas fall into excellent category for irrigation purpose.

3.4.2 Piper Diagram

Piper diagram is the method of comparing the results of chemical analyses of ground water (Piper, 1944). This diagram in Fig 5 shows two lower triangles that exhibit the percentage distribution of major cations (Mg^{++}, Ca^{++}, and Na^{+} + K^{+}) and anions (Cl^{-}, SO_4^{2-} and CO_3^{2-} + HCO_3^{-}), on the milliequivalent basis, and the dominance of cations and anions are summarized by diamond-shaped part above to suggest the final water type.

This classification system demonstrated the anion and cation facies in terms of major-ion percentages. The water types are classified according to the area in which they occur on the diagram segments. The cation distribution indicates that the most of samples of Aurangabad and Lucknow in composition predominantly is Calcium type, where as some samples of Aurangabad is Na^{+}, K^{+} type. In the anion triangle, for the ground water samples of Lucknow there is a tendency more towards carbonate/bicarbonate type water and samples of Aurangabad ranges from Carbonate/ bicarbonate to mixed anion-type water.

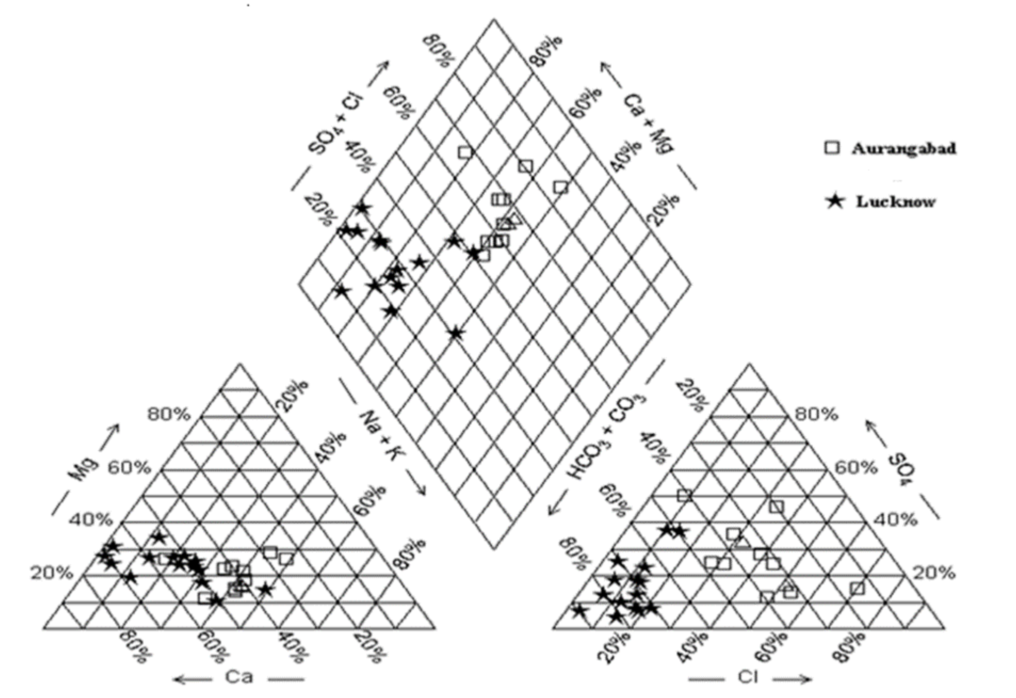

Fig 5. Piper diagram of ground water quality of Aurangabad and Lucknow

4. Conclusion

In Aurangabad the host rock type is basaltic which comprises mainly Quartz, Feldspar, Muscovite, Biotite, Olivine and Amphibole etc. The clay minerals (Biotite, Muscovite) are important because they provide very reactive surfaces and it releases Ca^{++}, Mg^{++}, SiO_2, HCO_3^- in the water aquifer. However, in Lucknow, an alluvial plane which is made up of mainly sedimentary rocks comprises Calcite, Quartz, Clays, Dolomite etc thus here also the dominant anion is bicarbonate HCO_3^- and calcium (Ca^{++}) and magnesium (Mg^{++}) are the dominant cations. This theory is supported by the results given in Table 5 which, shows that the dominant anion is HCO_3^- and cations are calcium (Ca^{++}) and magnesium (Mg^{++}) in the ground water of Aurangabad and Lucknow. Usually in ground water the Cl^- concentration is low but the Table 5 demonstrated that samples collected from the locations which are in proximity to industrial site or with in the industrial sites e.g. Chikalthana industrial area, paper mill, industrial area on the Jalna road, Aurangabad are showing excessive Cl^- concentration and Sodium Na^+ which is evidently shows the impact of paper mill and distillery on the ground water quality**.**

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A REVIEW ON SOURCES OF DYES, SUSTAINABLE ASPECTS, ENVIRONMENTAL ISSUES AND DEGRADATION METHODS

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Abstract

Dye an organic coloring substance has been used for ages and the most commonly used were indigo and turmeric. Natural sources of dyes were used until the 19th century but post industrialization use of synthetic dyes became more prevalent. Now more than 7500 dyes are used in various industries such as food, textile, pharmaceuticals, cosmetics and leather. Natural dyes are renewable and biodegradable so they are eco-friendly but to cater demand for huge population of the world, their production is not sustainable. Agricultural land is primarily required to feed the world population and if this will be used for the purpose of natural dyes it will surely create conflicts over land use applications. While considering the requirement of the huge population we started looking for synthetic dyes as a viable option. However, the uses of synthetic dyes by replacing the natural dyes have caused major concern towards the human health and environment. The use of synthetic dyes over a period of time has reported toxic effects which can cause hyperactivity in children and dermatitis. It also causes teratogenic and carcinogenic effects. It's environmental impacts can be soil pollution and water pollution which will disturb the ecology of aquatic system and will reduce carbon dioxide sequestration efficiency of various water bodies. Hence, it becomes necessary to remove or to reduce the concentration of dyes at various stages of its usage and in water bodies. The dye removal processes are numerous such as phyto-remediation, photochemical degradation, adsorption, filtration, ionic separation and many more, so they can be classified broadly into physical, chemical and biological methods of dye removal. Advancements have been done in their removal methods like the use of nanomaterials, activated carbon and sugarcane pulp. In this chapter we have discussed natural and synthetic dyes along with their sources, impacts on human health and various environmental concerns associated with them and methods for dye removal and degradation.

Keywords: synthetic dyes, health hazards, biotransformation, environmental impacts, dye degradation.

1. Introduction

The annual effluent discharge of about 0.4-0.5 million tones, containing dyes and its derivatives, flow into the water bodies and has been causing pollution, health problems and causing other environmental problems (Bhavsar et al., 2018). Generally organic compounds do not exhibit different colors like dyes. It is due to various reasons like dyes have at least one-color bearing groups which are chromophores, the light absorption by the dyes occur in visible spectrum, presence of alternate single and double bonds in their structure which gives them conjugated structure and a stabilizing force called resonance in electrons (Lyon, 2010). But the absence of any of the above properties causes the loss of color of a dye. The dyes consist of one or more compounds called auxochromes which are color helpers and have compounds like sulphonic and carboxylic acid along with hydroxyl and amine groups. The organic colorants corresponding to their solubility are of two types which are dyes and pigments. The dyes are soluble in organic solvents and water however; the pigment is not soluble in either of them. The largest family of organic dyes is azo dye and some other are acid dyes (used for protein and polyamide substrates), disperse (for hydrophobic substrates) dyes and reactive dyes (for cellulosic substrates) (Lyon, 2010).

The natural dyes based on chemical composition can be categorized as Indigoid dyes, Anthraquinone dyes (red color), Naphthoquinone dyes (henna, walnut shells), Benzoquinone dyes, Flavonoid dyes (yellow dyes have a hydroxyl or methoxy substituted flavones structure), Carotenoid dyes (orange color) and Tannin-based dyes (Saxena and Raja, 2014). The dyes on the basis of their origin can be categorized as natural and synthetic dyes. Natural dyes are extracted from natural resources includes plants, minerals, animals and microbial organisms like insects (Lyon, 2010). The chemical composition of natural dyes is a mixture of two or more chemical compounds unlike synthetic dyes. Plant based dyes are derived from various parts of a plant like fruits, flowers, roots, leaves, stems, heartwood, bark and husk. The blue colored dye is generally obtained from indigo plant, red colored dye from madder, morinda, safflower and yellow dye can be obtained from various plants like turmeric, saffron, annatto, barberry, myrobolan, marigold, kamala, weld, dolu. The red colored dye is extracted from insects which act as main source for dyes of animal origin. Tyrian purple which was used by royal family was the oldest dye of animal origin obtained from sea mollusk. Some colored secondary metabolites produced by a few bacteria also serve the purpose of dyes. The use of microbes for the production of dyes can be a better option as they can be grown under controlled conditions and on small surfaces. Fungi *Monascus purpurous* also provides pigments which were used for traditional food items (Saxena and Raja, 2014). India has a huge diversity of flora and fauna which can provide us raw materials for dye production and will add special aesthetic significance to that product. This will also provide an additional environment to handicraft and cottage industries (Tripathi et al., 2015).

The natural dyes are used to color textiles but for a few decades due to heavy load of population and its ineffective coloring, synthetic dyes have replaced a major portion of natural dyes (Saxena and Raja, 2014). The production of synthetic dyes is done in laboratory using various compounds like amines, toluene, benzene and naphthalene. Synthetic dyes can meet the demand of growing population while the production of natural dyes in huge amount will take a larger portion of flora and fauna. A small amount of synthetic dye is enough to provide a bright color however the natural dyes have limited range for various shades of different colors. Various metallic mordants used in synthetic dye production can also be a cause of concern that has health hazards and it also increases the dyeing time. The pure extracts used in natural dye synthesis may be suitable for machines but will make it costly and non-economical. However, the production of synthetic dyes is cost-effective and easy. Any secondary color can be produced by over dyeing, but change in pH can change the color of natural dyes, so color fastness is also a major concern in natural dyes. While the synthetic dyes are resistant to pH and various other factors that affect it are temperature, sunlight, biological attacks and chemicals (Saxena and Raja, 2014). The secondary metabolites produced by the plants are also used as a source of dyes and such colors would provide resistance against parasites and microorganisms. The natural colors also provide protection from harmful ultraviolet radiations. The natural dyes are obtained from natural biodiversity so they are eco-friendly, biodegradable, some have curative properties which are of medicinal values and their residues can be used in fields as a source of fertilizer. However, inefficient dye transfer to substrate, like inefficient dyeing procedures in synthetic dyes, inadequate and poor treatment of dyes containing effluents cause environmental pollution after it get mixed with water reservoirs and soil. It also impacts the human health as it may induce dermatitis, respiratory problems, other occupational hazards like mutagenicity and carcinogenicity as well as destruction to biodiversity (Saxena and Raja, 2014). The GOTS- global organic textile standard has recommended the use of synthetic dyes within safety limits and not to destroy the natural resources for dye extraction. So, the extraction of natural dyes cannot be a sustainable option by using natural resources when the whole world is facing the adverse impacts of climate change hence the synthetic dyes are preferred over natural dyes (Muthu, 2014; Chengalroyen and Dabbs, 2013).

In the effluents, dyes are present in various concentrations when these are discharged, the dyes are present in different concentration in the effluents due to various steps involved in the dyeing procedures and diverse variety of fabric used by various textile industries. The discharged waste water has concentration of dyes between 20 to 200 ppm (Gita et al., 2019). In our everyday life we use dyes at a very large scale such as in textiles, food additives, and cosmetic products and even in stationery like pens. When all these materials are discarded, it enters into our rivers and disrupts our aquatic system which reflects teratogenic, carcinogenic and mutagenic effects (Chowdhury and Saha, 2010). Synthetic dyes along with their toxic and carcinogenic effects decrease the intensity of light into the water bodies which interrupts the photosynthetic activity of phytoplankton and causes the decrease in dissolved oxygen (Gita et al., 2019). There are various studies on effects of dyes like when the dose of 4-aminobiphenyl dye was tested on mice in drinking water, it reflects the incidence of carcinogenicity in bladder, hepatocellular carcinoma and angiosarcoma, chromosomal instability and initiation of DNA damage in human lymphocytes (Lyon, 2010; Chen et al., 2003). The "International Agency for Research on Cancer" directs that dyes like benzidine are carcinogenic towards humans and other mammals. When reactive dyes are inhaled, bronchial problems occur and make a person prone to bladder cancer which was studied as an occupational disease (Lyon, 2010). Intake of sunset yellow dye causes gastro-intestinal problems and quinoline yellow dye used in pharmaceutical industry may cause itching, sneezing and hyperactivity in children upon its consumption (Chung, 2016). The consumption of methylene blue induces headache, high blood pressure and vomiting. However, the presence of toxic substances in the dyes causes serious health hazards like bleeding, skin ulcers, nausea and cardiac risks. In plants, dyes may cause oxidative stress, lowers the rate of photosynthesis and regeneration (Khandare and Govindwar, 2015). The synthetic dyes show harmful impacts on microbial world as well, such as slow down the bacterial luminescence and various azo dyes reduce the algal growth and cause mutagenic effects on various microbes (Lyon, 2010; Lade et al., 2015). So, change in color of water due to dyes can reduce the rate of photosynthesis among algae, phytoplankton and cause less carbon dioxide sequestration which can cause more global warming. According to the international standard for discharge of effluents into the environment, the biological oxygen demand must be less than 30 mg/l, chemical oxygen demand should be lower than 50 mg/l, pH can be 6-9, temperature can vary up to 42 degrees and suspended solids should be lower than 20 mg/l (Katheresan et al., 2018).To prevent the harmful effects of dyes various countries took various measures and Germany became the first country to prohibit the manufacturing and applications of specific azo-dyes. India, the Netherlands and a few countries have prohibited them but still synthetic dyes are used at large scale in various industries (Sanjeeda and Ansari, 2014). Indigo farming being introduced during the period of modern world left a large part of agricultural land as unfertile and also left Indian population without sufficient supply of food grains. But the introduction of artificial dyes to save the land, left people with respiratory problems, carcinogenic effects and also polluted marine life. So it becomes necessary to reduce or to remove the toxic effects of artificial dyes as we cannot completely replace them with natural one so as to serve the whole population. The removal of dyes takes place through various processes like physical, chemical and biological methods which are discussed ahead.

2. Removal Methods

The textile industries and various other industries release effluents which consist of variety of dyes and its derivatives. This leads to increase in biological and chemical oxygen demand of a water body, reduces the rate of photosynthesis and ultimately disrupts the biological balance and interrelation between various species. As per the world health organization report, the dyes show toxicity, mutagenic and carcinogenic effects on animals and microbes. So, it becomes necessary to degrade dyes and lowers their concentration in the environment. There are various methods for dye degradation like oxidation, adsorption, sedimentation, electrolysis, coagulation, sedimentation, neutralization, membrane treatment and bioremediation (Lellis et al., 2019). All these methods can be categorized into three groups for the ease of their study which are physical, chemical, and biological methods, which are shown below as different types of methods for dye degradation:

Physical methods

- Membrane Treatment
- Incineration
- Adsorption
- Coagulation and Foam Fractionation
- Sedimentation
- Floatation
- Catalysis, Reduction Neutralization, Oxidation

Chemical methods

- Catalysis
- Neutralization
- Reduction
- Photochemical-Oxidation
- Ion Exchange
- Electrolysis

Biological methods

- Microbial remediation
- Phyto-remediation
- Enzymatic remediation

2.1. PHYSICOCHEMICAL METHODS

This includes several conventional methods such as adsorption, oxidation, coagulation, flocculation etc. which are mostly used at various small scale industries. Nowadays combinations of various processes are utilized for dye removal called state of the art technologies, which include processes like membrane separation, photochemical, ultrasonication and electrochemical processes. The conventional methods are now used in combination with various new adsorbents and coagulants which enhance the efficiency of older methods (Arslan et al., 2016). However, such techniques also have disadvantages like incomplete combustion during incineration which causes the production of dioxins and furans (Hassaan and Nemr, 2017).

2.1.1. *Adsorption*

It is the most commonly used method for wastewater treatment and is based on surface phenomenon. This method doesn't require much training and efficient skill power in terms of its ability to separate both dissolved and undissolved chemical compounds. Here contaminants get adsorbed on the surface of the adsorbent materials like active carbon which provides larger surface area for adsorption (Arslan et al., 2016).

2.1.2. *Coagulation and flocculation process*

In this process coagulating agents are used to destabilize the colloidal material which later forms small aggregated particles with polymers. The large particles are removed by methods like sedimentation and the most commonly used inorganic coagulant is aluminum sulphate (Arslan et al., 2016).

2.1.3. *Advanced oxidation process (AOP*)

The wastewater treatment techniques required for removal of dyes and purification of water are also becoming a major concern to improve the quality of treated waste water. In this method oxidation of organic pollutants present in effluents occurs which produces hydroxyl free radicals. These free radicals produced by using oxidants destroy the compounds which were not destroyed by conventional oxidation method. The AOP can be used in combination of various other processes like ozone, ultraviolet, photo-fenton and hydrogen peroxidases for better results. This process results in mineralization of dyes and also low waste generation technology because of its high oxidation power (Hassaan and Nemr, 2017).

2.1.4. *Ion-exchange method*

This is a reversible interchange of ions between solid and liquid, while the structure of solid doesn't change. The ion exchanging material is solid while the effluents are ion containing materials out of which ions as contaminants are extracted. The ion exchangers are cationic and anionic where the cations are exchanged by weak acid cation exchange resins (Arslan et al., 2016).

2.1.5. *Membrane processes*

In this method permeable and non-permeable membranes are used to remove the contaminants or dyes from the wastewater. For various types of separation processes, membranes of different pore sizes are used such as for nanofiltration, microfiltration (for suspended solid particles) and ultrafiltration (for separation of macromolecules). The major benefit of this method is very less use of chemicals but, after some time pores of the membranes get clogged which can cause fouling and may hamper the efficiency of this process (Arslan et al., 2016).

2.1.6. *Photochemical oxidation*

It is an advance oxidation method, which can also be used to produce highly reactive radicals like hydroxyl radicals. These highly reactive radicals then degrade the dyes and can also be performed under sunlight (Arslan et al., 2016). The use of chemicals in various methods would help in dye removal but later the coagulation of chemicals becomes another problem as sludge. Photo-Fenton process has been used extensively for treatment of reactive dyes and mineralization occurs along with oxidative degradation of dyes (Hastie et al., 2006).

2.2. BIOLOGICAL METHODS

The effluents from various industries like textile, pharmaceuticals have organic and inorganic compounds. Textile industries that majorly produce biodegradable organic compounds can be mineralized with the use of plants and microorganisms such as fungi, bacteria and algae (Arslan et al., 2016). In a plant, various parts plays an important role in phytoremediation, like roots, shoots, leaves and provide an environment to the microorganisms to grow which also play an important role in dye degradation. The plants having deep and fibrous roots with faster growth rate are preferred to dye degradation such as annual herbs, creepers and grasses. Water hyacinth also shows better efficiency for degradation of dyes especially methylene blue and methyl orange (Tan et al., 2016). The microorganisms, through mineralization help in dye removal and other harmful metal ions. The microbes like algae, bacteria, fungi and cyanobacteria utilize organic dyes as a source of their nutrient in their growth and cause degradation of dyes present in effluents. The process performed by the microbes for dye removal can be anaerobic, aerobic or combination of both (Kandelbauer and Guebitz, 2005)**.** Various parameters need to be maintained to provide optimum growth condition for the microorganisms such as dye concentration, temperature of the medium, aeration and homogenization, pH, oxygen transfer levels, incubation period, holding time, supplements like carbon, nitrogen and inoculums size (Bhavsar et al., 2018).

The microbial degradation in few cases becomes less effective due to the presence of refractory compounds that are biologically hard and non-biodegradable. So, in those instances degradation by microbes can occur in synergy of various other physical and chemical methods. When the degradation of dye caused by different strains of an individual species of a microorganism likes algae or bacteria then they attack on dye at different sites and at different bond positions. This would play a crucial role in complete mineralization of dyes in wastewater (Arslanet al., 2016). The process of bioremediation can be improved by some biotechnological tools and techniques that would enhance the degrading efficiency and makes them resistant towards harmful dyes.

3. Bioremediation of Dyes

Bioremediation of dyes follows either of the two pathways biodegradation process or biosorption process. The biodegradation involves breakdown of dye compounds or contaminants into small size molecules called mineralization. The process mineralization refers to the conversion of organic compounds into different mineral forms which contain carbon dioxide or methane and inorganic compounds present in that original structure. The biosorption process is the uptake of dye molecules or contaminants with the help of dead or inactive biological materials (Singh, 2015).

3.1. PLANTS

The degradation of dyes when performed by plants is referred as phytoremediation. Phytoremediation is the process to degrade and detoxify the contaminants from air, soil and water with the help of enzymes and microbes associated with a plant. This adaptability in plants to remediate the contaminants makes them autotrophic bioreactors to combat the environmental stress. Various plants do phytoremediation by using different principles such as rhizofilteration, phytoextraction or phytoaccumulation, phytodegradation and rhizodegradation. When degradation occurs without the use of soil but with the help of plants in water for dye degradation it is termed as hydroponics system (Lellis et al., 2019).

Table 1: Biotransformation of various plants caused biodegradation of dyes (Imron et al., 2019; Morad and Ooi, 2016).

PLANT	DYE DEGRADED
Nasturtium officinale (Brassicaceae)	Basic Red 46
Pennisetum purpureum (Poaceae)	Poly R-478
Tagetes patula (Asteraceae)	Red 198
Sesuvium portulacastrum (Aizoaceae)	Reactive Green 19A-HE4BD
Blumea malcolmii (Asteraceae)	Remazol Red, Red HE8B, Methyl Orange, Red Reactive 2, Red HE 7B, Golden Yellow HER and Scarlet GDR
Medicago sativa L.	Azo dyes
Sesbania cannabina Pers	Azo dyes
Eichhornia crassipes	Methylene blue (MB) and methyl orange

The process of phytoremediation can be monitored by the study of hairy roots; callus and cell suspension culture which also helps to understand the metabolism and toxicity tolerance of plants (Lelliset al., 2019). The roots of plants are known to produce secondary metabolites so they will store the contaminants or dye in their roots. These roots then can be used to study and research about the tolerance and mechanism of different plant species against dyes and other pollutants or contaminants. So, the hairy roots of plants can be biotransformed like incase of *Tagetes patula* (Asteraceae) which was mediated by *A. rhizogenes*. This causes the stimulation to the production of lignin peroxidases, Mn peroxidases, tyrosinases and azoredutases which lead to the biodegradation of textile dye Red 198. Various plants are biotransformed to enhance the efficiency of biodegradation and some are mentioned in the above table. The consortia of plants and rhizospheric microorganisms are used at a large scale for phytoremediation of wastewater. In the consortia, different microorganisms such as algae, fungi, bacteria interact with different dyes at different bond which helps in complete degradation of effluents or contaminated water. Hence it is environmentally sustainable to degrade dye through phytoremediation alone or in the consortium system, as it does not require much substrate for the growth and presence of abundant biomass (Lellis et al., 2019).

3.2. MICROORGANISMS

The microbes such as algae, bacteria, fungi and cyanobacteria do bioremediation of effluents or wastewater through biostimulation or bioaugmentation by in-situ transfer of the microorganisms. This is called in-situ-bioremediation while the microorganisms already present in the wastewater also cause bioremediation. Ex-situ bioremediation is remediation with the help of bioreactors, bio-transformed plants and microbial consortia, composting or land farming.

3.2.1. *Bacteria*

Degradation occurs in two phases, anaerobic phase and aerobic phase. The anaerobic phase consists of reduction and pyrolysis which leads to decolorization of dye with the production of aromatic amines as harmful end products. In the second phase, aerobic bacteria utilize these amines for protoplasm synthesis and produces carbon dioxide and ammonia (Gao et al., 2018). In bacterial degradation, two processes play very crucial role which are adsorption and biosorption. The biodegradation of azo dye starts with the breakdown of azo bond (N=N) which is supported by some enzymes such as azoreductase, peroxidase and Malachite green (MG) reductase. The organic dye when mineralized, then carbon and nitrogen serve as a nutrient source for the bacteria which makes them good biosorbent material for biodegradation. The degradation process here starts with the interaction between dye and dead or living bacterial biomass due to the electric charges present on them to cause adsorption (Srinivasan and Viraraghavan, 2010). Bacterial degradation can be enhanced by using pure culture and hybrid absorbents (Lellis et al., 2019). The biodegradation by various species of bacteria are shown in the table 2.

Table 2: Different bacterial species which degraded various dyes

Bacterial species	**Dye**	**Reference**
Streptomyces DJP15	Azo blue	(Pillai, 2017)
Aeromonas hydrophila	Triarylmethane dye	(Ogugbue and Sawidis, 2011)
Brevibacillus laterosporus MTCC2298	Navy blue 3G	(Pillai, 2017)
Klebsiella oxytoca NR041749-1 and *Klebsiella* spp. DA26	Methyl Orange	(Da26, Radhakrishin and Saraswati, 2015)
Aeromonas punctata and *Shewanella putrefaciens*	Azo textile dyes Acid Red88, Reactive Black 5, Direct Red 81 and Disperse Orange3	(Khalid et al., 2008)
Pseudomonas aeruginosa	Navi-tan Fast Blue S5R	(Nachiyar&Rajkumar et al., 2003)
Aeromonas hydrophila	Crystal Violet dye	(Bharagava et al., 2018)
Proteus vulgaris and *Micrococcus glutamicus*	sulfated textile dye GreenHE4BD	

Nanoparticles generated by the bacteria can be used for biodegradation, under anaerobic conditions by an electron transfer system between the textile dye acceptor and hydride ion donors (Singh et al., 2017).When the co-culture, hybrid culture and consortia (bacteria and fungi) are used, the efficiency of biodegradation get enhanced as various microorganisms act upon different bonds of a dye (Lellis et al., 2019). Such systems can be used as microbial fuel cell to generate electricity; however, the toxic compounds produced during such processes should be monitored.

3.2.2. *Fungi*

Mycoremediation is the decolorization of dye due to the action of fungi to make them less harmful to the environment. The fungi perform bioremediation under the mechanisms such as biosorption, bioaccumulation, adsorption, enzymatic degradation and combination of them. In this method less sludge is generated as compared to the other methods of bioremediation. The fungal strain also produces some extracellular enzymes such as laccase and lignin peroxidase. These enzymes may enhance the efficiency of fungal degradation and possess capability to degrade molecules of dye and toxic compounds. The presence of ligninolytic enzymes in the fungal environment (*Phanerochaete chrysosporium* and *Trametes versicolor*) served to degrade various dyes such as azo, heterocyclic, reactive or polymeric dyes from wastewater (Sen et al., 2016). Some dyes are resistant to bacterial degradation like sulfonatedphthalocyanine but such dyes were reported to get degraded by fungi. The fungi provide large surface area for adsorption and its metabolic activities help it to sustain in high temperature conditions. In some cases of mycoremediation, biosorption and biodegradation occurs together like in case of *Aspergillus flavus* A5p1 and due to this it was used to decolourize at least 15 dyes (Reemtsma and Jakobs, 2001).

3.2.3. *Algae*

An alga performs the function of decolourization of dyes called mineralization through the process of biosorption and adsorption. The degradation of dyes using algae is called Phyco-remediation which can be done with the help of dry and wet algal biomass. An alga uses the organic dye as a source of substrate for its growth which leads to the removal of colour from a dye. The dry biomass is a good example of biosorbent which has high binding efficiency and large surface area for the absorption of dyes (Pathak et al., 2015). When the algae are exposed to the high concentration of dyes their specific growth rate and pigment concentration get reduced (Gita et al., 2019). The cell wall of algae acts as a site for electrostatic attraction and plays a vital role in the process of adsorption. Various researches have been done to study the interaction of algae with dyes such as removal of reactive dye was performed by using dead biomass of *Spirogyra*. The bioconversion of colour has also been reported with the use of *Chlorella vulgaris*, in which the colour of mono-azo dye changes due to its conversion into aniline (Pathak et al., 2015). It was reported that macrophytes *Lemna minor* can cause 80% degradation of Acid blue 92 dyes within six days (Imron et al., 2019). The ability of biodegradation can be improved by the use of certain enzymes like Azoreductase, which facilitate the reductive cleavage of azo groups and degrade the dye by decolorizing and making it less harmful (El-Sheekh et al., 2009). It was reported that *Lemna minor* can tolerate high concentrations such as 200-300 mg/l of Triphenylmethane dye and can absorb Crystal violet and Malachite green by accumulating them in its cell wall (Török et al., 2015). Cyanobacteria have also been reported to cause degradation of dyes and consortia of cyanobacteria and algae can be used for bioremediation.

3.2.4. *Derived Products or Enzymes*

Mineralization is the degradation of organic compounds such as dyes into carbon dioxide and inorganic compounds by reductive cleavage which make dyes less harmful to the environment. An azo-reductase enzyme can carry out this reductive cleavage by a direct mechanism or indirect mechanism (Pathak et al., 2015). In the direct method, it would interact with the dye molecule through the transfer of electrons and in the indirect method coenzymes help in the transfer of an electron from the enzyme to the dye compound. The coenzymes such as adenine dinucleotide (FAD), Nicotinamide adenine dinucleotide (NAD^+), flavin and many more also help to accelerate the degradation of dyes (Guo, 2010; Senet al., 2016). When these coenzymes get oxidized, receive the electrons from azo-reductase enzyme and through reduction, NADH and FADH formed. They can transfer back to their native state by donating the electron to the dye molecule. Laccase enzyme helps in the degradation of polycyclic aromatic hydrocarbons, sulfonated aromatic amines, anthraquinonic dye Remazol Brilliant Blue. This enzyme causes the breakdown of the chromophore group and decreases their molecular weight which is not considered harmful. This method produces free radicals and helps to remove contaminants or dye molecules. The disadvantage of carrying bioremediation through enzymes is that the enzymes through the action of inhibitors may become adaptable to inactivation in severe conditions such as contaminated water. However, biotransformation can be done by expressing the gene of interest in the host microorganism to improve the efficiency of enzymatic bioremediation (Pathak et al., 2015).

4. Conclusion

Clean water is the basic need of civilization as mentioned in our sustainable development goals. However, the daily discharge of effluents into the water bodies from various industries particularly textile, food and pharmaceuticals make it unfit for domestic use. Here we have discussed the dyes and its sources, sustainable issues and methods to remediate them. Dyes include synthetic and natural dyes, as their name suggests they are synthesized from chemicals in laboratories and from natural sources like plants, insects, microbes and minerals respectively. The natural dyes are ecofriendly but unable to meet the demand of the population at a time when there is global call for climate action. But in some instances, flower waste of temples can be used to synthesize dyes and the residual biomass can be used in agricultural fields. The synthetic dyes are mostly organic compounds but they are harmful to the environment and humans as they can raise the BOD and COD of water. In order to mitigate the detrimental effects of dyes various physical, chemical and biological methods are available. But biological methods are often preferred over other methods as it involves natural processes and in chemical methods, a lot of sludge gets produced and in membrane method, the chances of clogging of membrane pores are obvious. Biotransformation plays a vital role in making phytoremediation more efficient method however when the remediation occurs with the help of algae, fungi, bacteria and the consortia system, then use of enzymes such as azoreductase, peroxidases enhance their remediating capacity. Biotechnology plays a crucial role in improving the biological methods and to make them more effective to combat the harmful effects of various compounds in order to improve the quality of life.

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