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Review Article *Natural Resource Management*

Bioremediation Trends on Mitigation of As(III), Cr(VI) and Organic Dyes From Aqueous Medium using Plant and Microbial Biomass: An Overview

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Abstract

Arsenic, chromium and organic dyes are the prominent carcinogenic agents, posing a serious health hazard. In current scenario, groundwater as well as surface water mostly contaminated by chemical complexes of As (III), Cr (VI) and organic dyes, these are leading hazardous threat to eco-system. Several mitigation techniques of As (III), Cr (VI) and organic dyes are available but efforts are going on to devise a novel method of removal of these toxicants. This review takes into account all the recent advances in the detoxification of contaminated water exploring removal mechanism by biosorption and bioaccumulation. The possibility of the removal of toxic heavy metals from an aqueous medium by plant and bacterial biomass has been discussed. Now a days, bioaccumulation and biosorption from plants and microbial sources has emerged as simple, effective and eco-friendly techniques for decontamination of these chemical compounds from water resources at very low cost. Many agricultural products and solid wastes have also been found suitable decontaminant of toxic heavy metals and dyes. A wide spectrum of medicinal and aromatic plants as well as aquatic plants available in abundance may also be utilized as potential remover of As (III), Cr (VI) and organic dyes. This article explained mechanism and application on detail aspects of bioremediation technology including conventional techniques with recent development. This review shows the trends and development of mitigation stretagies by bioremediation with latest updates.

Keywords: Arsenic, bioaccumulation, biosorption, chromium, organic dyes

1. Introduction

Water is distinctive from all substances naturally found on earth because water has a unique property to renew and clean itself by the water cycle. In this process, pollutants settle out or break down, but this method is time taking. Heavy metals, metalloids and dyes present in higher concentrations in water resources are posing a serious problem to the entire eco system. The presence of Arsenic(III), Chromium(VI) and Organic dyes in water bodies affectsthe entire food chain and raises serious health issues due to their toxicity and carcinogenicity. Arsenic and chromium are listed as one of the major carcinogenic agents globally (Jha and Gupta, 2017; Jha and Kumari, 2021).

The quality of life on the earth depends upon the overall quality of the environment. In recent years water resources have been contaminated by

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different heavy metals and different dyes discharges. Arsenic (III) and Chromium (VI) are the main metallic contaminant that dissolves in water resources by natural or anthropogenic activity. The major amount of water consumption is based on groundwater resources or river water. In the last few decades, groundwater has been contaminated due to natural as well as industrial release of Arsenic(III), Chromium(VI) and organic dyes. Arsenic and Chromium contamination in water resources has become a hazardous environmental challenge worldwide, as reported by different countries. The Gangetic basin has also been widely affected by these metallic contaminants (Oliveira et al., 2008). The population of the Gangetic basin region has not been just drinking the contaminated water, but also using this water for crop irrigation. Arsenic is a naturally occurring metalloid that is widely distributed in water, soil, air and biota from natural and anthropogenic sources, while Chromium is the 17th most abundant element of the earth's crust (Singh, 2015). One of the important sources of chromium is the occurrence of different types of ores of chromium present in nature. One of the important ores is chromate in serpentine rocks. The ores of chromium may be complexed with other metals. The most important oxidation state of chromium is (VI). Out of (+III) and (VI) oxidation state of Cr, Cr(III) is the inactive state. Cr(0) produced in industry and solid with high fusion points is usually used for the manufacturing of steel and other alloys. Cr(VI) in the form of chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) is considered the most toxic form of Chromium, as it possesses high oxidizing potential, high stability, and mobility across the membranes in living organisms and the environment. Hexavalent chromium is soluble in water and so migration of Cr(VI) ion takes place in the aqueous medium. Cr(III) is inert in comparison to Cr(VI) and remains in soil bound with humus. Cr(III) has thus lower mobility in aquatic medium and so less detrimental to health in comparison to Cr(VI) (Avudainayagam et al., 2003; Zayed and Terry, 2003).

There are a number of organic dyes which adversely affect aquatic life. Some of the organic dyes worth mentioning are malachite green, methylene blue, crystal violet which find their way in water bodies through effluents and thus have become a matter of great concern for the environment. The effect of such dyes is depletion of depleting dissolved oxygen but make a biological change also. Moreover, some dyes and their degradation products may be carcinogenic and toxic (Tang et al., 2012; Blackburn, 2004). Therefore, it is necessary to treat the dye effluent prior to the discharge into the river. As a result, serious efforts of researchers all over the world focused on the field of pollution control and management.

In view of the above statement and management of groundwater as well as other water resources like surface water quality has become essential. Some of the traditional methods being adopted for remediation are electrocoagulation, electrolysis, ion exchange, adsorption from active charcoal and bone charcoal process (Shi et al., 2007; Adam, 2001). This article explains all aspects of bioremediation of As(III), Cr(VI) and organic dyes which provides information about various plants and bacterial biomass as a mitigator of heavy metals.It also explains the research trends and developments of bioremediation. This review paper explains bacterial biosorption as well as phytoremdiation alongwith the fundamental mechanism.

2. Arsenic, Chromium and Dyes in the Environment

2.1. Arsenic

Arsenic is a metalloid introduced into groundwater and soil through weathering of rocks and minerals followed through the leaching of runoff. It also enters in the environment through anthropogenic sources (Ngah and Hanagiah, 2008). Natural arsenic is commonly associated with metal ores is of copper, lead, iron and gold (Anonymous, 2014). It has been reported that groundwater of Ganga–Brahmaputra–Meghna basin are widely affected by arsenic contamination and there is no exact finding of the natural emission of arsenic in the Gangetic plain but many researchers estimated that the release of arsenic in the environment through natural processes are occurring from holocene sediments comprising sand, silt and clay (Jha and Mishra, 2012).

It is found in four inorganic oxidation states i.e. +5, +3, 0 and -3 in which arsenic tri valent (III) and arsenic penta valent (V) are most common in nature (Satyapal et al., 2016). Inorganic occurrence in groundwater is a serious menace worldwide like flood and delta plains of Mekong River in Laos and Cambodia (Poyla et al., 2005). Indus river of Pakistan (Iqbal, 2001), Upper end of red river delta in Vietnam (Berg et al., 2001) and Irrawaddy delta in Myanmar (Mandal et al., 1996) including Gangetic basin (Nickson et al., 1998) Arsenic is introduced into the aquatic environment through natural and anthropogenic sources. However, majority of arsenic contamination is due to natural sources because arsenic is found as a major constituent in more than 200 minerals (Petrusevaki et al., 2007).

There are a number of findings and hypothesis regarding the source of arsenic and possible reasons for the occurrence of groundwater (Ghosh and Singh, 2010; Kumar and Jha, 2020). Arsenic contamination in groundwater in India has also been reported as natural groundwater calamity to the population. It was initially reported from West Bengal in 1983. Groundwater arsenic contamination occurs in a wide range of the Gangetic plain of India., which shares its boundary with Nepal and Bangladesh, Panjab, West Bengal, Bihar and Assam are severely affected by this problem. Bihar and West Bengal are the worst affected arsenic contaminated states of India due to their siltation in the middle Gangetic plain (Singh et al., 2015).

Total 89% of the geographical areas are covered by the middle Gangetic plain (~94,000 Km^2) that holds potential alluvial aquifers. These middle and upper Gangetic plains covering the upper stream part from Rajmahal hills, are highly affected by arsenic contamination (Saha, 2009).

2.2. Chromium

Chromium enters into various environmental matrices mostly in Cr(III) and Cr(VI) forms. The behaviour of chromium in the environmental system is affected by the oxidizing and reducing condition in the environment and their mobility in an aqueous medium (Gary et al., 2001). Cr(III) is stable and immobile, hence its bioavailability decreases. Literature reports the presence of inorganic species of chromium in both oxidizing and reducing environments at different pH. The type and condition of the soil are responsible for the dynamic exchange of chromium forms, like pH, presence of organic matter, micro-organism, Fe (III) and Mn oxides in the soil horizon (Langlois and James, 2015). The solubility of chromium depends upon the pH of the environmental system. Cifuentes et al reported that above pH 7, chromium oxides (Cr_2O_3) and hydroxides ($Cr(OH)_3$) are formed which settles. At pH 7 Cr_2O_3 and chromium hydroxide $Cr(OH)_3$ are formed which disrupts the mobility of $CrOH^{2+}$ and Cr $(OH)^{2+}$ (Cifuentes et al., 1996; Hansel et al., 2003). Electron donor organic matter may form complex with Cr (III) even in an acidic environment and alter the solubility of Cr(III). These complexes are considered to be insoluble in terms of their bioavailability (Barlett and Kimble, 1976; Remoundaki et al., 2007). Although the complexes themselves are soluble at acidic to circum neutral pH (Sinha and Bhattacharyya, 2017; Rai et al., 1987).

Chromium is categorized to be environmentally toxic element and classified as a class-A human carcinogenic (Dhal et al., 2013; Dawodu et al., 2019). It has been considered as an environmental hazard by environmental protection agencies as one of the 129 priority pollutants and of the 14 most noxious heavy metals (Sharma et al., 2012). Naturally, chromium is found as Cr(III), Cr(V) and Cr(VI) in which Cr(V) is chemically inactive in nature while Cr (III) and Cr(VI) are widely distributed in nature (Al–Othman et al., 2012). Its contamination is increased in the environment due to rapid industrialization because the application of Cr(VI) is widely used in industrial processes including leather tanning, mining, metal processing, smelting operations, electroplating and pigment manufacturing (Karthikeyan et al., 2012). All these circumstances state that Cr(VI) contaminate and affect the environment through anthropogenic sources then natural emission, despite these, it enters into aquatic environment through some natural sources because it is naturally found in earth crust as hard, steel grey metal from chromate ore (Jobby et al., 2018).

Cr(VI) has been reported as the second most metallic contaminant in groundwater worldwide. The high concentration of Cr(VI) in soil and water bodies has become a major issue and threat to health and the environment (Singh et al., 2013). Tata Environmental Research Institute reported that the industries generated 7.2 million tons of hazardous waste per year in India, in which 5.2 million tons of hazards are improperly disposed off. Kanpur district of Uttar Pradesh in Indian state is a hub of industrial manufacturing and leather tanneries that produce Basic Chrome sulphate (BCS). Centre Leather Research Institute, India state that only 170 registered or officially recorded tanneries at Kanpur, while studies conducted in these areas find more than ~350 tanneries in just one tuning cluster (Schjolden, 2000). All these Chromium containing industrial waste is directly dumped in deep boring, open land and river. Another research reported that India alone releases about 2000–3000 t of Chromium into the environment annually from steel and leather tuning industries. These effluents contain 2000 to 5000 ppm concentration that exceeds the permissible limit of 0.05 ppm (Manivasagam, 1987). In South India roughly it is estimated more than 50,000 ha of productive agricultural land have been contaminated with Cr(VI) due to tannery effluents (Mahimairaja et al., 2000).

2.3. Organic dyes

Organic dyes used in huge amounts in textile industries are one of the critical environmental problems worldwide. Dye pollutant causes great concern to harm the human and environment (Dubey et al., 2010). A large scale of industrial development leading to the production of the huge amount of dyes effluents in India creates hazards for aquatic eco – system and environment. The great number of synthetic dyes used in textile and other industries are generally driven from organic bases. They are also called cationic dyes as they ionize in water producing coloured cations (Dubey et al., 2010). In India, the textile industry contributes 15–20% of dye effluents that lead to contaminate water resources and the environment. These dyes are consequences of high amounts of chemicals such as amine, azo, nitrile, sulphuric acid, acetic acid, chromium and other metals toxic compounds in their effluents (Cirini, 2006; Swami and Budhi, 2006).

The textile industries have always had a major involvement in the field of industrial production. In recent years due to development in textile industries, the dye discharge has increased unexpectedly (Vijayalakshmi, 2016). Organic dyes are the largest pollutant in the aquatic eco-system.

These compounds are widely used in various industries such as paper, textile, plastics, rubbers, foodstuffs and cosmetics to colour their products (Chowdhury and Viraaraghavan, 2009). Organic dyes belong to the synthetic compound category having aromatic structure and recalcitrant to biodegradation due to xenobiotic nature. Textile dye stuff has been grouped into 12 categories on the basis of their general chemistry. To understand its property, they may be mentioned as direct dyes, acid dyes, disperse dyes, azo dyes, reactive dyes, sulphur dyes, basic dyes, chrome dyes, oxidation dyes, solvent dyes, fluorescent dyes and vat dyes (Gita et al., 2017).

These dyes lead to hazardous impact on aquatic environment and health because it has high thermal and photostability to resist biodegradation. Therefore, it remains for long period in the environment. Some aromatic compounds, amino acids and azo dyes are responsible for carcinogenic effects in humans due to high concentration in water resources (Baan et al., 2008). The presence of organic dyes in the aquatic environment may cause disfunction of the liver, kidney, reproductive system, central nervous system and brain in the human population (Adegoke and Bello, 2015; Kadirvelu et al., 2003; Shen et al., 2009) because even a small quantity of organic dyes in water resources can be highly toxic for entire ecosystem (Lee et al., 2006; Ibrahim et al., 1996; Wijetunga et al., 2010). About 40% of organic dyes used worldwide contain organically bound chlorine which is also responsible for cancer. Chemical evaporation and dyes through contaminated water resources into the air may be adsorbed through our skin. These contaminations may harm children even before birth (Adegoke and Bello, 2015; Bains and Sethi, 2017).

It is roughly estimated that 10,000 dyes and pigments are extensively used globally. It is estimated that about 10–14% of the total used dyes may be found in dye effluents. These are considered to be toxic and recalcitrant. It resists microbial degradation so it is not easily biodegradable in water resources. Therefore, dyes drastically decrease the concentration of oxygen in water resources due to the presence of hydrosulphide. It blocks the passage of light through water resources which lead to decreased photosynthesis in aquatic plants (Gita et al., 2017; Kant, 2012).

3. Conventional Methods for Mitigation of Metal/Metalloid and Dyes from Water Resources

3.1. *Chemical reduction*

Water and soil contaminating ions such as arsenate, chromate and organic dyes ingredient have the least tendency for precipitation and cannot be removed successfully by another removal technique because they are selective for adsorption. To short out these problems many chemical reducing methods have been developed by researchers i.e. 1, 3 – benzenediamidoethanethiol dianion (BDET) (Matlock et al., 2002) has been developed and find that irreversibly bind heavy metals from aqueous medium. There are several chemical based reducing agents studied such as carbon based, iron based, photocatalytic nanomaterials. But these methods are costly and complicated. Another example of the chemical reduction process is the use of consumable iron electrodes and electric current for removal of Cr(VI) while sodium borohydride has been studied to be effective in the removal of arsenic and other ionic contaminates (Kiff, 1987).

3.2. *Cementation*

Cementation is a metallurgical process in which heavy metals/ metalloids are displaced from an aqueous medium by metal higher in the electromotive series. Cementation of metallic contamination from waste water includes both hydro and environmentally suitable metallurgical methods to remove metallic contamination from water. Alkaline leaching of the method of electric and furnace dust has been reported for many metallic removals (Orhan, 2005).

3.3. *Solvent extraction*

Solvent extraction is a heavy metal separation process from waste water. This method can be carried out by two methods – first is on–site, in which extraction set up is incorporated into the process and second is, Central extraction unit, in which different contaminated samples are brought from different contaminated site and mixed it before treatment (Cerna, 1995; Li et al., 2017). In solvent extraction of As(III) by spent electro fining sulfuric acid solution, As(III) exists into two hypothetical weak acids AsO_2 and H_3AsO_3, As(III) exists in the form of AsO^+ in strong acid solution. Recovery of As(III) from water through various reagents has been proposed by this method (Majumdar and Jha, 2020). Removal of Cr(VI) from aqueous sources by solvent extraction has been reported by aqueous acidic solutions using tri – n – butyl phosphate (TBP) in Kerosene (Zhang et al., 2007).

Organic dyes also have been successfully separated from wastewater resources from solvent extraction methods. The use of reverse micelles is reported as one of the solvent extraction applications. In this method, the dyes are in the aqueous core of reverse micelles that are present in the organic phase. These organic phases are afterward separated from the aqueous solution leading to notable removal of dyes. This mechanism follows the electrostatic interaction between oppositely charged particles (Pandit and Basu, 2002).

3.4. *Electrodeposition*

Electrodeposition is one of the established processes to decontaminate heavy metals from waste water. In this method oxidation occurs on sacrificial anode and reduction occurs at the cathode in an aqueous solution when current is applied. Electrodeposition is an electrochemical application that uses an electric current to remove metals from solutions. The metallic and dye contamination in wastewater is maintained in solution by electrical charges, when metallic ions and charged particles of dyes present in contaminated water are neutralized with ions of opposite electrical charges supplied by electric coagulation system, they become destabilized and participate in a stable form (Mahapatra et al., 2019). It has been reported that arsenic, chromium and textile dyes such as methylene blue, malachite green and many other heavy metals have been successfully removed by electrodeposition using graphene composition (Verduzcoa et al., 2019).

3.5. *Reverse osmosis*

Reverse osmosis is a membrane–based filtration technique. It is generally used in drinking water filtration. But it is also successfully implemented on the removal of heavy metals and dyes from contaminated wastewater sources (Yoon et al., 2009).

Reverse osmosis has two different types, i.e. nanofiltration unit and hyperfiltration, in which nanofiltration works on relatively low pressure and removes primarily large dissolved solid as compared to hyperfiltration. Hyperfiltration works at higher pressure with a higher removal efficiency of all dissolved ions (Kartinen and Martin, 1995).

4. Biosorption Technology

The above mentioned conventional method for mitigation of arsenic, chromium and dyes from an aqueous medium is often expensive to maintain their chemical parameter and operational cost.

Biosorption is highly efficient and selective at a low cost that involves physical and chemical adsorption. Electrostatic interaction, ion exchange, chemical adsorption, chelation, complexation and microprecipitation also play an important role (Okenicova et al., 2016). Biosorption takes place in the cell wall of the biomass of plants, algae, bacteria and different natural materials. It precedes the anaerobic and aerobic biodegradation process.

It is a biotechnological physicochemical approach, independent from metabolism and utilizes the mechanism of adsorption, surface complexing, ion exchange and precipitation process that is spontaneous. It works as the passive adsorption of heavy metals or toxic ions by biologically dead or inactive substances to decontaminate the environment (Pagnanelli et al., 2009, Jha et al., 1015). These techniques are accepted for all metabolic and energy dependent processes of the cell membrane. Despite this, bioaccumulation is defined as the phenomenon of absorbing contaminants by living organisms including plant and microbial species in which metallic contaminant ions are actively or passively transported into cells. It is transported and accumulated inside them. It may enter in the metabolic system through the cell membrane. Therefore, bioaccumulation is generally a cell metabolism dependent process (Gadd, 2004).

While biosorption of heavy metals and other aquatic contaminant such as organic dyes separated due to the presence of functional groups at biosorbent surface, this mechanism is dependent on ion exchange, physical and chemical adsorption. All these mechanisms are not related to metabolism (Ribeiro et al., 2015).

The first research article on biosorption techniques was published in 1951, and since then many efforts have been made to implement, effective and efficient biosorbent to remove metallic stress from water resources (Volesky, 1990). Although, the massive research concerning these technologies is an unsurprising fact, in fact, this technique has been discussed in the literature for 60 years with over 13,000 scientific papers in peer–reviewed journals (Matlock et al., 2002). But, the majority of research has been conducted on a laboratory scale using either batch operation or column experiment and it has not been successfully implemented on field or industrial scale (Joo et al., 2010). Although, biological materials have ability to adsorb heavy metals from wastewater through metabolically mediated use of ATP or spontaneous by a physicochemical process of uptake that is without the use of ATP (Joo et al., 2010; Gabr et al., 2008; Hassan, 2009). Advantages of bioremediation or biosorption techniques are such as the minimum ratio of disposal sludge volume, low operation cost, technically easy to operate, no need for chemical reagents and ability to detoxify very dilute effluents, etc. (Choudhary and Sar, 2009; Volesky and Schiewer, 2000; Valls and Lorenzo, 2002).

The biosorption techniques have lots of advantages that attract researchers to establish it as a sustainable method for decontamination of toxic elements from aqueous medium, because – plants and microbial biomases are easily available as biosorbents. Biosorbents are able to remove multiple contaminants. Biosorption or bioaccumulation requires no chemical reagents and sophisticated apparatus to operate removal operations.In addition to this it is easily applicable and functional over a wide range of temprature, pH and other dissolved solvents. After removal operation is over, disposal or desorption of attached metals or contaminants to biomass is easier.

4.1. Mechanism of metabolic independent biosorption by dead plant biomass

Biosorption almost occurs in the dead cell of biomass because it is membrane independent process (Aksu et al., 1992). The physicochemical mechanism and ionic interaction are the main keys behind the removal of contaminants through biosorption, bacterial and plant cell walls. The hydroxy, phosphate, carboxyl group and amines play an important action during metal biosorption. Rapid biosorption occurs at metabolically extinct biomass than living biomass because living biomass has ability to carry continuous metal uptake and self–replenishment (Malik, 2004; Hajdu et al., 2010).

4.2. Metal detoxification mechanism by live plant biomass

Large green plants have the capability to move large amounts of soil solution into the plant body through the roots and evaporate this water out of the leaves as pure water vapour during transpiration. Plants transpire water to move nutrients from the soil solution to leaves and stem as a result of which photosynthesis takes place. During this process, contaminants present in the soil and water are also taken up and vapour from leaves comes out (Raskin et al., 1997; Frankenberger et al., 1995). Heavy metals are generally transported and deposited in the vacuole as metal chelates. Plant tissues take up free metal ions from the solution as metal chelates using specific high affinity ligands (like oxygen–donor ligands, sourdine ligands, and nitrogen–donor ligands), for example, carboxylic acid anions which are abundant in the cells of terrestrial plants and form complexes with divalent and trivalent metal ions of reasonably high stability (Girhepuje et al., 2015). The anions present in the cell vacuoles of photosynthetic tissues are carboxylates of tartaric acid, malic acid, citric acid, etc which may combine with metal ion concentrations in plants. Metallothioneins and phytochelatins are ligands having sulphur as donor atoms that donate to heavy metals to form stable complexes and thus heavy metals are removed by the formation of complexes and these ligands are better because of the fact that the donor capacity of sulphur is more than oxygen.

Metallothioneins are gene–encoded low molecular– weight, cysteine–rich peptides found in fungi and mammals recently shown to be induced by metals. In fungi and mammals, metallothioneins are involved in metal detoxification but their role in plants is not yet well understood (Ma et al., 1997; Ma et al., 2001; Homer et al., 1995). These mechanisms include chelation, biotransformation, and cellular repair (Salt et al., 1998). The external mechanisms include exudations which change rhizosphere pH, metal speciation and binds metal ions on the cell walls. The intracellular mechanism of live plants for removing heavy metals is based on the fact that transports of metals take place to the vacuoles where removal of toxic heavy metals involves two steps (i) Ligands bind with the metal ions in the cytosol to form complexes. (ii) Metals bind to the cell walls of the plants.

There are a number of micropores in root cell walls that take up many types of contaminants from the solution. Cellulose, hemicellulose and glycopattern are present in cell wall micropores whose negative charges bind with heavy metals cations. There are cation exchange sites within the root cell walls that remove heavy metals by the exchange of cations also. Metal ions from the root of live plants move to other parts of the plant by transport from the plasma membrane of the cell and this mechanism of uptake of heavy metals from soil/solution to roots and different parts of plants e.g. stem and leaves has been very well explained. The inner limit of the root cell wall is the endodermis, which forms the outer limit of the root vascular system or stele (Winkle et al., 2011). Some medicinal and aromatic plants also have the capacity to remove arsenic and chromium from an aqueous medium (Jha and Kumar, 2017).

5. Arsenic, Chromium and Dyes Removal by Dead Plant Biomass

After the attention to biosorption techniques by scientists in the 1970 decade for removal of metal ion contamination from the aqueous medium, plant material become important and valuable for biotechnologists because plant biomass can easily be available and prepared everywhere for adsorption treatment (Debnath et al., 2016). Plant biomass constitutes cellulosic content that is effective in the biosorption of heavy metals from an aqueous medium. Approximately all parts of plant biomass can be applied for biosorption phenomena such as leaf (Shafique et al., 2012; Reddy et al., 2012; Babu and Gupta, 2008) seeds (Gutha et al., 2011; Jayaram and Prasad, 2009), root (Li et al., 2013), bark (Munagapati et al., 2010; Sarin and Pant, 2006; Aoyama et al., 2005) and peel (Owamah, 2014; Feng et al., 2011; Saha et al., 2013; Rao et al., 2012).

Many agriculturally based plant biomasses have been explored as biosorbent such as husk (Ahmaruzzaman and Gupta, 2011; Oliveira et al., 2008; Imamoglu et al., 2014) stalk (Zheng et al., 2010; Jalali and Aboulghazi, 2013) bagasse shell (Velazquez–Jimenez et al., 2013; Mohan and Singh, 2002; Krishnani et al., 2009) (Kumar et al., 2011; Vamerali et al., 2009) and fibres (Jalali and Aboulghazi, 2013; Bhatti et al., 2010). These biomasses are abundant which are locally available, economic, eco-friendly and renewable. These are composed of lignin and cellulose; hence they make a feasible option for metallic decontamination from waste water. Despite this, various aromatic and medicinal plants have been reported for their bios orbing potential of heavy metals. These plants are basically non-food crop, so they can play a key role to utilize in heavy metal contaminated areas to inhibit the entry of metallic ions in the food chain by irrigation and bioaccumulation through crop yielding plants (Verma et al., 1990; Zheljazkov et al., 2005; Sridhara et al., 2008).

Researchers suggested that the use of medicinal and aromatic plants for clean-up of metallic contaminants from the polluted site may be a better effort to other plant biosorbent, because some medicinal and aromatic herbs significantly removed heavy metals from contaminated areas which are removed after harvesting (Chiang et al., 2006; Divrikli et al., 2006). There is no significant risk of metal contamination in the essential extract by product of medicinal and aromatic plants and no change takes place in their product’s basic concentration because various methods have been suggested recently in which bios orbed metallic ions from harvested biomass can be extracted efficiently (Lal et al., 2013; Siddiqui et al., 2013).

5.1. Arsenic biosorption by dead plant biomass

After 70s–decade, arsenic contamination in aqueous resources has gradually increased. Now it has been considered as the world’s most toxic substance in water resources which adversely affects lively hood and the environment. Several technologies have been successfully applied and available for the treatment of arsenic from water resources (Mohan and Charles, 2007). But these are operationally complex, require technical skills, cost effective, equipment and other chemical reagents (Jain and Singh, 2012). This bioremediation of arsenic through plant biomass involves a solid phase (adsorbent) and liquid phase containing dissolved arsenic to be adsorbed easily. Many agricultural wastes and plant products are composed of lignin, lipids, cellulose, polysaccharides, proteins, ashes, hydrocarbons and various other compounds, that have different functional groups (Sud et al., 2008). These functional groups on the biomass create a strong affinity to adsorb the metallic ions present in aqueous solutions. This phenomenon depends on the bond linkage between the metallic ion of the adsorbate in the solution and molecules present in the biomass. Any solid material may be applied as an adsorbent if it has sufficient affinity to adsorb the target species. Due to local abundant availability, low cost of preparation and high affinity to adsorb metallic ions, plant biomass makes an effective biosorbent (Tiwari et al., 2015).

The bond linkages between the metallic ions of contaminated water and molecules interact with biosorbent surface and its inner pores. Different mechanisms have been studied and reported to explain the removal properties at the biosorbent surface and pore involving ion exchange, complexation, chemisorption, physical forces, and chelation in inter and intra fibrillar capillaries, etc. (Kelaiya and Rank., 2019).

To understand the proper biosorption mechanism, rate of adsorption, adsorbing capacity, effective pH range, the effect of time on biosorption and initial biomass concentration are an essential parameter that is needed for batch operation system design. Various leaves biomass have successfully experimented on biosorption of As(III) from an aqueous medium. Recent researches have reported that Guava leaf biomass and Mango bark and bagasse have the capacity to treat arsenic containing water (Mohan et al., 2019).

Reviews show that *Moringa oleifera* Lamarck seed powder tested and fitted all parameters for biosorption of arsenic. Leave biomass of *Eucalyptus* reported as good adsorptive properties to remove the arsenic and mercury from aqueous medium (Alimohammadi et al., 2017). Some agricultural waste biomass such as rice husk has also been reported as arsenic remover biosorbent (Mimouni, 2018). Various plant leaves have been found as biosorbent and tested their arsenic removal efficiency by experimenting with different batch and column operations such as leaves of *Acacia auriculiformis* (Al–Mamuna et al., 2013), Soya been biomass as novel arsenic biosorbent (Gupta et al., 2007). Other studies of arsenic removal efficiency using biomass like Solid *Psidium guajava* Leaf (Zolotova, 2021) and leaves of *Bambusa vulgaris* have been reported.

These are some recent researches that reported different plant biomass as a remover of arsenic contamination from aqueous medium. Many other plant species are also under continuous investigation for remediation in different parts of the world.

5.2. Chromium biosorption by dead plant biomass

The Cr(VI) removal from the contaminated water by lead plant biomass has been tested among various species of plant varieties. Adsorption mechanism through biomass takes place by cellulosic and lignocellulosic present on biosorbent. Various plant biomass like leaves, stem, roots and their derivatives have been reported as the effective potential remover of Cr(VI) through the biosorption phenomenon. These include saw dust, maize cob, Sugar cane bagasse (Sharma and Forster, 1994), rice husk (Mechmet and Keles, 1990) and sugar cane bagasse (Sharma and Forster, 1994).

Different published literature state that inexpensive materials from plant biomass have been used for Cr(VI) removal including Osage orange biomass (Pehlivan et al., 2012), wheat bran biomass (Nameni et al., 2008), maize tassel powder (Zvinowanda et al., 2009), pine needle powder, different wheat based biosorbents (Farooq et al., 2010), biomass of *Beal fruit* (Anandkumar and Mandal, 2009) cone of *Pinus sylvestris* (Ucun et al., 2002) and *Arachis Hypogea* shell (Mahajan and Sud, 2011). All these biomasses have been experimented and reported as effective biosorbent for Cr(VI). These biomasses can be used *In situ* trial for Cr(VI) removal from an aqueous medium because these are cheap and abundant in nature.

5.3. Dye removal by dead plant biomass

Waste water release from textile industries has been a major environmental issue for society today. These effluents represent a serious problem all over the world. They contain different types of organic dyes. Most of these are toxic, mutagenic and carcinogenic. It is very stable to light, temperature and microbial attack making the recalcitrant compound from an environmental point of view (Barka et al., 2011). Plant biomass has the presence of functional groups like alcohols, aldehyde, ketones, carboxylic acids, phenols, ester groups and ionization of these helps in cationic bonding with dyes dissolved in the waterbodies (Lal et al., 2018). Generally, textile effluents containing dyes block the penetration of sunlight due to their dark colour into the water and that affects the water ecosystem (Choi et al., 2004; Sanmuga and Priya, 2014; Bhatnagar and Minocha, 2010). In–plant biomass, dye substances can bind to the substrate by adsorption. Molecules containing dyes consist of two chemical groups that are chemophores and auxochromes. Chemophores are electron harnessing and colour producing compounds, other auxochormes are electron donating and colour – intensifying compounds (Grande, 2015).

Biosorption of organic dyes by plant–based biomass is a chemical bonding process. The key role includes ion exchange due to surface ionization. Studies reported that this is pH dependent and generally covalent bonds are formed between biomass and dyes. Reactive dyes from the covalent bond to biomass with fibres, causing the dyes to be easily adsorbed onto biomass. Basic dyes have ionic charges, so they have higher biosorption potential than acid dyes (Ho and McKay, 1998). Reports state that the polyhydroxy phenol group of tannins is a very active binding species.

Rice husk and *Eucalyptus* bark also have a good adsorbent capacity of dyes (Morais et al., 1999). Several studies suggested that different biomass had been successfully analyzed to remove different dyes from aqueous medium. Rice husk contains carbon and cellulose that is also responsible for dye adsorption, whereas hemicellulose and cellulose present in their biomass also assist dye adsorption phenomenon (Hashem et al., 2006; Baldikova et al., 2015; Sadaf et al., 2015). Investigations have reported that raw rice husk and modified risk husk are able to treat safranin–T from water resources (Gupta et al., 2006) acid yellow and acid blue dyes also have been decontaminated by activated rice husk (Mohamed, 2004) and crystal violet by unmodified rice husk (Mohanty et al., 2006).

Similarly, ashes of rice husk have also been successfully treated on the removal of methylene blue from aqueous medium. Other studies show that Congo red has been removed by rice bran (Asuquo et al., 2017).

A review of the literature shows that cotton stalks were also applied to decontaminating agents in a considerable amount of variety of dyes from aqueous solutions such as Congo red, rhodamine B, methyl violet, methylene blue and malachite green (Saba et al., 2016; Kadirvelu et al., 2003). Among all types of cotton biomass, the cotton hull has also proven to be the most promising adsorbent with the higher removal efficiency such as removal of Remazol black by cotton hull (Tune, 2009).

Jute is an important fiber crop, which contains cellulose and lignin, like cotton. Literature explain that Jute industries generate a large amount of Jute fibres and their activated carbon from waste jute. They can widely be used in the mitigation of dyes contaminated water through biosorption (Senthilkumar et al., 2006) whereas, sugarcane bagasse is also widely applied and found appropriate for the removal of the dye's contamination like neutral red dye from acidic media. The main advantage of this biosorbent is that it has the best effective removal efficiency without any modifications (Elhami et al., 2012). Similarly, Sugarcane bagasse fly ash has also an effective removal efficiency of Congo red, Orange – G, methyl violet and malachite green (Mall et al., 2005).

Maize cobs, corn stalks and maize husk leaves are lignocellulosic – rich plant waste that is widely available worldwide. However, the residual of maize products often decomposes in fields or are burned (Sonawane and Shrivastava, 2009). Corn cubs have successfully experimented with as biosorbent for the removal of textile dyes including Congo red, rhodamine B, malachite green, methyl violet and methylene blue from aqueous medium (Mohanty et al., 2006; Robinson et al., 2001). It shows better results with a combination of other biosorbent like bi–valve shells for removal of Congo red (Jalil et al., 2012).

Barley husk biomass also achieves a high degree of removal efficiency of dye effluents through biosorbent mechanism, because it is abundantly available in many countries. It can reduce the cost of dye mitigation on an industrial scale. Some literature reports that barley husk is able to adsorb many dyes such as Cibacron red C–2G, Cibacron yellow C –2R, remazol – black B, cibcron blue C–R and remazol red RB onto their different residues (Robinson et al., 2001). Another dye biosorbent found in literature is sawdust. The adsorbing property of saw dust varies from adsorbate. Modified biomass of sawdust shows great efficiency to remove acid yellow 36 (Malik, 2003) whereas, sawdust from wood species like cherry, walnut, oak and pitch – pine tested removal possibilities on methylene blue and acid blue. It performs poorly with respect to hazelnut shells (Ferrero, 2007). Little work was done on sawdust but it has great potential to be used as a biosorbent.

6. Removal of Arsenic and Chromium by Bioaccumulation through Live Plant Biomass

6.1. Arsenic bioaccumulation

Arsenic is found in both arsenate and arsenite forms at naturally occurring sites. Arsenic can be mitigated through bioaccumulation by live plant species from its root. It depends upon the availability of arsenic contamination occurring in soil or water and arsenic accumulating properties of plant species. Arsenic sequestration by plants takes place primarily through the root system (Jha and Gupta, 2017). After uptake by the root system arsenic is transferred from the root through translocation in shoot without creating any toxic symptoms (Ross and Kaye, 1994; Prasad, 2008).

It is easily absorbed by roots because arsenic is phosphorous analog and phosphorous is an essential nutrient for all types of plants. So it competes with phosphorous and enters into the root (Kumar et al., 2015). Arsenic is translocated up to leaves of plant species by their metabolic transporter. Various experiments have been examined and reported arsenic remover plant such as *Amaranthusbilitoides*, *Chamaemelum fuscatum*, *Convolvulus arvensis*, *Cynodon dactylon* and *Malva nicaensis* (Dabrowska et al., 2011).

Another study on *Salix atrocinerea* aangiosperms plant, *In-vitro* cultured and experimented in an aqueous medium to evaluate their arsenic accumulating capacity. Results have shown that it is a good arsenic accumulator plant (Navazas et al., 2019). Many other plants have been tested *In-vitro* and *In -situ* trials of arsenic accumulating potential such as *Populus alba*, *Populus nigra*, *Populus tremula* and *salix alba* (Vamerali et al., 2009). Despite these, Arsenic hyper accumulator plants are those which have the capacity to accumulate up to 1000 mg kg^{-1} or above the arsenic concentration in their plant body. Many arsenic hyperaccumulator plants have been reported, examples of these being *Pteris vittata* (Ma et al., 2001; Srivastava et al., 2009) *Pteris cretica*, *Pteris multifida* and *B. orintala* .

6.2. Chromium bioaccumulation

Chromium is not an essential element for plants (Huffman et al., 1973). The pathway for chromium transport in the plant is not yet clearly evaluated. So, chromium uptake by plants has no energy expenditure (Chandra et al., 1997; Skeffington et al., 1976). Chromium uptake by plants is performed by an active mechanism along with essential elements such as sulphate (Kim et al., 2006; Cervantes et al., 2001). It is found that both forms of Cr are translocated root to shoot but the rate of translocation is very low. It has been studied that Cr concentration in root is 100–fold higher than shoots (Zayed et al., 1998). The rate of Cr distribution in the plant through translocation varies by different plant species. At higher concentration of Cr species, roots accumulate a very high level of Cr and translocation was mainly to cut small number of hypocotyls and cotyledonary leaves (Skeffington et al., 1976), whereas, *Brassica deracea* show low level of Cr translocation from root to shoot (Chatterjee and Chatterjee, 2000).

Other studies on Cr bioaccumulation show *Alba* and *Populous* translocate Cr up to their leaves (Rafati et al., 2011). *Dyera costulata* have the potential to accumulate a high level of chromium in their leaf, *Pluchea indica* (Sampanpanish et al., 2006), *Amaranthus dubius* and *Convolvulus arvensis* (Gardea–Torresdey et al., 2004) has also been found good Cr accumulator plants. *Ipomoea aquatica* reported as a hyper accumulator of Cr(VI) have no toxic effect when they are exposed to high levels of Cr(VI) (Weerasinghe et al., 2008).

7. Bacterial Biosorption of Arsenic

Microorganisms play a key role in the biogeochemistry of influencing the mobility and bioavailability of various metals (Gadd, 2004). In the natural environment, bacteria respond to arsenic in a variety of different ways that is depending on the species of different bacteria. The response could be biosorption, compartmentalization, exclusion, chelation and immobilization (Tsai et al., 2009). Developing efficient and selective arsenic bioremediation approaches through bacteria, it is necessary to understand the arsenic metabolism in bacteria at the molecular and biochemical level (Ordonez et al., 2005).

Since the early 80s of the 20th century, the removal of heavy metals through bacterial biomass from waste water had been formulated and recognized as a novel biotechnological mechanism with biosorption. The data of "ISI Web of Science" state that nearly 2700 journal papers have been published yet with biosorption and metal in their subject matter. Although it is continuously increased in research publication day by day, especially during the start of the 21st century, there was 96 metal biosorption by a microbial biomass research report published in 2000. This figure nearly doubled in 2005 to 178 articles. In 2009, the number of articles jumped to 393 so that these versatile studies on biosorption inspected and covered multidisciplinary angles from biotechnology, biochemistry, microbiology and physical chemistry to process engineering point of view and significantly contribute to the elucidation of the biosorption phenomenon and its biotechnological potential (Kotrba et al., 2011).

Biosorption using bacterial biomass has been reported that it has better potential than plant biosorbent (Volesky, 1990). In this mechanism bacterial cell wall is the first component to contact with metallic ions, where the solute can be deposited on the surface or within the cell structure. Functional groups present in bacterial cells are primarily responsible for the metal binding capabilities of the cell wall. Peptidoglycan, teichuronic acid and teichoic acid are the main anionic functional groups present in the cell wall of gram–positive bacteria whereas, lipopolysaccharides, phospholipids and peptidoglycan are present in gram negative bacteria (Sherbert, 1978).

Arsenic biosorption is also supported by the capabilities of extracellular polysaccharides present in bacterial surfaces (Newman et al., 1998). However, the viabilities of these components depend on the bacterial species and growth conditions. They can be easily removed by simple mechanical disruption or chemical washing (Mullen et al., 1989). During biosorption, metallic ions contacted the bacterial cell wall. The mechanism behind this interaction is the cellular structure of bacteria, phosphonate, carboxyl, hydroxyl and other functional groups present on their cell wall. These compounds can be determined for their potential of biosorption in which, negatively charged carboxylic groups abundantly available on bacterial cell walls actively participate in the binding of metal cations.

The omnipresence of arsenic in the environment has forced the bacteria to evolve the irdefense mechanism (Yee and Fein, 2001). Many bacteria are able to have developed the necessary genetic components which help them to survive and grow in high arsenic contaminating environments (Rehman et al., 2007; Liao et al., 2011). Bacterial biosorption has been generally recognized as fast interaction between arsenic ions and the electronegative surface of the cell membrane. Some genetically modified strain of *E. coli* has been reported for removal of arsenate (Bates et al., 1982). Several other bacteria and microbial biomass have been studied on arsenite (Wu et al., 2010) and arsenate (Pokhrel and Viraraghavan, 2006) removal as adsorbent. A detailed study reported on diverse microbial flora that has arsenic resistance potential including *Pseudomonas fluoreseens* (Teclu et al., 2008), *Deinococcus indicus* (Seki et al., 2005). *Thermus aquaticus*, *Thermus thermophilus* (De-vicente et al., 1990), *Bacillus subtilis* (Prithivirajsingh et al., 2001), *Yersinia enterocolitica* and *Yersinia intermedia* (Suresh et al., 2004), *Desulfitabacterium* (Gihring et al., 2001) and *Steptomycesnoursei* (Sato and Kobayashi, 1998).

The arsenic defense mechanism in certain bacteria evolved when the load of arsenic presence increased in their environment. Those conditions permit the cell to neutralize its toxic effects. This mechanism is well established and reported that many bacteria survive in the presence of arsenic by increasing or inducing an array of resistance proteins which are found either in plasmids (Bansal et al., 2000) or chromosomes (Niggemyer et al., 2001). The basis of arsenic biogeochemical lies primarily in bacterial biosorption, microbial mediated oxidation reduction (Drewniak et al., 2013) and methylation - demethylation processes (Bhat et al., 2011). Arsenic resistance mechanism in gram negative and gram-positive species of bacteria operate due to energy-dependent efflux of either arsenite or arsenate from the cell through *ars* operon (Shrivastava et al., 2015). *arsA* – *arsB* complex in *E. coli* is responsible for arsenate pump. In bacterial strain *S. aureus*, it is reported that *ars*B only is sufficient to act (Shrivastava et al., 2015). This way researcher has explored the possibilities of removal of toxic heavy metals from aqueous medium by bacterial biomass and my study also aims at finding and isolating new bacterial biomass for remediation of heavy metals. This is a novel approach for the removal of heavy metals from an aqueous medium and will prove a boon to the suffering rural population in particular for potable water.

8. Conclusion

Bioremediation and Phytoremediation of toxic metals and dyes by plant or bacterial biomass have emerged as a potential accumulator of As(III), Cr(VI) as well as organic dyes in comparison to the traditional methods of removal. Dead plant biomass and aquatic plants available in abundance may provide a suitable alternative of As(III), Cr(VI) and organic dyes removal. Many plant biomass and bacterias have been established as sucesssful remover of As(III), Cr(VI) and organic dyes in experimental condition.

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