Use of Low Cost Adsorbents for the Remediation of Heavy Metals from Waste Water

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Abstract: - **The problem of water pollution is alarming due to various anthropogenic activities. Heavy metals are being released in the water bodies causing heavy metal pollution and also accumulate in the food chain and ultimately affecting human health. Various activities like manufacturing of fertilizers, industrialization, mining, electroplating, smelters etc are responsible for the release of heavy metals in the water bodies. Various heavy metals include Pb, Cd, Cu, Zn, Ni, Cr, and metalloids like arsenic in drinking water causes harmful effects on human health like allergies, hyper pigmentation, skin cancer, neurological disorders, hypertension, cardiovascular diseases, etc. Therefore there is a need to develop and focus on methods to remove heavy metals from the waste water using techniques which are environment friendly, cost-effective and easily available in nature. Bioadsorbents have come up as one of the promising substitute for heavy metal removal because it is readily available in nature and most importantly the waste residues from agricultural activities is utilized in the manufacturing of bioadsorbent for heavy metal ion removal. Various agricultural residues used to remove metal ions are rice husk, sawdust, peanut husk, groundnut husk, wheat bran, sugarcane bagasse, pine needle, salseed husk, coconut coir, cotton stalks etc. The main objective of this paper is to study about bio-adsorbents derived from agricultural wastes and their applications to remove metal ions from waste water**

Keywords: **Adsorption, Heavy metal, Bioadsrobents, Agricultural by-products, Waste water.**

I. INTRODUCTION

The availability and quality of drinking water has a huge impact on people's life especially in the rural and remote areas which is essential for a healthy living (Gupta et. al., 2006). Water resources all over the world have been severely affected by human activities leading to water quality deterioration and also shortage in potable supply of water (Tripathi et al.,2015).Water pollution especially due to heavy metals and minerals in the waste water is becoming a severe problem in India (Rashmi et al.,2013). Major contributing industries which release heavy metals are mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products (Malil et al 2004). From the industrial sites these heavy metals contaminate the downstream water bodies through run off. Therefore it is essential to remove themfrom waste water before they are discharged in a water body to prevent various health hazards as they are toxic and carcinogenic in nature (Srivastava et al., 2006).

Heavy metals are non-biodegradable in nature and their constant presence in the environment leads to its accumulation in the food chain ultimately posing a threat to human health(Babel et al 2004). This gives us a global challenge to develop methods which are most suitable for the treatment of metal-contaminated wastewater. Most common techniques used to remove heavy metals include precipitation, ion-exchange, adsorption, filtration, reverse osmosis etc. (Rao et al., 2000). But these techniques are quite expensive and sophisticated in terms of their operation for a developing economy like India (Raji et al., 1997). This has led to an increased interest in developing novel methods that are cheap and efficient for heavy metal removal from waste waters (Gloaguen,et al.,1997). In this regard, agricultural wastes are one of the most promising materials which can be used as a potential bio-adsorbent for heavy metal removal from waste water as it is abundantly present in nature (Low et al.,2000). These wastes can be used to produce Bioadsrobents and also bio-hydrogels to remove heavy metal ions from waste water.

1.1 Heavy Metal Pollution: A Global Risk for Human Health

The heavy metal can be defined as "any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations" (Duruibe et al., 2007).Such elements possess higher atomic weights ranging from 63.5 and 200.6, and a specific gravity larger than 5.0g/cm^3 (Srivastava et. al., 2008).Mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr [VI]), Zinc (Zn), Arsenic (As), Nickel (Ni) etc., are known to be toxic heavy metals from ecotoxicological point of view(Ake et al. 2001; Babel et al., 2003; Farrag et al. 2009; Gupta et al. 2009 a, b ; Kapoor et al. 1999; Lo et al. 1999; Tunali et al. 2006;).

Heavy metals are natural components of the Earth's crust. They are non-biodegradable and are able to reach our body system through drinking water, air and intake of food. Although as trace elements some heavy metals are required to maintain the human body metabolism. But, poisoning naturally occurs at higher concentrations of such heavy metals (Jarup et al.,2003). Heavy metals are dangerous and toxic in nature because they tend to **bioaccumulate**in living cells.Bioaccumulation refers to an increase in the concentration of a specific chemical or a heavy metal which is toxic and non-degradable in nature. Due to which it tends to accumulate in the biological cells over time. Such compounds accumulate in living cells and are stored faster than they are broken down or excreted out of the biological system (David et al., 1999).

Heavy metals in industrial wastewater contain lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel. Most of the heavy metals are dangerous to health and to the environment (Ngah et al.,2008). Soil acts a sink for heavy metal ions through which they enter the food chain via water, plants or by reaching the ground water through leaching (Okoro et al.,2012). Major health implications of heavy metals are due to exposure to lead, cadmium, mercury and arsenic as per the studies by WHO. Major sources of heavy metal in the environment are geogenic, industrial, agriculture, pharmaceutical, domestic effluents, and other atmospheric sources (Tchounwou et al., 2012). This kind of pollution is very critical in areas where activities like mining, foundries and smelting, electroplating, petroleum refiningis done.

Table 1.Types of heavy metals and their effects on human health with their permissible limits. (As per BIS Standard, I. 1991)

Pollutants	Sources	Effect on Human Health	Permissible limit (ppm)
Lead	Paint, pesticides, automobile emission, burning and mining of coal	Liver and kidney damage, gastrointestinal problems, mental illness in children	0.1
Mercury	Pesticides, batteries, paper and pulp industry	Nervous system is affected badly	0.01
Cadmium	Electroplating, pesticides, fertilizer, Cadmium, Nickel, batteries, nuclear plants.	Kidney damage, bronchitis, gastrointestinal disorder, cancer of bone	2.0
Arsenic	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis	0.2
Zinc	Refineries, brass manufacture, metal Plating.	Skin problem arises due to zinc fumes; Nervous system is also affected badly.	5.0
Manganese	Welding, fuel addition	Central nervous system is badly affected by inhaling Manganese.	2.0

There are millions of people who are suffering with disorders from heavy metal poisoning and therefore it has become a worldwide menace. Clean drinking water is the second most important requirement after oxygen. Hence, there is a critical need to develop efficient, low-cost methods for heavy metal removal from water bodies to ensure improved water quality for population.

1.2 Contemporary Techniques for heavy metal removal: Merits and De-merits

Since heavy metal pollution is becoming a serious issueit is essential to find passive and efficient matrix to remove heavy metals from potable and waste water, in this regard a low cost bio-adsorbent is well suited as it provides a better surface for adsorption.Production of cheaper adsorbents to replace costly wastewater treatments is the need of the hour (Babel et al., 2003). Most common methods for heavy metal removal includes methods chemical precipitation, microfiltration, ion-exchange, adsorption, coagulation, flocculation, electrochemical treatment, membrane-separation, reverse osmosis, electro-dialysis. (Wang et al., 2004) (Carlos et al.,2013)

Activated carbon, silver beds, charcoal, sand is highly used in portable filters for filtration and disinfection of water.

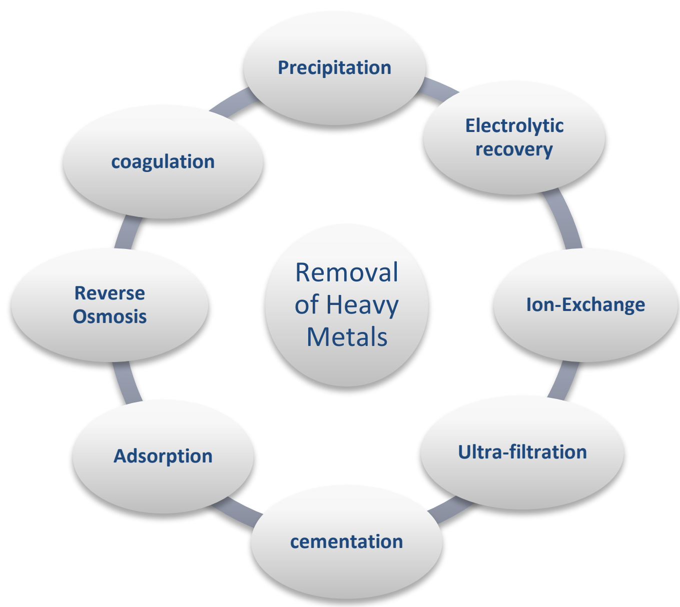

Figure 1. Available remediation technologies for water decontamination

1.2.1 Electrolytic recovery or electro-winning is a technology used to remove heavy metals by passing electric current through an aqueous solution containing a cathode plate and an insoluble anode plate. Positively charged metallic ions attach to the negatively charged cathode leaving behind deposits of metal which can be recovered. A significant disadvantage observed with this technique was of corrosion which destroys the electrode and therefore needs to replace frequently (Kurniawan et al., 2006).

1.2.2 Reverse Osmosis is also meant for heavy metal removal in which a pressure gradient greater than the osmotic pressure is created by dissolved solids across a semi-impermeable membrane. Ujang et al 1996 studied usage of low-pressure RO membranes for the removal of Zn^{2+} and Cu^{2+} by applying pressures significantly below 690 kPa. The experiment revealed that removal of both Zn^{2+} and Cu^{2+} was enhanced in the presence of sulphonated polysulphone RO membranes. The percentage removal of metal ions of Zn^{2+} was slightly greater than that for Cu^{2+} (Ujang et al.,1996). The major disadvantage is that it is an expensive technique. (Kurniawan et al., 2006.).

1.2.3 Electro-coagulation: It is an electrochemical approach that utilizes electrical current for the removal of heavy metals from aqueous solutions and is also capable in removing suspended solids, dissolved metals, tannins and dyes from waste water. The metal ions become destabilized and precipitate in a stable formwhen they are neutralized with ions of opposite electrical charges provided by electro-coagulation system (Rajemahadik et al., 2014)

Removal of cadmium (Cd), copper (Cu) and nickel (Ni) from an artificial wastewater was investigated by Umran et al., 2015 using electro-coagulation (EC) method . The results revealed that electro-coagulation for 90 minutes was helpful in removing highest concentrations of Cd, Ni, Cu up to 99.78%, 99.98%, 98.90% from waste water. This study was conducted at current density of 30 mA/cm2 and pH of 7 using supporting electrolyte (0.05 M Na_2SO_4) respectively (Un et al.,2015). The formation of metal hydroxides leads to clogging of the membranes which is a huge limitation of this method (Pedersen, 2003)

1.2.4 Ultra-filtration use porous membranes for the removal of heavy metals driven by very high pressure gradient. The main disadvantage of this process is leads to production of sludge which again is difficult to manage (Owlad et al., 2009). Juang and Shiau (2000) ,studied the removal of Cu (II) and Zn (II) ions from wastewater by using chitosan-enhanced membrane filtration. Amicon-generated cellulose YM10 was used as the ultra-filter which was highly efficient in removal of Cu (II) and Zn (II) ions at a pH of 8.5 to 9. This experiment revealed that the efficiency of heavy metal removal is enhanced manifolds by using chitosan membranes.

1.2.4 Ion-exchange: In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include: high cost and partial removal of certain ions(Fu et al., 2011).Ion exchange is the most effective process known for the removal of toxic substances at very low concentrations released from chemical industries into drinking water making it the most promising technique used (Dabrowski et al.,2004).Various ion-exchange resins are available for adsorption purpose. Dowex 50W isone such gel resin which contains sulfonate groups and it was used for removing of Cd^{2+} ions from aqueous solutions(Pehlivanet al.,2006).

1.2.5 Chemical Precipitation: Metals or heavy metals are coagulated by using coagulants like alum, lime, iron salts and other organic (Ahalya at al., 2013). These coagulants lead to the formation of an insoluble precipitate which can be easily separated out by sedimentation or filtration. Further, the treated water is either discharged or reused (Pehlivan et al., 2006.). The ordinary chemical precipitation is done by hydroxide precipitation and sulfide precipitation. Hydroxide precipitation is done by using Ca(OH)2 and NaOH for the removal of Cu(II) and Cr(VI) ions from wastewater. This study was conducted by Mirbagheri and Hosseini (2005).

The large amount of sludge containing toxic compounds produced during the process is the main disadvantage of chemical precipitation (Kurniawan et al., 2006).

1.2.6 Phytoremediation is the removal of metal ions from water, soil and sediments using certain plants. Bioremediation includes the use of microorganisms, plants and their products to remove contaminants. Phytobioremediation is the use of plants to remove heavy metals especially from wastewater. In this technique selectively engineered pollutant accumulating plants are used for the clean-up of environmental pollution (Raskin et al., 2000). Mojiri in 2011 investigated that Typha *domingensis* was able to eliminate heavy metals from municipal waste water by Phytoremediation. The study shows that the usage of Typha *domingensis* was efficient against the concentration of heavy metals in municipal waste water. The disadvantages of this method is that it is a time taking process and the regeneration of plant for another cycle of biosorption is difficult which leads to improper metal removal and high energy requirements, also huge amount of toxic sludge and waste products is produced which makes it difficult for disposal (Fenga et al 2004).

1.2.6 Cementation is the displacement of a metal from a solution by a metal higher in the electrochemical series. Electromotive force is required to facilitate cementation capability. Since contact time is required for cementation process is long, it is suitable for small waste water flows. Examples of cementation in wastewater treatment includes the precipitating copper from printed etching solutions, and chromium plating for the reduction of Cr(VI) in and chromate-inhibited cooling water discharges (Case 1974). The removal and recovery was done by cementation of lead ion on an iron sphere packed bed (Angelidis et al.,1988, 1989). A less toxic metal replaced Lead in a harmless and reusable form.

According to study conducted by Eltaweelin 2014 cementation method offers various advantages like recovery of metals in its pure metallic form, low energy demand, and cost effective in nature. The study showed that cementation is the most affordable and simple method for the recovery of copper using scrap iron to produce metallic copper sediments suitable for metallurgical processing (Eltaweel et al.,2014)

1.2.7 Activated carbons have high adsorption capacity but its cost is too high to bear making it great barrier for practical applications majorly in terms of industrial effluent treatment.

Adsorption has proved out to be the most promising alternative for metal ion removal from waste water. Adsorption is a process of transferring a substance from the liquid phase to the surface of a solid, and hence the substance becomes attached by chemical or physical interactions (Kurniawan and Babel, 2003). For the effective removal of heavy metals from wastewaters low-cost adsorbents are used which can be derived either from agricultural waste, industrial by-product, natural material, or modified biopolymers(Bailey et al.,1999)

Table 2.Comparative analysis of conventional methods for heavy metal removal with hydrogel

S.No.	Method	Advantages	Diadvantages	References
1.	Membrane filtration	Small space needed for operation, can be done at low pressure, it has high separation selectivity	Less production of wastes occurs.	*Babel and Kurniawan, 2003* and *Aklil et al., 2004*
2.	Electrodialysis	Highly selective in separation.	High capital cost, Energy intensive	*Mohammadi et al.* 2005
3.	Chemical precipitation	Cost effective technique, requires less capital. It is simple in terms of operation.	Generation of sludge and high operational cost	*Kurniawan et al.* 2006
4.	Photo catalysis	Metals and organic pollutant can be removed at the same time using this technique. By-products, generated by this process are less harmful in nature.	long duration of time required	*Barakat et al., 2004*
5.	Adsorption with new adsorbents	Inexpensive, less sophisticated and can work within wide range of pH. High affinity for binding metals.	High byproducts and disposal of waste	*Babel and Kurniawan, 2003* and *Aklil et al., 2004*

II. LOW-COST ADSORBENTS: A PROMISING METHOD FOR METAL ION REMOVAL

Most of the above mentioned methods have various drawbacks like higher cost of operation, disposal of residual sludge generated by these techniques, non-regenerative approach etc. Cost-effective adsorbents for metal removal are needed to deal with the above mentioned drawbacks. Natural adsorbents from agricultural wastes are readily available in large quantities and also inexpensive in nature. Low-cost adsorbents which are developed from agricultural wastes, industrial by-product, natural material, or modified biopolymers, are used for the removal of heavy metals from wastewaters. Amongst all these commonly used methods, adsorption is very effective in purifying waste water due to advantages like low-cost, eco-friendly and minimum maintenance required (Bhattacharya et.al,.2008).

It is considered as the most appropriate method for the removal of organic and inorganic pollutants since it is convenient at higher concentration and cost-effective (Demirbas 2008).

Use of low cost adsorbent to remove heavy metals is found to be more promising as there are several varieties of agricultural wastes present in abundance (Abas et al 2013). There are various advantages of adsorption over other old methods of heavy metal removal. Few of them are: Cost effective, metal selective in nature, easily regenerative, and do not produce toxic sludge, easy recovery of metals can be done and above all efficient too (Sud et al.,2008).

Agricultural materials, specially having good amount of cellulosic content have higher sorption abilities for various pollutants(Mohan et al., 2002). It is because cellulose is insoluble in water therefore giving it great adsorptive properties. Agricultural waste generally consists of hemi-cellulose, lignin, lipids, proteins, sugars, hydrocarbons and starch (Yuvaraja et al.,2012). They are cost-effective, recyclable, and biodegradable because of their chemical compositions and also a great alternative for waste water treatments and removal of metal ions. Therefore, the use of agricultural wastes as low-cost adsorbents is a promising alternative to solve environmental problems in the simplest way possible.

2.1 Adsorption by Agricultural Wastes

The bio-adsorbents have higher affinity for heavy metal ions as they form complexes due the presence of functional groups like carboxyl, hydroxyl, sulphydryl, amino, phosphate, sulphate, phenol, carbonyl and amide etc (Lata et al.,2014)and their chemical treatment increases the number of these functional groups. Nowadays various agricultural byproducts are used to as adsorbents for the removal of heavy metals from waste water (Sayedet al 2012). A lot of focus has been done on plant wastes like rice husk and neem bark (El-Said et al 2012) (Bhattacharya et al 2006) Black gram husk (Saeed et al 2003), Waste tea, (Orhan et al 1993) Turkish coffee, Walnut shell etc.

Various other adsorbents include papaya wood (Saeed et al., 2005); maize leaf (Babarinde et al.,2006); teak leaf powder (King P et al.,2006), *coraindrum sativum* (Karunasagar et al.,2005) ,lalang (*Imperata cylindrica*); leaf powder

(Hanafiah et al 2007), peanut hull pellets (Johnson et al.,2002), etc. are also studied in detail. The major advantage of using these as adsorbents for waste water treatment is that they are easily available, needs very little processing, high adsorption rate, specific adsorption for a metal ion, regenerative and easily available in nature. Consequently, plant wastes require be modifying or treating ahead of being applied for the cleansing of heavy metals. Various agricultural wastes which can be used as a promising bioadsorbent are discussed.

2.1.1 Adsorption by palm oil fuel ash: Palm Oil Fuel Ash (POFA) is a by-product obtained from palm oil mill boilers by burning of palm oil fibres; empty fruit bunches and shells. It consists of 85% fibers, 15% shells and empty fruit bunches which can be burned at a temperature of about 900- 1000°C to produce energy to make crude palm oil. During the course of this method 5% of waste ash is produced which is usually disposed in open leading to a lot of health hazards like bronchitis and other lung diseases. To prevent these health issues, various researches have examined the use of palm oil fuel ash as a remediation for waste water treatment (Bamaga et al., 2013)

2.1.2 Coconut shell as a bioadsorbent: Coconut shell is a very common agricultural waste available mainly in tropical countries all over the world. In order to effectively manage the solid waste generation from coconut shells, the waste of this material has been explored by researchers for the treatment of waste water from industries. Recently, it was investigated that coconut shells can be used to remove low concentrations of heavy metals in aqueous solutions. Heavy metals like Cu (II), Pb(II), Ni(II), Zn(II), Cr(VI), were found to be efficiently removed from waste waters. Therefore, coconut shells can be used as a low cost adsorbent for the removal of heavy metals in aqueous solutions (Aziz et al.,2005)

2.1.3 Mangos teen (Garcinia *mangostana*): The mangosteen tree is abundantly present in Thailand and Indonesia and is popularly known as "queen of fruits" as it is rich in taste and is used for medicinal purposes too. More than 6 kg of the fruit peel is generated for every 10 kg of the mangosteen fruit. The large quantity of fruit peel is utilized to extract pulp juice and the peel is also in lignocellulosic content. This makes it a promising material for heavy metal ion removal from waste water. It was found that this fruit peel was effective in the removal of Cu (II) ions from waste waters (Chen et al., 2012)

2.1.4 Durian peel as adsorbent: Durian (Duriozibethinus Murray) is an agricultural waste prominently available in the south eastern Asian region. Being consumed in higher amounts, huge amount of peels are generated, causing difficulty in disposal. Research has been conducted to analyze the efficiency of these peels to remove heavy metal ions from aqueous solutions. It was found that durion peels are quite effective in this regard (Hameed et al.,2008)

2.1.5 Rice Husk as an adsorbent: Rice husks accounts for about one fifth of the annual gross production of rice and is the most abundantly found in India, and 545 million metric tons of the world. Huge quantity of rice husk is generated from rice mills which are a threat to environment, due to which efforts are being put to utilize this highly generated waste in some good direction like energy generation, used as a cementing material, and also to be used as a bio adsorbent. Rice husk was found effective in the removal of metal ions like Ni(II), Cr(VI), Zn(II), Pb(II), Cu(II) (Mohammad et al.,2012)**.**

Rice husk is an agricultural waste material and its annual worldwide production is approximately 500 million metric tons, of which 10–20% is rice husk. Dry rice husk contains 70–85% of organic matter (lignin, cellulose, sugars, etc.) and the remainder consists of silica, which is present in the cellular membrane (Premalal et al.,2002).

Recently a lot of focus has been applied on the use of unmodified or modified rice husk as an adsorbent for the removal of pollutants from waste water. Batch studies were performed using tartaric acid to modify rice husk as adsorbent for the removal of lead and copper and have reported the effects of various parameters such as pH, initial concentration of adsorbate, particle size, temperature etc. (Wong et al 2003). Modified rice husk is a potentially useful material for the removal of Cu and Pb from aqueous solutions as reported from this study.

III. BIO-ADSORBENT: POTENTIAL ALTERNATIVE FOR HEAVY METAL REMOVAL

The main feature of this paper is to study about the properties of an inexpensive adsorbent derived from agricultural wastes and its application to remove metal ions from waste water. However the efficiency of adsorption depends upon the nature of the adsorbents used for metal ion removal. Recently hydrogels have attracted the attention of the researchers due to their high adsorption ability (Gariepy et al.,2004).

IV. CONCLUSION

Activated carbon is generally used to remove heavy metals from waste water through adsorption process. But it is quite expensive in nature therefore it needs to be replaced with a technique that is inexpensive and easily available in nature. As agriculture is the main occupation in India, a large amount of agricultural waste is generated so we can easily utilize this waste to produce low-cost adsorbents and also produce hydrogels from agricultural wastes. Further research is required to be done in this direction to enhance maximum removal of heavy metals at a reduced cost. Also behavior of the hydrogel needs to be tested with real industrial effluents where different types of heavy metals are present and analyzing the adsorption capacity

This review has majorly reflected the use of various bio-adsorbents derived from agricultural wastes and also focused on the promising attributes of low cost adsorbents present naturally which are more competent in terms of adsorption process. These Bioadsrobents can be effectively used for treatment of waste water contaminates with various metal ions and dyes. Bioadsrobents prove out to be non-toxic in nature and have higher mechanical strength. It has higher regenerative abilities which further reduce the cost of waste water treatment process.

V. FUTURE SCOPE

Development of low-cost adsorbents is the need of the hour. Bioadsorbents from agricultural resources are highly competent as compared to other conventional methods as conventional methods are quite complicated, demands lot of input like energy, manpower and infrastructure. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purpose in the future.

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