International Journal of PharmTech Research
CODEN (USA): IJPRIF, ISSN: 0974-4304
Vol.9, No.1, pp 90-96, 2016

An Overview of Research Trends in Remediation of Heavy Metal Ion from Polluted Water

Shanmugam. S and *Arabi Mohammed Saleh M.A.

School of Bio Sciences and Technology, (SBST), VIT University, Vellore. India.

Abstract: In the present scenario because of rapid industrialisation, the environmental problems are more and more nuisance for world population. Efficient and effective methods for the removal of pollutants present in water are the need of the industries. Heavy metals present in waste water and industrial effluent is major concern of environmental pollution. Most heavy metals are well-known toxic and carcinogenic agents and it represent a serious threat to the human population and the fauna and flora of the receiving water bodies. These inorganic species are persistent and non-biodegradable pollutants that should be eliminated from water. The need to find alternative inexpensive and effective methods for heavy metal removal from waters becomes inevitable. Bio sorption is an emerging field in this regard and has great potentials for application in developing economies. It involves the use of living or non-living biological materials for pollutants removal from wastewater. In this review an attempt is done to summarize the research work done related to use of bio sorbents for the remediation of water and waste waters.
Key words: Heavy metals, waters, pollution, bio sorption.

Introduction

Water is the most important and essential component on the earth for vital activities of living beings. Unfortunately, water quality of our water resources is deteriorating continuously due to geometrical growth of population, industrialization, domestic and agricultural activities, and other geological and environmental changes (1- 3). Therefore, water pollution has become a serious issue in the present scenario, affecting all living organisms and all human activities (4). The government authorities, scientist's academicians are worried and serious on this issue. Enormous number of organic, inorganic, and biological pollutants has been reported as water contaminants (5). Some of them have serious side effects and toxicities with a few being life threatening and cancer causing. The numerous metals which are significantly toxic to human beings and ecological environments include chromium, copper, lead, cadmium mercury, nickel (6).

Metal ions are released into the environment from many sources. Wastewaters such as those generated during dyes and pigments production, film and photography metal cleaning, plating and electroplating leather and mining release undesirable amounts of chromium (VI) anions (7). Metals ions reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity (8). The most important problem is metal ions are not biodegradable and are highly persistent in the environment. Thus metal ions can be accumulated in living tissues, causing various diseases and disorders (9). heavy metals toxicity can result in damage or reduced mental central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver n other vital organs(10).

Increased knowledge about toxicological effects of heavy metals as well as increased legal requirements for reduction in industrial emissions necessitates research and development in the area of waste water treatment. Since heavy metals accumulate in the food chain and because of their persistent nature, it is necessary to remove them waste water. The need for economical and effective methods for removing heavy metals from wastewater therefore resulted in the search for materials that may be useful in reducing the levels of heavy metals in the environment (11).

The present technologies for metal ion removal waste water are costly. They include ion exchange resin solvent extraction, electrolytic and precipitation processes electro dialysis and membrane technology (12). Other convention technologies which have also been used ranged from granular activated carbon to reverse osmosis. These processes are however, not economically feasible for small scale industries prevalent in developing countries (13). Precipitation processes which are the most widely used techniques for treating wastewater with high metal concentrations often results in production of large volumes of sludge containing high levels of heavy metals. Thus additional treatment such as ion exchange, reverse osmosis or adsorption processes are required in order to purify the effluent prior to discharge (14). Comparison of different technologies for removing heavy metals from waste water is given in table 1.

New methods are essential to reduce heavy metals to environmentally acceptable levels at affordable cost. Bio removal is the accumulation and concentration of heavy metals from aqueous solution using biological materials (15). Metals removal has been achieve by adsorption on different materials such as activated carbon, agricultural waste, moss peat, minerals, etc.(16) Researchers have also used groundnut husk, fluted pumpkin used for removal of heavy metals(17).

Table 1 Comparison of different methods for removing heavy metals from waste water.

No	Methods	Disadvantages	Advantages
1	Chemical precipitation	Large amount of sludge	Simple operation, inexpensive, can remove most of metals
2	Chemical coagulation	Extra operational cost for sludge disposal High cost large consumption of chemicals	Sludge settling
3	Ion exchange	High cost, less number of metal ions removed	High regeneration of materials, metal selective
4	Electrochemical methods	High capital and running cot Initial solution pH and current density	No consumption of chemicals Pure metals can be achieved.
5	Adsorption using activated carbon	Cost of activated carbon No regeneration	Most metals can be removed High efficiency (99%)
6	Bio sorption	Early saturation, limited potential for biological process improvement, no potential for biologically altering the metal valence state	Low cost, high efficiency, minimization of sludge, regeneration of bio sorbents, no additional nutrient requirement, metal recovery

The term bio sorption is used to describe passive non-metabolically mediated process of metal binding to living or dead biomass (18). Bio sorption of heavy metals from aqueous solutions can be considered as an alternative technology in industrial waste water treatment. The technique is an emerging technology based on the ability of biological materials to accumulate heavy metals for wastewater by either metabolically mediated or physico-chemical pathways of uptake (19).

More researches had been done to develop low cost biomass for pollution control from diverse sources in different countries. Some of them are anaerobically digested sludge, bacteria, fungi and algae. Agricultural wastes have also been used these include rice bran, soybean, ground nut husk, coconut shell etc. (20, 21).

Bio sorption uses inexpensive dry biomass to extract toxic heavy metals from industrial effluents, the biomass can be shredded or ground to yield stable bio sorbent particles or it can be immobilised on polymer or fixed onto an inorganic support material, the bio sorbent particles can be packed in columns which are the most effective devices for continuous removal of heavy metals, once the metal binding reaches saturation the biomass can be regenerated with acid or hydroxides solutions which discharge small volumes of concentrated heavy metal, the advantages of bio sorption are low operating costs, minimal volumes of chemical disposal and or biological sludge and high efficiency in detoxifying very dilute effluents, these advantages constitute the priory incentives for developing full scale bio sorption processes for the removal of heavy metals form contaminated solutions.

The use of dead biomass is of particular economic interest because the biomaterials are used the same way as synthetic absorbents or ion exchangers and repeated regeneration is possible (22). Bio sorption has been found to be a more rapid mechanism hence it has a more significant role in metal sorption from waste water. Biological treatment processes for removing heavy metals from wastewater are most effective when contaminant concentrations are below and above 100mg/L (23).

Adsorption

Adsorption is a process in which pollutants are adsorbed on the solid surface. Basically, it is a surface phenomenon adsorption takes place by physical forces but sometimes weak chemical bonding also participate in adsorption process. A molecule adhered to the solid surface is called adsorbate, and the solid surface as an adsorbent. adsorption is controlled by various parameters such as presence of other pollutants along with the experimental conditions(pH, concentration of pollutants, contact time, particle size, and temperature. an equilibrium is established when the concentrations of pollutant adsorbed and in water become constant the relationship between amounts of pollutant adsorbed and in water at equilibrium is called an adsorption isotherm. The adsorption is treated for calculation of various adsorption parameters. The important models are Langmuir, Freundlich, Henderson and Smith inter particle diffusion. These some well-known models used to explain the results of adsorption studies. These models are based on almost similar principle with little difference in their approaches (24, 25). The kinetic study is carried out by calculating enthalpy, free energy, entropy, and energy of activation. The adsorption technology is developed by batch process followed by the column studies. The developed adsorption technology is applied first at pilot and after on industrial scales by using large size columns.

In Nano technological treatment process, the first step involves the preparation and characterisation of nanoparticles. Some of the common preparations methods are solgel method, solvo thermal method, precipitation method, thermal decomposition etc. Sol gel method is used for the preparation of nanoparticles of alumina, alumina-silica, and cadmium sulphide Zinc sulphide nickel oxide (26). The nanoparticles are characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Transmission electron microscopy (TEM) techniques. Basically the reported methods are used for the preparation for different types of nanoparticles for various applications such as biomedical, electronics optical, mechanical, environmental science, etc. the selection of the technique depends on the size properties starting materials, and required applications of nanoparticles.

The particles of 1.00 nm size are called nanoparticles which offer the potential for the treatment of contaminated water. Some nanoparticles have been prepared and used for treatment. Nano particles have proven themselves as excellent adsorbents due their unique features, the most important characteristics of these particles ; which made them ideal adsorbents, are small size, catalytic potential, high reactivity, large surface area, ease of preparation and large number of active sites for interaction with different contaminants. Activated carbon loaded Nano zero valent iron removed Arsenic pollutant (27). They also studied various factors affecting the adsorption process. Nano scale zero valent iron has been used to remove hexavalent chromium (28).

Microbes

The accumulation of metals by microbes has been extensively studied over the past few years. There are three general categories that describe the biological process of removing metal ion from solution. They include bio sorption of metal ions onto the surface off microorganism, intracellular uptake of metal ions and chemical transformation of metal ions by microorganisms.

The bio sorption studies on marine algae have extensively studied because of more availability. The algae remediation involves both surface adsorption and internal diffusion (29). In the case of dead cell usage in bioremediation some advantages include, no requirement for growth media and nutrients, easy desorption of metals from biomass, possibility of biomass re-use.

Fungal, microbial yeast and micro algal biomasses have also been widely investigated and found to provide efficient systems for accumulating metals. Micro algal biomasses have the advantage that they are relatively easy to grow and produce in large quantities; however, the medium, age, and growth phase of the culture influence the metal binding efficiency of algae. Another potential problem is that growth and bio removal efficiency of micro algal biomass may be limited by toxic effects of heavy metals in solution.

Bio sorbent matrix was developed using *Carica papaya* plant dry stem to colonize the fungal strain *Fusarium oxysporum* to facilitate bio absorption process. Maximum efficiency of chromium removal by bio sorption up to 90% was achieved at the end of 5^{th} day of incubation. FTIR spectroscopic analysis revealed that the main functional groups involved in the uptake of chromium by fungal strain were carbonyl, carboxyl, amino and hydroxyl groups (30). The ability of yeast to reduce hexavalent chromium was studied. The in vitro reduction of hexavalent chromium using Crude Chromate Reductase of *Pichia jadinii* M9 and *Pichia Jadinii* M10, two yeasts isolated from a textile dye factory effluent (31).

Spent biomass has been used by several researchers around the globe for the removal of the Cr (VI) from effluents. Biomass including spent *Pleurotus ostreatus*, *Rosa damascene*, *Termitomyces clypeatus*, *Phanerochaete crysosporium*, pistachio hull, Cyanobacterium *Oscillatoria laete-virens* and *Citrus cinensis* have been used for the removal of Cr (VI) ions. Recent research has been conducted to investigate the efficacy of chitin immobilized *Mucor racemosus* sorbent (CIMRS) sorbent, impregnated in the modified rotating disc contactor (MRDC) blades for the sorption of chromium (VI) contained in the electroplating effluent. The optimum time, pH, temperature and CIMRS dosage were found to be 8 h, 7.0, 323 K and 0.7 g/150 mL, respectively, for MRDC sorption studies. Desorption studies were also carried out in MRDC at 60 8C. Seven isotherms were applied to model the experimental data. The study revealed highly promising nature of CIMRS for Cr (VI) sorption from electroplating effluent. In this study, a modified RDC is employed for the removal of Cr (VI) ions from the electroplating effluent. The fungi *Mucor racemosus* was pretreated, immobilized and impregnated into the MRDC blades for the removal of Cr (VI) ions. Kinetic studies were carried out by varying the initial Cr (VI) ion concentration, pH, sorbent dosage, particle size, and temperature. Studies were carried out under batch operation in a modified RDC. The paper as well aims to study and model the sorption isotherms of Cr (VI) from the effluent onto chitin immobilized M. racemosus sorbent (CIMRS). The representation of the sorption isotherms onto CIMRS is based on various sorption models with two, three, or more parameters .Langmuir, Freundlich, Temkin, Fowler– Guggenheim, Kiselev, and Hill–de Boer models were used for the determination of the energy of sorption, interaction energy between sorbed molecules, and complex formation between sorbate (32).

Sorption properties of bio-chars have been explored for the removal of organic and inorganic contaminants from water. By product of bio-chars generated during bio-oil production have been used for removal of metal ions. In this research oak bark chars has the more chromium adsorption over the oak wood char. Their work includes batch studies at various values of pH, contact time, dosages. They observed that the biosorption process fits Sips adsorption isotherm model. They were able to remove 90 % Cr at the optimum pH value of 2.0. The Chromium removal capcity of biochar increased with increase in temperature. Their investigation suggests that byproduct chars from bio-oil production might be used as inexpensive adsorbents for water purification (33). Saw dust has been modified by incorporating L-cysteine in saw dust by Nilisha *etal.* Batch studies were conducted by researchers. They found optimum pH as 3.0. (34)

Animal by-products were also used to remove pollutants from solution *viz*. Coconut shell, oyster shell, maize cob, keratin fibre. Among these keratin fibre is stability over a wide range of pH, structural toughness and high surface area renders it's as best for bio sorption. The application of animal by products in the field of bioremediation is very few because such products have useful applications (35).

Plant Based Materials

Amine functionalized magnetic corn stalk composites were used by scientists reduce hexavalent chromium. Various factors affecting the adsorption has also been studied. XRD, SEM, FT-IR BET VSM XPS studies were conducted to explain the mechanism of metal ion absorption. The research showed the interaction between metal ion and composite might include electrostatic attraction chemisorption, adsorption. (36)

Cellulosic materials and their derivatives have shown quite good metal ion adsorptive capacity. although, the efficiency of activated carbon in absorbing heavy metal ions from wastewater is high enough, because of significant costs involved in preparation of activated carbon and its regeneration. It is only used as a tertiary step in the treatment of waste water. Among all heavy metal removal techniques reported so far, ion exchange technique using cellulose based agricultural waste appears to be most attractive since it is an effective and relatively simple method for removal of heavy metal ions. Also the adsorption capacity is reduced at every stage of regeneration (37).

Cr (VI) removal from industrial waste water by different low cost abundant adsorbents had been studied by researchers. Wool, Olive cake, sawdust, pine needles, almond shells, cactus leaves and charcoal were used at different adsorbent/metal ion ratios. The influence of pH, contact time, metal concentration adsorbent nature and concentration of the selectivity and sensitivity of the removal process was investigated (38).

Nut Shell Carbon

Prunus amygdalus (Almond nutshell) which belongs to *Rosaceae* family is adsorbent can be used efficiently to treat Cr (VI) contaminated wastewaters. The maximum uptake capacity of the adsorbent was observed at pH 1.8. The percentage adsorption as well as uptake capacity of the adsorbent increased with decrease in pH. The percentage adsorption was found to be increased with adsorbent dose whereas decreased with adsorbate concentration. The percentage adsorption increased with increase in the adsorbent dosage. The percentage removal of Cr (VI) by this adsorbent was found to be 60 %.(39).

Plant Leaf Powders

Powdered leaves of various plants have extensively studied by various researchers. Powdered leaves of *Bhringraj Aerva lanata, Trianthema Portulacastrum* leaves have been used for extracting Cr (VI) from polluted water. (40) Plants leaves and their ashes of *Tephrosia purupurea* and *Solanum Nigrum* have been used for the removal of Cr (VI) from industrial effluents and polluted lakes (41).

Conclusion

This paper highlighted current studies on the use of various adsorbents obtained from biological materials for heavy metal removal from waters. Such materials include biomass of algae, fungi, animal by-products and cellulosic materials. All of these have good adsorbent capacity for heavy metals. The mechanisms of uptake include chemisorption and physio sorption. The materials are readily available and relatively cheaper than various synthetic resins. This field may therefore be utilized by developing countries to alleviate or at least reduce the impacts of industrial water pollution on the aquatic environment. Despite existing limitations, various modifications either by chemical or biological methods may result in remarkable enhancement in their metal uptake capacities. Thus more attention should be paid to improving pre-treatment methods. Most of bio sorption studies using biological waste products involved in single metal systems. Hence, further work is required in multi metal systems and real waste water to make industrial usage of biological products more feasible, particularly there is a need to develop versatile bio sorbents for the simultaneous decontamination of several pollutants.

References

1. Nemerow, N.; Dasgupta, A. Industrial and Hazardous Waste Treatment, Van Nostrand Reinhod: New York, 1991.
2. Tchobanglous, G; Franklinn, L. B. Waste ater Engineerig: Treatment, Disposal and Reuse; McGraw Hill, Inc.: New York, 1991.

3. Ali, I.; Abul-Eneir, H.Y. Chiral Pollutants: Distribution, Toxicity and Analysis by Chromatography and Capillary Electrophoresis; John Wiley & Sons: Chischester, UK, 2004.
4. Franklin, L.B. Wastewater Engineering: Treatment, Disposal and Reuse, McGraw Hill Inc.: New York, 1991.
5. Laws, E.A. Aquatic Pollution: An Introductory Text, 3rd ed.; John Wiley & Sons: New York, 2000.
6. Meena AK, Kathirvelu K, Mishraa GK, Rajagopal C, Nagar PN. Adsorption of Pb(II) and Cd(II) metal ions from aqueous soluutions by mustard husk. J Hazard Mater 2008, 10, 619-25.
7. Vinodhini V Das N, Relevant approach to assess the performance of sawdust as adsorbent of chromium (VI) ions form aqueous solutions. Int. J Environ Sci Technol 2010, 7, 85-92.
8. Demirbas A. Heavy metal adsorption on to agro-based waste materials; a review. J Hazardd Mater 2008, 157, 220-9.
9. Wan Ngah WS, Hanafiah MA KM. Removal of heavy metals from wastewater by chemically modified wastes as adsorbents: a review. Bioresource Technol 2008, 99, 3935-48.
10. Ahmaruzzaman M. Industrial wastes as low-cost potential adsorbents for the treatment of waste water laden with heavy metals. Adv. Colloid Interface Sci. 2011, 166, 36-59.
11. Okeimen FE, Okundia EU, Ogbeifun DE .Sorption of cadmium and lead ions on modified ground nut (*Arachis hypogea*) husk. J. Chem. Technol. Biotechnol., 1991, 51, 97-103.
12. Strik WA, Staden JV. Removal of heavy metals from solution using dried brown seaweed material, Botanic Marna, 2000, 43, 467-473.
13. Horsfall M, Spiff AI .Studies on the Effect of pH on the Sorption of Pb^{2+} and Cd^{2+} ions from aqueous solutions by Caladium bicolour Biomass. ISSN 0717-3458 Electronic Journal Biotech. 2004, 7(3), 313-323.
14. Ulmanu M, Maranon E, Fernandez Y, Castrillon L, Anger I, Dumitriu D .Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material adsorbents. Water air soil pollut. 2003, 142, 35-373.
15. Strik WA. Staden JV. Removal of heavy metals from solution using dried bron seaweed material. Botanica Marina.2000, 43, 467-473.
16. Shukla SR, Pai RS. Removal of Pb (II) from solution suing cellulose containing materials. J.Chem. Technol. Biotechnol., 2005, 80,176-183.
17. Horsffal M, Abia AA, Spiff AI Removal of Cu (II) and Zn (II) ions from waste water by cassava (Manihot esculenta Cranz) waste biomass. Afr. J. Biotechnol., 2003, 2, 1246-1255.
18. Rangsayatorn N, Upatham ES, Kruatrachue M, Pokethitiyook P, Lanza GR, phytoremediation potential of spirulina (*Arthrospira)* Plantensis: Biosorption and toxicity studies of Cadmium. Environ. Pollut. 2002, 119, 45-53.
19. Kaesarn P,Yu Q. Bioremoval of cadmium (III) removal from aqueous solutions by pre-treated biomass of marine algae (*Paina sp*). Environ.Pollt. 2001, 112, 209-213.
20. Okiemen FE, Ogbeifun DE, Nwala GB, Kumsah CA Binding of cadmium , copper and lead ions bby modified cellulosic materials Bull. Environ Contam. Toxicol.,1985, 34, 86-870.
21. Marshall WE, Johns MM Agricultural byproducts as metal adsorbents sorption properties and resistance to mechanical abrasion. J chem technol biotechnol., 1996, 66 192-198.
22. Kilmmek S, Stan HJ, Wilke A, Bunke G Buchholz R. Comparative analysis of the biosorption of cadmium, lead nickel and zinc by Algae. Environ. Sci.Technol. 2001, 35, 4283-4288.
23. Rangasayatorn N, Upatham ES, Kruatrachue M Pokethitiyook P, Lanza GR. Phytoremediation potential of Spirulina (Arthrospira) Platensis: Biosorption and toxicity studies of Cadmium. .Environ. Pollut.2002, 119, 45-53.
24. Masel, R. I. principles of Adsorption and Reaction on Solid Surfaces; John Wiley Sons; New York .1996.
25. Lewinsky, A.A, Hazardous Materials and Wastewater: Treatment, Removal and Analysis, Nova Science Publishers: New York,1996.
26. Binns. C. Introduction to Nanocience and Nanotechnology; Wiley C& Sons: New York 2010.
27. Zhu, H.J.; Jia. Y.F.; Wu, X.; Wang, H. Huan Jing Ke Xue 2009, 30,1644
28. Ponder, S.M, Darab,J.G., Bucher,J.D., Craig, C.I DavisL., Stein, N.E,, Luken, W., Nitsche, H. Rao,L.F., Shuh,D.K., Mallouuk T.E. Sep.Purif. Technol.2007,s7, 161
29. Zhou JL, Huuang PL, Lin GG.Sorption and sesorption of Cu and Cd by microalgae Environ.Pollut. 1998. 101:67-75.

30. Amatussalam.A, Abubacker M.N, and Babu Rajendran, "In Situ Carica PaPaya stem matrix and Fusarium Oxysporum(NCBT—156) mediated bioremdieation of chromium" Indian Journal of Experimental Biology, 2011.49, 925-931.
31. Maria M. Martorell, Pablo M. Fernandez, Julia I. Farina, Lucia I.C Figueroa Cr(VI) reudction by cell-free extracts of Pichia jadiniiand pichia anomala isolated from textile-dye factory effluents' International Journal of Biodeterioration & Biodegradation ol. , 2012, 71,80-85.
32. Anuradha J.S., Lalith. D, Pavithra G., Sorption of Chromium (VI) from electroplating effluent onto chitin immobilized Mucor racemosus sorbent (CIMRS) impregnated in rotating disk contactor blades. J. of Industrial and Engineering Chemistry 2015,23, 79-92.
33. Dinesh Mohan, Shalini Rajput, Vinod, K.S., Philip H. S, Charles U.P, Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. J. of Hazardous Materials .2011, 188, 319-333.
34. Nilisha Itankar, Yogesh Patil, Management of hexavalent chromium from industrial waste using low-cost waste biomass. Procedia- Social and Behavioral Sciences 2014, 133, 219-224.
35. Kar P, Misra M, Use of keratin fibre for separation of heavy metals from water. J.Chem.Technol.Biotechnol. 2004, 79:1313-1319.
36. Wen Song, Baoyu . G, Tengge. Z, Xing Xu, Xin Huang, Huan Yu, Qinyan Yue High-capacity adsorption of dissolved hexavalent chromium using amine-functionalized magnetic corn stalk composites, Bioresource Technology 2015, 190, 550-557.
37. Shukla SR, Pai RS Removal of Pb (II) from solution using cellulose containing materials. J. Chem. Technol. Biotechnol. 2005, 80, 176-183.
38. Dakiky M, Khami M, Manassara A, Mereb M. Selective adsorption of chromium(VI) in industrial waste water using low-cost abdundantly available adsorbents. Adv.Environ. Res., 2002, 6(14),533-543.
39. Mosleh M Manfe SJ, Attar M Parande, Niraj S Topare.Treatment of Cr (VI) contaminated water using biosorbent *prunusamygdalus* (almond) Nut shell carbon. Int J Chem Sci.2012,10(2), 609-618.
40. Sekhar KPC, Vishnu Babu RV, Rohini T, Ravindhranath k. New biosorbents in the control of chromium (VI) pollution in wastewaters. Inter J App Bio Phar tech.2012, 3(2), 115-125.
41. Krishna Reddy RH, Naga Malleswara Rao N, SumarnKrishna JV, Ravidhranth K. Removal of Chromium (VI) from Polluted waters. J Bio Phy Sci. 2012, 2(3), 1621-163.

*****