Review Article

A REVIEW ON ORGANIC ADSORBENTS FOR THE REMOVAL OF TOXIC METALS FROM WASTE WATER

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ABSTRACT

The contamination of water due to explosive population growth rate, industrial operations, various toxic components particularly trace metals are affecting on the flora and fauna including on the human well-being. Water is essential requirement for process, developmental activities and all the living being. Due to manmade activities, there is an instant necessity to find different techniques for the removal of toxins in wastewater. Industrial processed effluent contains like nickel, lead, chromium, zinc, arsenic, cadmium, selenium and uranium. So far, a various type efficient methods are available for the removal of heavily metals such as chemical precipitation, ion exchange, reverse osmosis, ultrafiltration, electrodialysis, nanofiltration, coagulation, flocculation, floatation, etc. However available methods have numerous disadvantages like more reagent requirement, random removal of metal ion, generation of toxic sludge etc. At present, treatment of water in the economical process is very important. So the various natural adsorbents were used for the treatment of water. Adsorption techniques being very simple, economical, successful and flexible has become the most ideal methods for removal of toxic metals from wastewater. In this paper reviewed on readily available about 99 published articles (1990-2020) various natural materials as adsorbents for removal of heavy metals from wastewater. It is evident from the review of articles that ion-exchange, adsorption and membrane filtration are the most frequently apprised for the removal of heavy metal in wastewater. As these industries disposes untreated or poorly treated waste water containing toxic metals to the water bodies which in turn affect the human health those who are consuming it causing serious carcinogenic health effects. In this paper an attempt is made to study the effort done by the various researchers those who have made an attempt to treat the toxic waste water by using natural adsorbents and the results are discussed.

Keywords: various method, adsorption, toxic metals, Adsorbents

INTRODUCTION

Environmental pollution is presently one of the major important issues due to undesirable effects of industrialization, urbanization, population growth and human attitude towards the environment. At present, environmental protection is the main need of the society. Oyaro, *et al.,* (2007), reported heavy metals are essential for human health. They are significant for the many functions of living beings and regulate the different biochemical processes. However, more trace metals affects and changes in the immune system like stomach pain, skin irritation, vomiting, nausea and anemia. Metals also required for metabolic activities in animals, it exceed in the animal system may cause cramps, convulsions and finally death (Paulino, *et al.,* 2006). Sources of water contaminants by trace metals are presented in Figure 1.

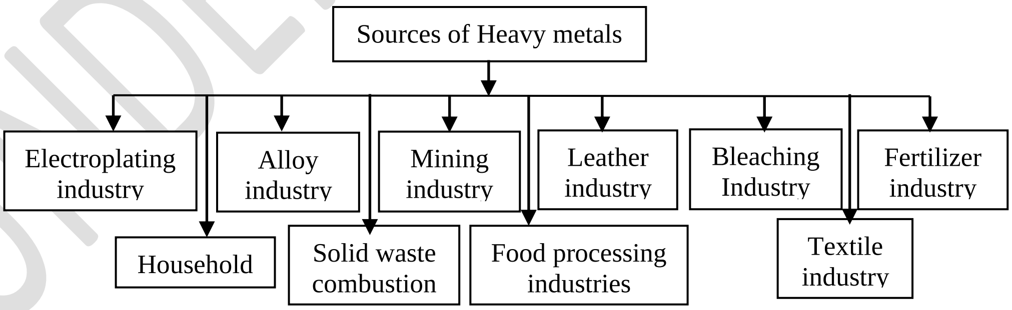

Figure 1 Sources of water contaminants by trace metals

In India, the environmental pollution has become a cause of concern at various levels. Due to lack of sewage treatment plants, generally untreated sewage effluents are released either on agricultural land for irrigation or disposed of to nearby water bodies. Toxic metals are chemical elements like arsenic, iron, chromium, cadmium, lead, cobalt, nickel and mercury which are having specific gravity multiple times the specific gravity of water and arepoisonous even at low concentrations. These toxic metals are from electroplating industry, electronic goods manufacturing industry, battery industry and so on. For low level heavy metals wastewater, the conventional treatments are commonly used like ion exchange and precipitation methods are having the disadvantages since low efficiency, more cost and easy to form secondary pollution in the atmosphere (Wang, *et al.,* 2019). Hence, probable low-cost adsorbents like clay, zeolites, chitosan and other have been widely used for the removal of heavy metal

(Asere, *et al.,* 2019; Uddin, 2017; Zhang, *et al.,* 2016; Egashira, *et al.,* 2012; Zhang, *et al.,* 2012; Wang and Chen, 2009; Gadd, 2010; Bradl, 2004). Table 1 predicts the maximum allowable limits toxic metals in drinking water. Several conventional treatment methods of removal of heavy metals through electro-coagulation, flocculation, co-precipitation, filtration, reverse osmosis, membrane bioreactor, electro-dialysis, ultra filtration, bio-sorption, solvent extraction, ion exchange, and wetland technology (Radhakrishnan, 2014; Sudarsan, 2015; Ali and Peer, 2017; Ahdoum, *et al.,* 2004 and Yavari, *et al.,* 2016) amongst others are not effective for the treatment of heavy metals in the range of 1to 100mg/L. The reduction of contaminants by conventional techniques is complex and a need for a novel technique is preferred. Adsorption technology is typically applied to sequester different bio-degradable and non-biodegradable contaminants from wastewater (Elsehly, 2016).

Table 1 Standard allowable Maximum Contamination Level (MCL) for Toxic Metals

Toxic Metal	MCL (mg/L)
Arsenic	0.050
Cadmium	0.01
Chromium	0.05
Copper	0.25
Nickel	0.20
Zinc	0.80
Lead	0.006
Mercury	0.00003

LITERATURE REVIEW

Agricultural waste as adsorbent

Varieties of agricultural wastes used as adsorbent like wool, rice, straw, coconut husks, peat moss, tired coffee (Bhattacharya, *et al.,* 2006; Eccles, *et al.,* 1999 and Orhan, *et al.,* 1993), waste tea (Ahluwalia, *et al.,* 2005), rice hulls (Ajmal, *et al.,* 2003; Marshall, *et al.,* 1993 and Tarley, *et al.,* 2004), cork biomass (Chubar, *et al.,* 2003), seeds of Ocimum basilicum (Melo, *et al.,* 2004), coconut shells (Babel, *et al.,* 2004), soybean hulls and cotton seed hulls (Bailey, *et al.,* 1999), saw dust of walnut (Bulut, *et al.,* 2003) untreated coffee dust Oliveira, *et al.,* 2008), papaya wood (Saeed, *et al.,* 2005), peanut hulls (Johnson, *et al.,* 2002), citrus peel (Ajmal, *et al.,* 2000) were used as adsorbents for removal of metals. However, sea weeds, molds, yeasts, bacteria have been used for metal bio-sorption with hopeful values (Moustafa Moustafa, *et al.,* 2003; Ahluwalia, *et al.,* 2007; Wu J, Zhang, *et al.,* 2010 and Mane, *et al.,* 2011). Mohd Rafatullah, *et al.,* (2012) did a study on Meranti wood, an inexpensive material, utilized as an adsorbent for the removal of Cadmium (II) from aqueous solutions. Various physicochemical parameters such as equilibrium contact time, solution pH, initial metal ion concentration and adsorbent dosage level were studied. Most of agricultural wastes were used without chemical modification reported that poor metal removal in accumulation to their nonmetal selectivity due to some nature of adsorbent, properties of solution, contact time and metal concentration factors are responsible.

Chemical adsorption technique

Chun, *et al.,* (2008), In this study, palm shell activated carbon was impregnated with polyethyleneimine (PEI) and the effect of impregnation on batch adsorption of Ni^{2+}, Cd^{2+} or Pb^{2+} as well as the equilibrium behavior of adsorption of metal ions on PEI impregnated AC were investigated. In the single metal adsorption capacities of Ni^{2+} or Cd^{2+}except for Pb^{2+}, where its adsorption capacities were reduced by 16.67% and 19.55% for initial solution pH of 3 and 5 respectively. Goran, *et al.,* (2009) studied the functions of multi layered carbon nano-tubes (MWCNTs) by ethylene diamine, via chemical alteration of carboxyl groups, using O-(7-aza benzotriazol-1-yl)-N,N,N',N'- tetra methyl uranium hexa fluoro phosphate. The resulting materials were characterized by different techniques, such as FTIR, TGA and elemental analysis. Biocompatibility studies indicated that the functions of MWCNTs, at concentrations between 1 and 50 gm/L, were not cytotoxic for the fibroblast L929 cell line. Mihaela Mureseanu, *et al.,* (2012) stated that Metallothioneins (MTs) are low-molecular weight proteins (1 -10 kDa), which are known to bind selectively metal ions such as Zn or Cd in metal thiolate clusters. The study describes the preparation of copper metallothionein (Cu - MT) and its immobilization by covalent grafting on meso-porous silica for the selective uptake and recovery of Cu^{2+} from water. The meso-porous silica used (SiDav) features 10nm pore size suitable to accommodate Cu-MT (6nm size) and 200 lm particle size adequate for flow processes. Adarsh, *et al.,* (2020) worked on diary wastewater treatment using low cost adsorbent. The orange peels are adsorbent used in their work, the effect of pH, time of contact, adsorbent dosage in removal of contaminants present in diary wastewater is appraised. Experiments were conducted for different dosages using water bath shaker with slow mixing contact time. Results have shown that the pH is reduced from 8.4 to 6.2, The BOD & COD removal is observed to be 70.79% & 74.58% respectively. Turbidity and sulphates removal is observed to be 35.53% and 47.61% respectively. There is a superficial increase in the chloride and total suspended solids level by 36.47% and 80.66% respectively. Total dissolved solids removal is observed to be 86.86 %.

Bioadsorbents

The main limiting factors of biosorbents for sensible heavy metal removal from wastewater is the efficiency of biosorbents, source of metals and reproducibility (Vijayaraghavan and Yun, 2008; Wang and Chen, 2009). Even though biosorbents are usually accessible, some of biosorbents can be reused many times, they ultimately reached to landfill / incineration. Hence, continuing to find an incessant source of biosorbent is the current research view of biosorbent for removal of heavy metal in wastewater. In addition, to this difficulty of handling genuine wastewater, the challenges of applying biological removal method of the genuine heavy metal in wastewater present. The improved techniques of biosorbents own its way for removal of heavy metals, but it cannot be restricted in single technique that have reviewed. Further, the addition of bioadsorbent as adsorbent is complex of handling actual wastewater; the challenges of applying biological removal technique of the actual heavy metal wastewater are still exist. The improved techniques of biosorbents own its way for removal of heavy metals is not limited for single technique. Further work should be based on biological techniques and it is believe that a combination of multiple methods may be suitable solution and also for broader application prospect (Huaqing Qina, et al., 2019).

Electro dialysis(ED)

The membrane is classified into basically into two types like cation-exchange and anion-exchange in which the cations move toward the cathode and vice versa crossing in a different way deliberate membranes respectively (Chen, 2004). Mohammadi, *et al.*, (2004) and Cifuentes, *et al.*, (2009) reported ED is very effective technique in the removal of Cu and Fe (removal efficiency up to 96.9 %) respectively. Lambert, *et al.*, (2006) and Mohammadi, *et al.*, (2005) reported with respect to zinc, lead and chromium ions, the performance of ED is not dependent on the type ions but the main factors are operating conditions and structure of ED cell. ED technology have many merits in analyzing the wastewater contaminated with heavy metals is removal of undesirable impurity from water also the ability to pick up the valuable metals but it required clean feed and high operating costs and daily maintenance since the efficiency is related with temperature and voltage.

Ion Exchange (IE)

Motsi, *et al.*, (2009) reported that naturally available silicate and zeolites are chief materials for removal of trace metal and low cost and prevalence as well as excellent metal adsorption capacity under various experimental conditions (Ostroski, *et al.*, 2009). Taffarel and Rubio (2009) reported loading of clinoptilolite with amorphous Fe^{-} oxide on the surface indicated that more adsorption capacity in most of the conditions (Doula 2009; Doula and Dimirkou, 2008; Inglezakis, *et al.*, 2002). Even though, the usage of zeolites and montmorillonites as ion-exchange resin to treat the heavy metal in waste water is restricted, since it is not published but still in the laboratory scale. With the above reviews states that IE is having more advantages like fast kinetics, removal efficiency is more and recovery of heavy metal including treatment capacity is also high (Kang, *et al.*, 2004), resin required to be revitalized on a standard basis which will enhance the cost of the operation along with sludge production as residue.

Membrane filtration (MF)

MF is a pressure driven separation techniques for removal heavy metals, it can be improved by treating the membrane with appropriate chemical materials (Barakat and Schmidt 2010; Kurniawan, *et al.*, 2006b).

Ultrafiltration

In the ultrafiltration technique, the particles are larger than the porous size of UF membranes will be ensnared while the metal ions is converted into hydrated ions and also low molecular weight mixture will pass easily through the UF membranes (Vijayalakshmi, *et al.*, 2008). It is evident that some supplementary chemical agents like surfactants / polymer formation agents improved UF (Landaburu, *et al.*, 2009). The metal ions will be squeezed by aggregate of surfactant molecules then form large metal surfactant cycles (Liu, *et al.*, 2016; Zeng, *et al.*, 2011). From the investigation, predicts that the rejection coefficients up to 98% were attained when the surfactant to metal molar relation (S/M) is above 5 (Landaburu, *et al.*, 2009; Samper, *et al.*, 2009) and forthcoming 99% for Cr (III) were removed at pH is more than 7 when polymers were adopted in the analysis (Kim, *et al.*, 2005). Actually as per the study, the removal efficiency of heavy metal is depends on the properties like pH of the solution, the ratio of metal and surfactant / polymer also the presence of the metals content in the solution. However, a number of publications indicates, the usage of UF with the help of polymer agents not suitable in industries not yet also having demerits like its maintenance and operational costs is very high.

Nano-composites based on Biopolymers

Hybrid composites (organic and inorganic) of high stability can be obtained by forming a polymer shield over an inorganic Nano material along these lines joining the upsides of both materials. Composites made from various polysaccharides comprise another class of naturally safe materials for diverse biological and industrial applications. It was stated that magnetic Nano-materials functionalized with biopolymers, for example, chitosan (Pineda, *et al.*, 2014 and Tran, *et al.*, (2010), gum Arabic (Banerjee, *et al.*, 2007), β-cyclodextrine (El-Kafrawy, *et al.*, 2016) and cellulose (Carpenter, *et al.*, 2015), have been utilized for the exclusion of toxic metals from aqueous solution. Nano particles composed of modified starch polymer and Fe_3O_4 (modified potato starch magnetic nano particles, MPS-MNPs) were synthesized. The prepared Nano adsorbents were used for selective abstraction of Pb^{2+}, Cu^{2+}, and Ni^{2+} ions from water (Abdul-Raheim, *et al.*, 2016). The grafting reaction of acrylic acid onto starch is provided in. It has been shown that starch can effectively stabilize Nanoscale magnetite particles, and starch-stabilized magnetite nano particles (SMNP) are potent sorbents for in situ remediation of arsenic contaminated soils (Zhang, *et al.*, 2011). An, *et al.*, (2011) developed a new engineered strategy to minimize the production and arsenic leachability of the process waste left behind. They prepared and tested a new class of starch-bridged magnetite nano particles for removal of arsenate.

Reverse osmosis (RO)

RO is also depend upon the porous size of membrane (<2 nm), works on the principle of size and diffusion of solution with semi permeable layer, where water is passing then follow the twisted pathway to run off with netted structure (Greenlee, *et al.*, 2009). Number of work done by the researchers for removal of RO membrane and performance is at 5 atm operation pressure, RO can attain 99% removal efficiency of Cu^{2+} and Ni^{2+} (Mohsen Nia, *et al.*, 2007) is 99 and 98.6%, correspondingly (Zhang, *et al.*, 2009), but removal efficiency of Cu^{2+} could range from 75 to 96 % reported by (Ipek 2005). Many research work done on removal of heavy metals using RO systems; they have not been extensively applied yet since maximum high power is required and regeneration of membrane.

Coagulation/ flocculation

Ferric chloride is the chiefly effective coagulant for removal of turbidity, color and TOC removal percentages greater than 72% and a coagulant dose of 61 mg/L, while for the best metal removal doses were 229 mg/L and 498 mg/L aluminum sulfate, and 305 mg/L and 508 mg/L of ferric chloride, attaining removal percentages above 81% for the majority metals. Chitosan is not that much of did comparatively Chitosan showed removal efficiencies is less compare to other coagulants. The optimal for removal of metals, aluminum sulfate and ferric chloride are required in coagulation process in the water. The disadvantage of coagulation process is mainly high dosage of coagulants are required. The results warn that the best dosage of colloidal material removal gives dose for removal of metals in various procedures.

For the chitosan, clotting process is differing from Aluminum Sulfate and Ferric Chloride in coagulation process. Hence, author selected and reported as optimal doses of removal of organic matter is low solubility property (Sciban, *et al.*, 2009). If the Chitosan is used for removal of copper and cobalt, the optimal dose is 9.5 mg/L with a removal percentage are 15% and 50% correspondingly. Rodriguez, *et al.*, (2012) used ferric chloride plus polymer as supporter coagulation to remove Lead, Chromium, Copper, Zinc and Nickel metals. The percentage of removal of metals of about 94% Lead, 91% chromium, 78% copper, 56% of zinc and 16% Nickel. In this process predicts that coagulation will be encouraged biopolymers as coagulant in the process.

Various polymers are having merits over chemical coagulants since they are safe and easy to handle also easily biodegraded (Sievers, *et al.*, 1994 and Zhu, *et al.*, 2004). Author also expressed and reported In their work, addition of polymer to ferric chloride increases the coagulation process even at different polymer doses. The same trends were observed by other researchers (Santarsiero, *et al.*, 1998; Tatsi, *et al.*, 2003; Zhu, *et al.*, 2004 and Aguilar, *et al.*, 2005). Many research work done on removal of metals using coagulation process, mainly factor is volume of sludge will be produced more, if only ferric chloride used as coagulant in process; however, the maximum reduction in the volume of sludge (65%) was reached when the ferric chloride is replaced by polymer as coagulant.

Adsorption process

Awwal Musa, *et al.*, (2020) evaluated the contaminant removal efficiency of an improvised charcoal filter. The filter had four layers with 6.3mm, 2.0mm, 1.18 mm size, and powdered charcoal was used for the filtration process. The water sample was collected from river Challawa from the region believed to have the highest concentration of contaminants. The physicochemical and bacteriological characteristics of the water sample before and after filtration were determined and evaluated. It also showed high odor, hardness, and chloride removal efficiencies. However, an increase in conductivity was observed in the filtered samples which may be correlated to the ability of charcoal to enrich the water with elements like sodium and potassium. In addition to these the pH value of the sample before filtration was acidic (i.e. 5.7) but increased to 7.7 after filtration which is suitable for drinking water. Hence, it is recommended here that charcoal filters can be used to produce high-quality water.

Shameeda and RanaRahman (2020) stated that the textile industry is considered to have one of the most polluting wastewater effluents in the world, with regards to volume and composition, and large quantities of dye used for coloring fabrics are present in the effluent. Textile wastewater was diluted to get different concentrations from 790 mg COD/L to 1350mg COD/L and this was given as feed to microbes present in MFC. The COD removal efficiency increased with the increase in feed concentration. The maximum COD removal of 77.03% was achieved at the feed concentration of 1350 mg COD/L. MFC produced a maximum current of 4.8 mA and power density of 16.8 mW/m^2

The adsorption technique for removal of toxic waste from industrial processed water many by products from agricultural and industry has been extensively reported (Basu, *et al.*, 2006; Srivastava, *et al.*, 2006). Technically various low cost adsorbent for removal of heavy metals from waste water reported (Babel, *et al.*, 2003). As a substitute of commercial activated carbon, researchers have used inexpensive materials and locally available chitosan, zeolites, and other adsorbents, which have maximum adsorption capacity.

Among the various techniques, adsorption is presently reported as a suitable for removal metals from waste water, this process is cost effective and simple (Yadanaparthi, *et al.*, 2009, Kwon, *et al.*, 2010). Adsorption is commonly used method for the removal of toxic metal from different industrial processed water (Gottipati, *et al.*, 2012). Some widely used adsorbents for removal of toxic metal is activated carbon (Pollard, *et al.*, 1992, Satapathy, *et al.*, 2006), clay minerals (Wilson, *et al.*, 2006), bio-materials, solid wastes from industry and zeolites (Wang, *et al.*, 2008). Natural available material and industrial waste including agricultural waste are the resources for low cost adsorbents. In general, these adsorbents are locally and easily accessible in huge quantities. Therefore, these adsorbents are inexpensive and little economic value (Mohana, *et al.*, 2007).

CONCLUSIONS

Faced with more and more severe regulations, nowadays heavy metals are the environmental main concern pollutants and are becoming one of the most serious environmental problems. So these toxic heavy metals should be removed in the wastewater to protect the people and the environment. Various methods that are being adopted to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. The current review article deals with the present techniques for the removal of heavy metal ions from wastewater. Their advantages and limitations in application are also evaluated. This article reviews the past, present and future approaches for using organic adsorbents as effective techniques for the removal of heavy metal ions from wastewater along with advantages and disadvantages. The current trends of using natural organic materials as cost-effective and environmentally acceptable adsorbents for water decontamination were discussed in this review paper. This review highlights the applications of organic adsorbents because of it is cost effective, removal efficiency and various factors including thickness and filter bed. From the previous survey and review, an appraisal of various techniques and adsorbents for removal heavy metal indicates that adsorption techniques has huge probable and best for the removal of heavy metals from Industrial end liquid product using low cost adsorbents. Number of reviews carried out for low-cost adsorption techniques to encourage in large scale use of non-conventional adsorbents. Application of low cost adsorbents as adsorbent reduces the cost and maximizes removal efficiency of trace metals in waste water.

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