Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2018, Volume 9, Issue 8, Page 2345-2355

http://www.jmaterenvironsci.com

Heavy metal sequestration from contaminated water: A review

Hamida-Tun-Nisa Chisti*[a]

[a]*Department of Chemistry, National Institute of Technology, Srinagar 190006, India.*

Received 13 Oct 2017,
Revised 26 Nov 2017,
Accepted 01 Dec 2017

Keywords
- ✓ Heavy metals,
- ✓ Ion-exchange,
- ✓ Chemical precipitation,
- ✓ Bio-sorption,
- ✓ Low cost Bio-adsorbents.

hamida@nitsri.net
Phone: +91-9469668449

Abstract

Heavy metal pollution is currently one of the most threatening environmental problems faced by humanity. The removal/treatment of heavy metal ions is of great concern due to their intractableness and accumulative nature. In this article, the technical feasibility of various conventional physico-chemical and bio-sorption methods has been reviewed for the removal of various heavy metal ions from the contaminated wastewater. Keeping environmental sustainability in mind, the particular focus has been laid on biosorption, besides this the advantages and drawbacks of various conventional physico-chemical methods such as chemical precipitation, ion exchange and membrane filtration have also been highlighted in this article. It is evident from the literature survey that the low-cost bio-adsorbents have shown remarkable and outstanding removal capabilities as compared to other physico-chemical methods. In general, the technical feasibility, profitability, cost-effectiveness and efficiency are the key factors in selecting the suitable treatment method for the elimination of heavy metal ions from contaminated water.

1. Introduction

The fast-growing population, unmanageable urbanization, steep industrialization and improper utilization of water resources have led to the unmatched destruction of water quality throughout the globe. This problem is not only a particular region specific issue but has become a global menace. In the long run, the effect of water pollution alters the delicate balance of the nature. Basically, the water pollutants are classified as organic and inorganic pollutants. The inorganic pollutants mainly constitute the heavy metals. According to various environmentalists and researchers, the term "heavy metal" is oftenly used in research articles as a combined term for metals and semi-metals (metalloids) that have been associated with contamination and potential threat in terms of toxicity. However, as per the literature survey, the term heavy metal has never been appropriately defined by any established authoritative body such as International Union of Pure and Applied Chemistry (IUPAC) and reveals that the term "heavy metals" has been used inconsistently. Some authors define it in relation to density or specific gravity [1] others define it in terms of atomic mass or atomic number while some definitions have no clear cut explanation except toxic effects on the aquatic ecosystem. This term is a misnomer because these are not all "heavy" in terms of atomic weight, density, or atomic number and some are not even entirely metallic in character e.g. arsenic (metalloid). Depending on the view of interest and the environmental impact, metals are divided into four major categories (Figure 1**)**.

(1) Toxic heavy metals
(2) Strategic metals
(3) Precious metals
(4) Radionucleides.

In terms of environmental menace and toxicity, the metals in the categories 1 and 4 need to be removed from the aquatic environment.

Metals and metalloids due to their extensive use represent an important fraction of the pollutants. Several historical unforgettable episodes due to heavy metal contamination in aquatic environment increased the awareness about the heavy metal toxicity. Among these, Minamata tragedy due to methyl mercury poisoning and "Itai-Itai" disease in Japan due to cadmium toxicity are well known [2]. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in bio-systems, thus becoming dreadful for the aquatic as well as for human life. A variety of anthropogenic sources and industries are responsible for the release of heavy metals into the aquatic environment [3].

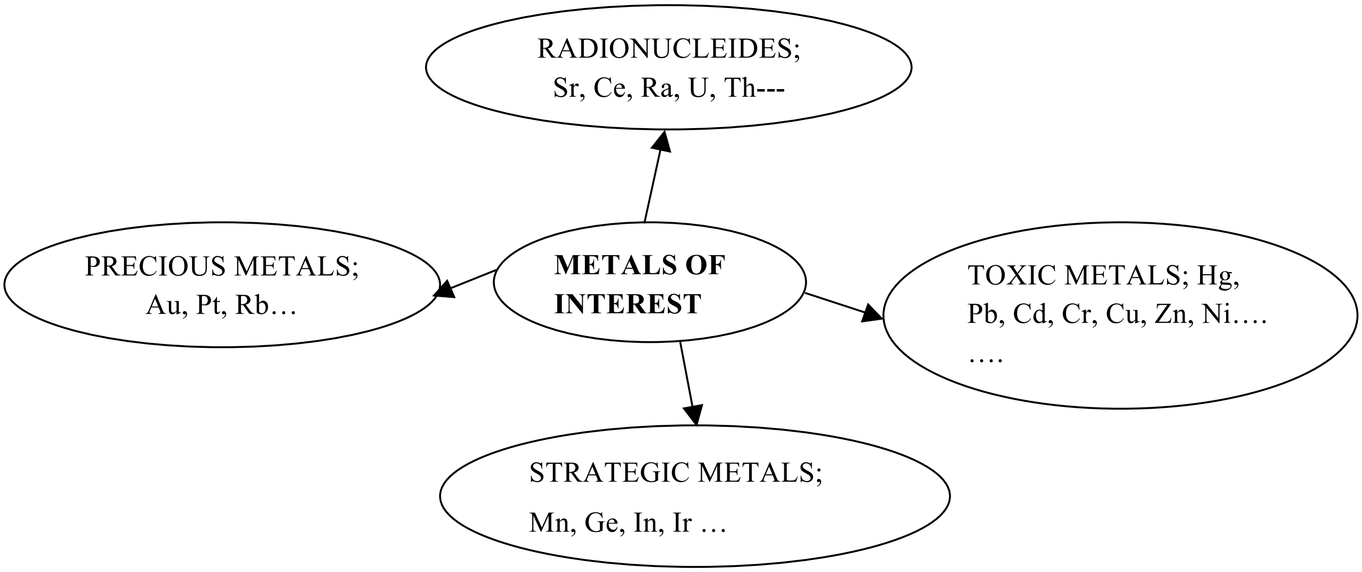

Figure 1: Metal classification

Conventional treatments for the removal of heavy metals from water and aqueous solutions include chemical precipitation, ion-exchange, reverse osmosis, coagulation–flocculation, electro-dialysis etc [4]. However, these technologies have been studied less extensively due to less efficiency, high cost, sensitive operating conditions and production of secondary sludge [5]. Since 1990's the adsorption of heavy metals by renewable biomaterials has gained great emphasis because of low cost, eco-friendly, high efficiency, minimum sludge formation, possibility of metal recovery [6].

Adsorption is an important process utilized in the removal of toxic metal ions from aqueous solutions. Adsorbent can be considered as cheap or low-cost if it is abundant in nature and requires little processing before its use. The plant wastes are low in cost and easily available. Plant wastes are inexpensive as they have no or very low economic value [7]. Adsorption studies mostly focused on untreated plant wastes such as grape stalk waste [8], neem bark, rice husk ash [9], pellets of peanut hull [10] , Sago waste [11] , Imperata cylindrical leaf [12], Moringa oleifera pods [13], tea waste [14] etc. The concentrations of the heavy metal ions is continuously increasing day by day than the permissible discharge levels from industrial effluents. It is therefore, of utmost importance to remove these heavy metal ions from the untreated waters by suitable methods.

This review article presents an overview of the technical applicability of various metal removal processes as well as utilization of agricultural waste materials and other biosorbents for heavy metal ion sequestering from water and waste water.

2. Toxicity of heavy metal ions

Due to high mobility, solubility, persistency, toxicity and bio-accumulation tendency of the metal ions in aquatic ecosystems creates adverse effects on human health and environmental degradation [2,15-17]. Heavy metal ions pose serious threat to human health, which includes impairment in growth, development and nervous system disorders. Exposure to certain metals like mercury and lead, may also cause autoimmune disorders such as rheumatoid arthritis, kidney diseases etc. Moreover, heavy metals are carcinogenic as well as mutagenic;

hence create lung cancer, skin cancer, whitening of hair etc. At higher doses, heavy metals can cause irreversible brain damage. Wastewater regulations have been established to minimize human and environmental exposure to hazardous chemicals. The Maximum Contaminant Levels (MCL) limits established by United States Environmental Protection Agency (USEPA) and the toxicities created in the aquatic environment by the discharge of heavy metals [18] are summarized in (Table 1).

Table 1: The MCL standards for the most hazardous heavy metals [18].

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease.	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen.	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic.	0.05
Copper	Liver damage, Wilson disease, insomnia.	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, Human carcinogen.	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst.	0.80
Lead	Damage the foetal brain, diseases of the kidneys, Circulatory system and nervous system.	0.06

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity of the surface water systems is largely reflected by its water chemistry and the ingredients deposited in it [19]. The metals are mineralized by microorganisms, which in turn are taken up by planktons and get further biomagnified in the higher trophic levels of the ecosystem. High concentration of the toxic metal ions in the natural waters give rise to many deleterious effects in aquatic organisms: physiologically as well as morphologically;

a) Alterations in physiology, such as retarded growth and development, poor swimming performance, changes in circulation;
b) Change in biochemistry, such as enzyme activity and blood chemistry;
c) Change in behavior;
d) Alteration in reproduction physiology [20].

3. Conventional treatment methods for removal of heavy metals

Several conventional methods have been devised for the treatment and removal of heavy metals from the water, the commonly used procedures for removing metal ions from aqueous systems include chemical precipitation, ion exchange, reverse osmosis and solvent extraction [4, 21] .

3.1 Chemical precipitation

Chemical precipitation is the most widely used technique for the heavy metal removal from inorganic effluent. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Equation(1) [18].

$$\mathbf{M}^{2+} + 2(\mathrm{OH}^-) \longrightarrow \mathbf{M}(\mathrm{OH})_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Precipitation of metals ions is carried out usually by the addition of various precipitating agents like alum, lime, iron salts etc. But the major drawback of this process is the large amount of sludge generation [21]. Lime precipitation can be used effectively to reduce the contamination level of the inorganic effluent having metal concentration greater than 1000 mg/L. The main merits of lime precipitation include the simplicity of the process, low-cost equipment setup, and convenient handling and safe operations. In spite of its advantages, chemical precipitation uses a bulk of chemicals to reduce the metal ion concentration to desirable level for discharge [22]. Other drawbacks are the post sludge formation treatment, slow metal precipitation, poor settling, and the severe environmental complications of sludge disposal [18]. The detailed removal performance of the precipitants is given in the (Table 2).

3.2 Ion exchange

Ion exchange being a reversible chemical reaction where there occurs the exchange of ions from a solution on to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins and are known as ion-exchangers. An organic ion exchange resin is composed of high-molecular weight poly-electrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin. Most of the resins used are synthetic because their characteristics can be fabricated to specific applications. Synthetic resins made by polymerization of organic compounds in a porous three dimensional structure. Ion exchange resins are classified as cation exchangers and anion exchangers [27]. Both anion and cation resins are produced from the organic polymers having same basic fundamental structure and differ only in terms of ionisable groups attached to it. On the basis of such groups, resins can be classified into strong or weak acid cation exchangers or strong or weak base anion exchangers [28]. Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluents. The main drawback of this method is that it cannot be used to decontaminate the effluents containing high concentration of metal ions because of destruction of its matrix. Moreover, ion exchange is nonspecific and is its efficiency is pH sensitive.

Table 2: Heavy metal sequestering by chemical precipitation method

Heavy Metal	Precipitant	Optimum dose of Precipitant (g/L)	Optimum pH	Removal Efficiency (%)	References
Zn^{2+}	$Ca(OH)_2$, Na_2S	10	11.0	99.77	[23]
Cu^{2+}	$Ca(OH)_2$, Na_2S, Na_2CO_3	10	11.6-12	99.9	[24]
Ni^{2+}	Na_2S	NA	5.81-11.6	71	[24]
Pb^{2+}	$Ca(OH)_2$,NaOH	NA	8.1-8.3	54-65	[25]
Cr^{3+}/Cr^{4+}	$Ca(OH)_2$,Na_2CO_3	11	8.3-8.7	50-96.6	[25]
Cd^{2+}	$Ca(OH)_2$,$Fe(OH)_3$	10	11	96-99.6	[26]

NA: not available

The physico-chemical interactions that may occur during metal removal by the sulphonic acid functional group ion exchange resin can be summarized as

$$\underset{\text{(Resin)}}{nRSO_3^{-}\text{—}H^+} + \underset{\text{(Solution)}}{M^{n+}} \rightleftharpoons \underset{\text{(Resin)}}{nRSO_3^{-}\text{—}M^{n+}} + \underset{\text{(Solution)}}{nH^+}$$

Where *n* is the coefficient of the reaction component, depending on the oxidation state of the metal ions[29].

The applicability of natural exchangers like clinoptilolite and synthetic zeolites (NaP1) to remove heavy metals from waste water was investigated. It has been reported that synthetic zeolite shows 10 times greater sorption capacity than that of clinoptilolite (Table 3a) even having almost similar surface area (20-28 m^2/g). This may be attributed due to the strength of hydration shell cations [30]. Moreover, other synthetic resins such as Amberlite-120 and Dowex 2-X4 have also been used by various researchers to observe the removal of heavy metal ions from the waste water containing Zn(II), Cr(II) and Cr(VI) ions [31].

Moreover, the cation selectivity and adsorption capacities of clinoptilolite zeolite has been investigated for the removal of various metal ions from the waste water. It was reported that the clinoptilolite selectivity for both single and mixed ion solution is $Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$ [34]. Therefore, for ion exchange with various heavy metals in waste water systems, cation selectivity of zeolite is important for selective ion removal. Cation-exchange selectivity of various metal ions on clinoptilolite zeolite is shown in (Table 3b). Generally, ion exchange is usually effective up to the range of less than 10-100mg/L metal concentration and pH 2-6. The pretreatment of secondary effluents, high capital and operational cost [35] are its main drawbacks.

Table 3a: Heavy metal uptake performance by ion exchange

Metal ion	Ion Exchanger	Dose (g/L)	Initial metal concentration (mg/L)	Adsorption capacity(mg/g)	Removal efficiency	References
Cr(III)	Clinoptilolite	10	100	4.10	90	[32]
	Synthetic (NaP1) Zeolite	2.5	100	43.58	100	
Ni(II)	Clinoptilolite	10	100	2.0	90	[33]
	Synthetic (NaP1) Zeolite	2.5	100	20.08	100	
Zn(II)	Clinoptilolite	10	100	3.47	90	[34]
	Synthetic (NaP1) Zeolite	2.5	100	32.63	100	
Cu(II)	Clinoptilolite	10	100	5.91	90	[34]
	Synthetic (NaP1) Zeolite	2.5	100	50.48	100	
Ni(II)	Clinoptilolite	10	51.6	8.89	75	[30]
Ni(II)	Zeolite tuffs	1.2	250	0.4	NA	

NA; Not available

3.3 Membrane filtration:

Membrane technology has become increasingly promising in removing heavy metals from wastewater and improving water recovery rate due to its high efficiency and low cost [36]. A multiple membrane processes were developed for selective separation to reduce cost and the alarming heavy metal pollution. Several metal ions (Cu^{2+}, Ni^{2+} , Cr(VI), As(V) have been removed efficiently by RO and NF [37-40]. The membrane processes were divided into three stages [41];

Table 3b: Cation-exchange selectivity of heavy metal ions on Clinoptilolite Zeolite [34].

Zeolite	Selectivity	Si/Al
Clinoptilolite	$Pb^{2+}>Ag^{2+}>Cd^{2+}>Zn^{2+}>Cu^{2+}$	2.7-5.3
Clinoptilolite	$Pb^{2+}> Zn^{2+}>Cu^{2+}>Ni^{2+}$	4.9
Clinoptilolite	$Pb^{2+}> Cd^{2+}>Zn^{2+}>Cu^{2+}$	4.2
Clinoptilolite	$Pb^{2+}>Cd^{2+}>Cu^{2+}>Co^{2+}>Cr^{3+}>Zn^{2+}> Ni^{2+}>Hg^{2+}$	-

(a) Membrane filtration (MF) and Ultra filtration (UF) were used to separate the possible organic and suspended materials.
(b) Electrodialysis (ED) was carried out for effective desalination.
(c) Nanofiltration (NF) and Reverse Osmosis (RO) was used to increase the recovery rate of water.
The various membrane processes, there comparison and driving force [42] is given in (Table 4)

Table 4: Driving forces for various membrane processes.

Driving Force	Membrane Processes
Pressure difference	Microfiltration, Ultra filtration, Nano filtration, Reverse osmosis or hyper filtration.
Chemical potential difference	Pervaporation, Per-traction, Dialysis, Gas separation vapour permeation, Liquid membranes.
Electrical potential difference	Electro-dialysis, Membrane electrophoresis.

4. Adsorption (Economical and Emerging Method)

Adsorption is a physico-chemical process where an adsorbate gets deposited over an adsorbent through various mechanisms and is totally different as compared to absorption. Adsorption is operative in most natural physical, biological, and chemical systems, and finds wide applications in every sphere of our day to day life. Adsorption being a surface phenomenon like surface tension and hence is a consequence of surface energy. The adsorption capacity of a substance is critically reflected by its bonding efficiency with the surrounding atoms in the bulk. However, the exact nature of the bonding depends on the type of the species involved, but the adsorbed material is generally classified as exhibiting physio-sorption or chemisorptions [43].

4.1 Adsorption dynamics

It consists of the following consecutive steps:

(i) Migration of adsorbate from the bulk solution to the surface of the adsorbent.
(ii) Transfer of the adsorbate by simple diffusion from the surface of the adsorbent to its bulk.
(iii) Adsorption of the adsorbate on the active sites of adsorbent.
The last step of the adsorption dynamics is found to be rapid one as compared to other steps [44].

4.2 Advantages of adsorption process [45]

Cheap: The cost of adsorbent is low since they are often made from locally, abundantly and easily available materials.

Metal selective: The metal sorbing performance of different types of bio-mass can be more or less selective on different metals.

Regenerative: Sorbent material can be reused after regeneration

No sludge generation: unlike the problems in other techniques (precipitation), there is any issue of sludge formation in adsorption process.

Metal recovery: If sorbate is a metal ion, it is possible to recover the metal ion after being desorbed from the adsorbent materials.

Competitive performance: Performance of adsorption process in terms of efficiency and cost is comparable with the other methods available.

4.3 Bio adsorbents

There is increasing research interest in using alternative low-cost adsorbents. Many such materials have been investigated, including microbial biomass, peat, compost, leaf mould, palm press fiber, coal, sugarcane bagasse, straw, wool fiber and by products of rice mill, soybean and cottonseed hulls etc. [9]. The low cost agricultural waste by-products such as sugarcane bagasse [46], rice husk [47], sawdust [48], coconut husk [49], oil palm shell [50], neem bark [51] etc, for the elimination of heavy metals from wastewater have been investigated by various researchers.

4.4 Mechanism of biosorption

The removal of metal ions from waste water by agriculture materials is based on the metal biosorption [52]. The process of biosorption involves the solid phase (sorbent) and a liquid phase (solvent) containing the dissolved species to be sorbed. Due to high affinity of the sorbent for the metal ions, which thereby are attracted and bound to the sorbent by complex process affected by several mechanisms involving chemisorption, complexation, adsorption by physical forces, ion-exchange, chelation and diffusion through cell wall and membrane [53,54] (Figure 2).

The agricultural waste materials are usually composed of lignin and cellulose; besides to it the agro materials contain various functional groups like acetamido, carbonyl, phenolic, amino, alcohols and esters [55]. The presence of these functional groups and their complexation with metal ions has been reported by various researchers using spectroscopic techniques [5,56].

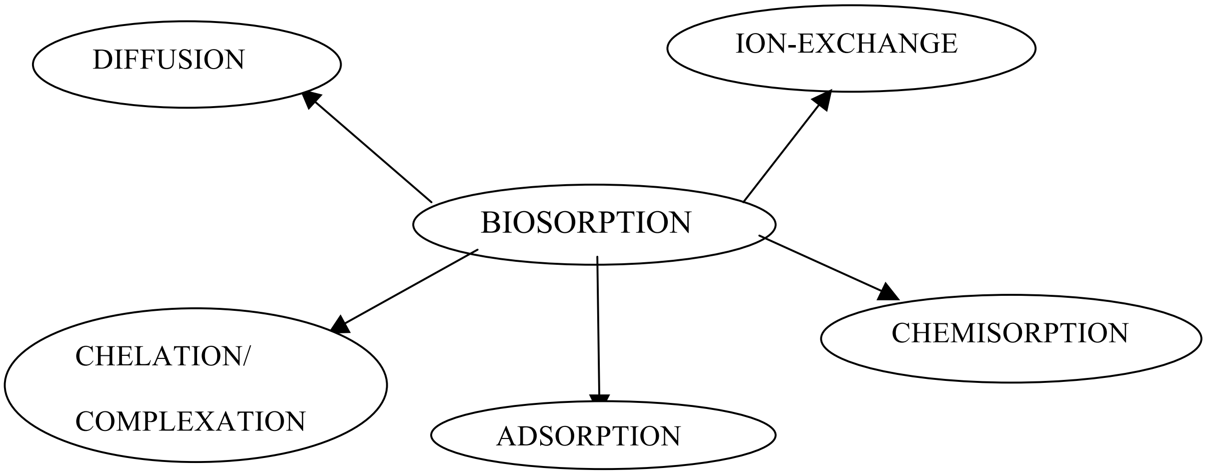

Figure 2: Plausible mechanism of biosorption

4.5 Heavy metal removal performance of agricultural waste materials as biosorbents

Removal of heavy metal ions from the aqueous streams by biosorbents is a relatively new innovative and promising technology. The removal efficiency of the agro-waste depends upon the capacity, affinity and specificity. Enormous amount of scattered research has been done on variety of biosorbents for the removal of various metal ions. In this section, various agricultural waste material and other biosorbents has been highlighted in terms of their removal efficiency for various heavy metal ions. Summary of the recent reported adsorption capacities along with certain experimental conditions are presented in (Table 5, 6).

Table 5: Summary of the recent reported studies using agricultural waste materials for the removal of various metal ions

Adsorbent	Heavy Metals	Initial concentration (mg/L)	pH	Maximum adsorption capacity (mg/g)	References
Almond shell	Cr(VI)	1.000	2-9	0.580	[57]
Neem leaf powder	Cd(II)	0.975	2–9.5	1.404	[58]
Hazelnut shell	Cr(VI)	0.580- 1.000	2-9	4.432	[57]
	Cu(II)	25- 200	2- 6	58.27	[59]
Palm Leaves	Zn(II)	0.306–4.587	4–5.5	0.225	[60]
Pomegranate peel	Cu(II)	0.157–1.256	1-8	0.020	[61]
Potato peels	Cu(II)	0.246-0.832	6	0.523	[62]
Tea factory waste	Ni(II)	0.455-0.754	4	15.26	[63]
Lignin	Pb(II)	-	5.5	89.51	[64]
Sawdust	Pb(II)	10	5	0.82	[65]
Livestock feed husk	Cd(II)	10-500	5	35	[66]
Olive stones	Cd(II)	10	11	2.606	[67]

4.6 Effect of modification on the biosorption

The use of untreated agricultural waste biosorbents have potential drawbacks such as low adsorption efficiency, high release of soluble organic compounds into the solution which there by causes increase in other parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC). So, for these reasons, it is highly recommended that agricultural waste biosorbents need to be pretreated before being used in biosorption processes [76] in order to increase the adsorption efficiency. Therefore, the pretreatment methods include physical pretreatment, chemical pretreatment and cell modification (Figure 3) must be carried out. But among all these methods, chemical method is preferred because of high efficiency and simplicity [77]. The modifying agents used in chemical pretreatment method can be acids, bases, organic compounds, oxidizing agents etc. Other pretreatment methods include enhancement of binding groups, elimination of inhibiting groups or graft polymerization.

However, from the literature survey it has been found that, chemically modified agricultural waste biosorbents exhibit far better adsorption capacities than unmodified forms [78].This can be attributed to the higher number of binding sites, better ion-exchange ability, and formation of new functional groups that favor metal uptake. Modifying agents used and adsorption capacities of various agricultural waste biosorbents after chemical pretreatment is summarized in (Table 7).

Table 6: Summary of the some reported studies using other adsorbents for the removal of various metal ions.

Adsorbent	Metal ion	Adsorption capacity (mg/g)	References
Chitosan/Clinoptilolite	Cu(II)	574.49	[68]
Cross-linked Chitosan	Cr(VI)	78	[69]
Crosslinked starch gel	Pb(II)	433	[70]
Alumina/chitosan composite	Cu(II)	200	[70]
Chitosan/coconut shell carbon	Zn(II)	50.93	[71]
Chitin (Natural)	Pb(II)	264	[72]
Chitin (Phosphorylated)	Pb(II)	258	[72]
Spheroidal cellulose	Cr(III)	89	[73]
Red mud	Ni(II)	160	[74]
Blast-furnace slag	Cu(II)	133.35	[75]

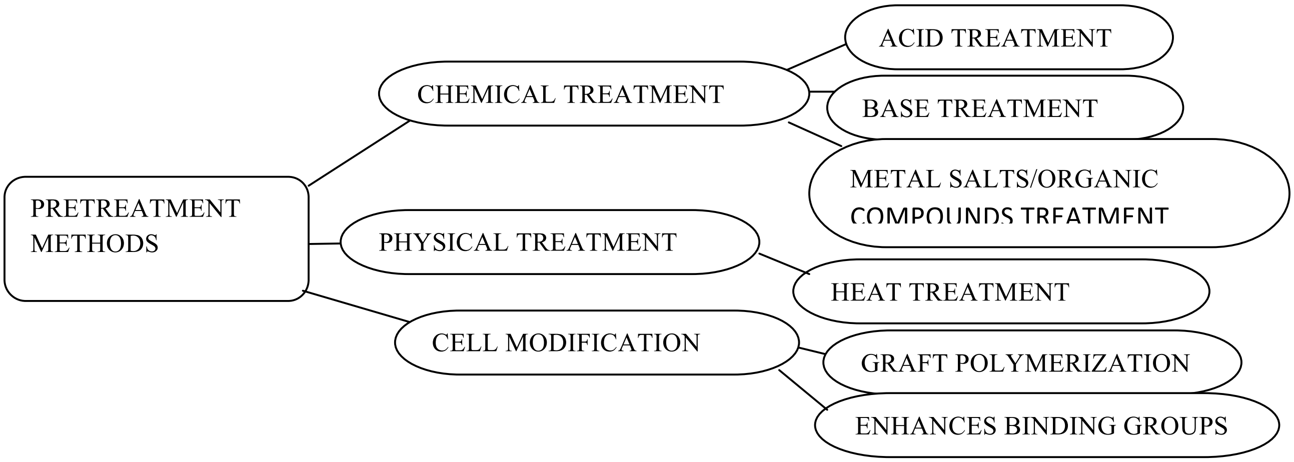

Figure 3: Pretreatment methods for agricultural waste biosorbents

However, on pretreatment of agricultural waste biosorbents with metal salts to enhance their removal efficiencies towards anions, the detachment of loading metal should be examined thoroughly. This is because it can not only affect the quality of aqueous solutions but also affect reusability of biosorbents. For that reason, it is very necessary to find out efficient methods to compensate the adverse effects of pretreatments while enhancing the adsorption capacity of agricultural waste biosorbents.

5. Evaluation of heavy metals removal processes

In general, physico-chemical treatments offer various advantages in terms of processing, operation and flexibility towards various conditions. There are numerous methods currently employed to remove and recover the metals from our environment and many physico-chemical methods have been proposed for their removal from wastewater [79]. These include chemical oxidation and reduction, membrane separation, liquid extraction, carbon adsorption, ion exchange, electrolytic treatment, electro-precipitation, coagulation, flotation, evaporation, hydroxide and sulfide precipitation, crystallization, ultra filtration, electro-dialysis etc. [80]. Chemical precipitation, reverse osmosis and other methods (ultra filtration, electrochemical deposition etc.) become inefficient when contaminants are present in trace concentration [81] and do not seem to be economically feasible for the removal of heavy metal ions because of their relative high costs [82]. Therefore, there is a need to look into alternatives to investigate a low-cost method which is effective and economic.

Table 7: Summary of recent studies for chemical treatment of agricultural waste biosorbents along with modifying agents and adsorption capacities

Adsorbent	Heavy Metals	Modifying Agent	Maximum adsorption capacity(mg/g)
Rice husk	Cd(II)	NaOH	20.24
Wheat straw	Cd(II)	Urea	39.22
Cashew nut shell Coir	Cd(II)	H_2SO_4	436.7
pith	Cr(VI)	Acrylic acid	196.00
Pineapple peel fibre	Cu(II)	Succinic anhydride	27.68
Orange peel	Cu(II)	NaOH and $CaCl_2$	70.73
Rice bran	Ni(II)	H_3PO_4	46.51
Onion skins	Pb(II)	Formaldehyde	200.00
Pine cone powder	Pb(II)	KOH	32.26
Cassava tuber	Zn(II)	Thioglycollic acid	83.30
Rosewood saw dust	Cr(VI)	Formaldehyde	62-86
Sugarcane	Cu(II)	Succinic anhydride	83.2

Conclusion

Finally, technical applicability, plan simplicity, and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment system for waste water effluent. All the factors mentioned above should be taken into consideration in selecting the most cost effective treatment techniques in order to protect the environment and human health from toxic and hazardous contaminated waste water in the present scenario. It is evident from the literature survey that adsorption is the most cost effective treatment method for removal of heavy metals from waste water. This aspect needs to be investigated and developed further in order to promote its large-scale usage over costly conventional methods. The widespread uses of agricultural waste biosorbents in industrial effluents and for waste water treatment applications today are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost effectiveness.

References

1. D.W. O'Connell, C. Birkinshaw, T.F. O'Dwyer, Bioresour. Technol. 99 (2008) 6709.
2. L. Friberg, C.G. Elinder, Encyclopedia of Occupational Health. Third ed. International Labor Organization, Geneva (1985).
3. K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Bioresour. Technol. 76 (2001) 63.
4. J.W Patterson, Industrial Wastewater Treatment Technology. Second ed. Butterworth Publisher, Stoneham, MA (1985).
5. S.S. Ahluwalia, D. Goyal, Eng. Life Sci. 5 (2005) 158.
6. N.T. Abdel-Ghani, G.A. Elchaghaby, Int. J. Environ. Sci. Technol. 4 (2007) 451.
7. S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, Water Res. 33 (1999) 2469.
8. N. Martnez, I. Villaescusa, M. Fiol, N. Miralles, J. Pocj, J. Serarols, Water Res. 38 (2004) 992.
9. S.K. Mandal, A.K. Bhattacharya, S.N. Das , Chem. Eng. J. 123 (2006) 43.
10. P.D. Watson , J. Brown, M.A. Johnson, I.A. Jefcoat, Waste Management 22 (2002) 471.
11. C.F. Wase, D.A.J. Forster, S.Y. Quek, Water SA 24 (1998) 251.

12. W.S.W. Zakaria, M.A.K. Hanafiah, Nigah, S.C. Ibrahim, J. Biol Sci. 7 (2007) 222.
13. O.A. Adelaja, I.A. Amoo, A.D. Aderibigbe, Arch. Appl. Sci. Res. 3 (2011) 50.
14. L. Kailas, Wasewar, Int. J. Res. and Rev. in Appl. Sci. (2010) 3.
15. U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Int. J. Res. and Rev. in Appl. Sci. 140 (2007) 60.
16. P.S. Kumar, S. Ramalingam, V. Sathyaselvabala, S.D. Kirupha, A. Murugesan, S. Sivanesan, Korean J Chem Eng. 29 (2012) 756.
17. A.B.P. Marin, M.I. Aguilar, J.F. Ortuno, V.F. Meseguer, J. Saez, M. Florenz, J. Chem. Technol. Biotechnol. 85 (2010) 1310.
18. M.A. Barakat, Arab. J. Chem. 4 (2011) 361.
19. B. Volesky, B. V. Sorbex Inc,sorption and biosorption, St. Lambert, Quebec, Canada 2003,316.
20. D.W. Connell, G.J. Miller, Chemistry and Ecotoxicology of Pollution. John Wiley & Sons, NewYork, (2003) 453.
21. N. Ahalya, T.V. Ramachandrl, R.D. Kanamadi, Res J Chem Environ. 7 (2003) 4.
22. K. Jüttner, U. Galla, H. Schmieder, Electrochim. Acta. 45 (2000) 2575.
23. A.H.M. Veeken, L. Akoyo, L.W. Hulshoff Pol, J. Weijma, Water Res. 37 (2003) 3709.
24. A. Lewis, R. Van Hille, Hydrometallurgy. 81 (2006) 197.
25. N. Meunier, P. Drogui, C. Montane, R. Hausler, G. Mercier, J. Blais, J Hazard Mater. 137 (2006) 581.
26. L. Charerntanyarak, Water Sci Tech. 39 (1999) 135.
27. X.J. Yang, A.G. Fane, S. MacNaughton, Water Sci. Technol. 43 (2001) 341.
28. H. Pendias, A. Kabata–Pendias, Trace Metals in Soil and Plants. CRC press, Boca Raton, FL, (1992) 75.
29. A. Dabrowski, Z. Hubicki, P. Podko´scielny, E. Robens, Chemosphere. 56 (2004) 91.
30. A. Papadopoulos, D. Fatta, K. Parperis, A. Mentzis, K.J. Harambous, M. Loizidou, Sep. Purif. Technol. 39 (2004) 181.
31. N. Sapari, A. Idris, N. Hisham, Desalination 106 (1996) 419.
32. E. Alvarez-Ayuso, A. Garcıa-Sanchez, X. Querol, Water Res. 37 (2003) 4855.
33. P. Kowalczyk, M. Sprynskyy, A.P. Terzyk, Journal of Colloidal Interface Science, 297 (2006) 77.
34. S. Wang, Y. Peng, Chem. Eng. J. 156 (2010) 11.
35. S. Ahmed, S. Chughtai, M.A. Keane, Sep. Purif. Technol. 13 (1998) 57.
36. M. Liu, H. Zhang, X. Zhang, Y. Deng, W. Liu, H. Zhan, Water Environ. Res. 73 (2001) 322.
37. B.K.C. Chan, A.W.L. Dudeney, Miner. Eng. 21 (2008) 272.
38. M.N. Mohsen, P. Montazeri, H. Modarress, Desalination 217 (2008) 276.
39. M. Muthukrishnan, B.K. Guha, Desalination 219 (2008) 171.
40. P.S. Sudilovskiy, G.G. Kagramanov, V.A. Kolesnikov, Desalination 221 (2008) 192.
41. M.A. Barakat, E. Schmidt, Desalination 256 (2010) 90.
42. B.V. Bruggen, J. Schaep, D. Wilms, C. Vandecasteele, J Memb Sci. 150 (1999) 29.
43. Q. Hui, L.V. Lu, P. Bing-cai, Z. Qing-jian, Z. Wei-ming, Z. Quan-xing, J. Zhejiang Univ. Sci. A 10 (2009) 716.
44. S. Uttam, K.K. Rajesh, Inter. Journal of Technical and Non-Technical Res. 4 (2013) 2319.
45. V.C. Renge, C.V. Khedkar, S.V. Pande, Sci. Rev. Chem. Commun. 2 (2012) 580.
46. D. Mohan, K.P. Singh, Water Res. 36 (2002) 2304.
47. K. Srinivasan, N. Balasubramaniam, T.V. Ramakrishna, Indian J. Environ. Health 30 (1998) 376.
48. M. Ajmal, R.A.K. Rao, S. Anwar, J. Ahmad, R. Ahmad, Bioresour. Technol. 86 (2003) 147.
49. W.T. Tan, S.T. Ooi, C.K. Lee, Environ. Technol. 14 (1993) 277.
50. M.N. Khan, M.F. Wahab, J Hazard Mater. 141 (2006) 237.
51. S. Ayub, S.I. Ali, N.A. Khan, Environ. Pollution Control Journal 4 (2001) 34.
52. B. Volesky, Z.R. Holan, Biotechnol. Prog. 11 (1995) 235.
53. M.C. Basso, E.G. Cerrella, A.L. Cukierman, Chem. Res. 41 (2002) 3580.
54. S. Qaiser, A.R. Saleemi, M.M. Ahmad, Environ. Biotechnol. 10 (2007) 409.
55. V.K. Gupta, I. Ali, Sep. Purif. Technol.18 (2000) 131.
56. V.K. Garg, R. Gupta, R. Kumar, R.K. Gupta, Bioresour. Technol. 92 (2004) 79.
57. E. Pehlivan, T. Altun, J Hazard Mater. 155, (2008) 378.
58. A. Sharma, K.G. Bhattacharyya, J Hazard Mater. 125 (2005) 102.

59. E. Demirbas, N. Dizge, M. T. Sulak, M. Kobya, Chem. Eng. J. 148 (2009) 480.
60. F.A.A. Al-Rub, Sep. Purif. Technol. 41 (2006) 3499.
61. El-Ashtoukhy, N.K. Amina, O. Abdelwahab, Desalination, 223 (2008) 162.
62. T. Aman, A.A. Kazi, M.U. Sabri, Q. Bano, Colloids Surfaces, 63 (2008) 116.
63. E. Malkoc, Y. Nuhoglu, J Hazard Mater. 127 (2005) 120.
64. X.Y. Guo, A.Z. Zhang, X.Q. Shan, J Hazard Mater. 151 (2008) 134.
65. F. Assadi, H. Shariatmadari, N. Mirghaffari, J Hazard Mater. 154 (2008) 451.
66. G.C. Panda, S.K. Das, S. Chatterjee, P.B. Maity, T.S. Bandopadhyay, A.K. Guha, Colloids Surfaces B: Biointerfaces, 50 (2006) 49.
67. G. Blazquez, F. Hernainz, M. Calero, L. F. Ruiz-Nunez, Process Biochemistry, 40 (2005) 2649.
68. E. S. Dragan, M.V. Dinu, D. Timpu, Bioresour. Technol. 101 (2010) 812.
69. R. Schmuhl, H.M. Krieg, K.A. Keizer, WaterSA 27 (2001) 1.
70. G. Crini, Progr. Polymer. Sci. 30 (2005) 38.
71. O.S. Amuda, A.A. Giwa, I.A. Bello, Biochem. Eng J. 36 (2007) 174.
72. S.H. Kim, H. Song, G.M. Nisola, J. Ahn, M.M. Galera, C.H. Lee, W.J. Chung, J. Ind. Eng. Chem., 12 (2006) 469.
73. M. Liu, H. Zhang, X. Zhang, Y. Deng, W. Liu, H. Zhan, Water Environ. Res., 73 (2001) 322
74. A.I. Zouboulis, K.A. Kydros, J. Chem. Tech. Biotechnol. 58 (1993) 95.
75. S.V. Dimitrova, Water Res. 30 (1996) 228.
76. N. Feng, X. Guo, S. Liang, Y. Zhu, J. Liu, J Hazard Mater. 185 (2010) 49.
77. D. Park, Y. Yun, J.M. Park, Biotechnol. Bioprocess. Eng. 15 (2011) 86.
78. J. Wang, C. Chen, Acta Sci. Circumstantiae 30 (2010) 673.
79. A. Saeed, M. Iqbal, N. Akhatar, Bioresour. Technol. 81 (2002) 151.
80. S. Manonmani, K. Selvaraj, S. Pattabhi, Bioresour. Technol. 89 (2003) 207.
81. N. Muhammad, P. Jeremy, P. Michael, D. Smith, A.D .Wheatley, 24th WEDC Conference, Islamabad, Pakistan, (1998) 346.
82. S.Y. Quek, D.A.J. Wase, C.F. Forster, Water SA 24 (1998) 251.

(2018) ; http://www.jmaterenvironsci.com