Heavy Metal Sequestration from Wastewater: Current Trends and Technologies - A Review

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ABSTRACT: *Heavy metal pollution has become a wide scale problem faced by all countries, with regard to the environment. Due to increase in anthropogenic activities like industrial operations and mining the concentrations of heavy metals have reached dangerous levels. The toxic, non-biodegradable, carcinogenic nature of heavy metals and its adverse effects on the plants and animals has rendered heavy metal removal important. Over the years various technologies have been developed and evaluated. The various existing methods for heavy metal removal are chemical precipitation, coagulation-flocculation, ion exchange, photo-catalysis, adsorption, electrochemical technique and membrane technology. This article reviews the current technologies for heavy metal removal along with their advantages and limitations. Despite the existence of a number of technologies for heavy metal removal, from literature survey it can be concluded that adsorption is the most widely used technology due to its economic feasibility, versatility and simplicity.*

KEYWORDS: Heavy metals, wastewater, adsorption, membrane technology, chemical precipitation, ion exchange.

1.1 INTRODUCTION:

Some of the reasons like excessive use of chemicals and metals by the process industries, rapid urbanization and industrialization and increase in the number of activities like mining and offshore drilling have increased the quantities of effluents laden with heavy metals[1, 2]. These heavy metal laden effluents have proven to be detrimental to living organisms and have caused a number of disposal problems. Characteristics of heavy metals like non biodegradability, toxicity and potential to accumulate in organisms distinguish them from other contaminants present in wastewater. But on the other hand noble metals like gold and silver which are of great value are also considered as heavy metals[2]. Therefore the removal and recovery of these heavy metals is crucial and there has been an increasing demand to develop cost effective and efficient technologies. Metals with atomic weight lies between 63.5 and 200.6 and those with specific gravity greater than 5.00 are considered to be heavy metals[3, 4]. Based on this criterion Arsenic, Lead, Mercury, Cadmium, Chromium, Zinc, Manganese, Copper, Selenium, Silver, Antimony, Iron, Gold and Molybdenum are considered as heavy metals.

Heavy metals affect flora, fauna and human beings. As the heavy metals have the capacity to accumulate in human beings, they cause health effects like cancer, nervous system damage, skin de-pigmentation and organ damage. Table 1 shows the maximum allowable levels of heavy metals as prescribed by World Health Organization and ill effects of various heavy metals. The waste water streams containing heavy metals are generated by process industries like refineries, coal fired power plants and municipal waste water for mercury, tanneries, electroplating, anodizing- coating, milling and etching industries for copper, batteries, metal plating, pigments and stabilizers for cadmium, brass and bronze manufacturing industries, steel plants, galvanizing, pigments, paints, insecticides and cosmetics produce high concentration of zinc laden wastewater[1, 2]. Small amounts of lead and arsenic are generated by printed circuit board industries and wood processing industries respectively. Petroleum industries generated conversion catalysts containing vanadium and photographic film operations generate silver and ferro cyanide. With the aim to reduce the hazards of these metals on environment and human beings strict regulations and limits have been imposed by UESPA[1]. Remediation of wastewater is utmost most importance before they are released into environment.

A number of methods- chemical precipitation, floatation, coagulation-flocculation, membrane-technology, adsorption on low cost adsorbents, photo catalysis and electrochemical treatment have gained attention for the removal of heavy metal ions from wastewater/ industrial effluents[5, 6]. This paper reviews the most recent technologies being used for heavy metal sequestration along with their advantages and disadvantages.

2. Removal of Heavy Metals from Wastewater

This section will review the currently used technologies for heavy metal removal along with their advantages and limitations

2.1 Chemical Precipitation

Chemical precipitation is commonly used technology for eliminating heavy metals from industrial effluents due to its simplicity and low operating costs. In the precipitation process the chemical referred to as precipitants react with heavy metal ions in the effluent which results in the formation of insoluble precipitates, which are separated from water using settling or membrane filtration. The commonly used precipitation processes involve hydroxide and sulphide precipitation[1, 7]. Some metal ions will not precipitate when they are present in their inherent form, therefore they need to be oxidized or reduced by chemical agents[6]. In some cases to increase the particle size and rate of sedimentation coagulants are added along with precipitant. The removal of metal ions may be optimized by varying parameters like p^H, temperature and initial concentration, for hydroxide precipitation p^H in the range of 8-11 is

Table 1: Potential Hazards of Heavy metals and Maximum Permissible Concentration

Metals	Toxicities	Maximum allowable(mg/L)
Arsenic	Carcinogenic, skin, gastrointestinal effects	0.01
Cadmium	Carcinogenic, Itai-Itai disease, anaemia, weight loss, dyspnea	0.05
Copper	Liver illness, dizziness, headache, stomach-ache	1
Chromium	Carcinogenic, lung tumours, dermatitis	0.05
Lead	Appetite loss, high blood pressure, joint pains	0.005
Mercury	Affects kidney, corrosive to skin and eyes	0.001
Nickel	Reduced lung function and damage to RBC's	0.02
Zinc	Metal fume fever and restlessness	5

preferred [1]. Hydroxide precipitation using lime is preferred over sulphide precipitation due to the additional costs associated with pre and post treatment for the removal of sulphide ions.

Sodium hydroxide, Calcium hydroxide and Sodium carbonate was applied to waste water containing Pb^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Fe^{3+}. A minimum removal percentage of 70 was achieved in case of majority of the metals and up to 100 was achieved in case of removal of Cu^{2+} and Fe^{3+} at a temperature of 50^0C, reaction time of 45 mins and pH =9 in case of hydroxide and p^H=10 in case of carbonate[8].

In order to avoid the costs involved in handling the secondary sludge, Ruiping Wu applied an integrated approach of precipitation and adsorption on a biofilm grown in a tricking bed reactor to remove Cu^{2+} ions from industrial wastewater. Studies on effect of change of pH, initial concentration, temperatures and contact time were conducted to evaluate their influence on removal percentage, rate of removal and adsorption capacity. Best results were reported under a pH of and contact time of 300 mins. An increase in adsorption capacity and decrease in removal rate with increase in initial concentration was reported[9]. Ibigbami T.B and co –workers conducted a similar study to remove metals like Fe, Zn and Ni from pharmaceutical waste water using hydrogen peroxide in addition to alum and bentonite clay as the precipitant and adsorbent respectively. Parameters such as pH, dosage of hydrogen peroxide and temperature were varied and highest removal percentages of 89.58, 92.30 and 94.22 was reported for Fe, Zn, Ni respectively at a temperature of 50^0C and pH of 8 for iron and pH of 10 for nickel and zinc[10].

Wang .P. L and Chen.Y.J applied a combination of hydroxide, oxidizing and sulphide treatment for sequential recovery of iron, copper and zinc. The difference in the solubilities of hydroxides of iron, copper and zinc was exploited to recover these metals sequentially. The wastewater containing Fe, Cu and Zn was treated with 0.1% (v/v) of H_2O_2, adjusting the pH to 3.5-4 using lime followed by the addition of 1g/L NaHS and finally achieving a pH of 9. Recoveries of 99.8%, 94% and 96.1% for Fe, Cu and Zn respectively have been reported[11]. This method rendered sludge disposal unnecessary.

2.2 Floatation

Floatation has found wide application in treatment of waste water laden with heavy metals, having its roots originate from mineral processing this method is employed to remove heavy metal ions from liquid phase via attachment to air bubbles. The various kinds of floatation techniques currently under use are hybrid floatation also known as dissolved air flotation (DAF), ion floatation, adsorptive floatation and hybrid floatation[7, 12]. Collector and frother are two commonly used chemicals in association with ion floatation. Collectors are commonly anionic surfactants, which interact with the positively charged ion in waste water and under the influence of air bubbles the complex is collected as froth. Commonly used collector is sodium dodecyl sulphate. Frother regulates the size of air bubbles and commonly used ones are ethanol, methyl esters and polypropylene glycol[13].

Blocher developed a hybrid system combining the advantages of membrane technology and floatation by submerging a micro filtration module in the floatation reactor to remove copper, nickel and zinc ions. Zeolite was used as the bonding agent and hexadecyl trimethyl ammonium bromide was used as the collector[14]. The system had many advantages like low operating cost, high membrane flux, easier recovery and disposal of heavy metals due to the presence of bonding agent in froth and lower energy consumption. Concentrations of copper, nickel and zinc were reduced below 0.05mg/ml. Hoseinian. F.S studied the effect of hydrodynamic parameters on removal rate of nickel ions from waste water. Oscillating grid floatation cell (OGC) was used with sodium dodecyl sulphate and the parameters studied were energy input, air flow rate, bubble diameter (130µm and 820µm) and ratio of surfactant to initial nickel ion concentration[15]. An energy input of 0.5 Watts per kg, bubble diameter of 130µm and isotropic and homogenous environment in the OGC has been reported to favour higher removal rates of nickel, while increase in surfactant ratio has a negative impact on the removal rate as the bubbles preferentially adhere to the unreacted surfactant molecules.

An integrated technique combining ion floatation and adsorption by MWCNT's was demonstrated by Dehgdani. M. H and co- workers to remove nickel ions from industrial wastewater. Similar to the previous study, studies on parameters like surfactant concentration, adsorbent dosage, p^H, aeration time, air flow rate and frother concentration. A removal percentage of 71.7 for a starting concentration of 30mg/l and reduction in time required to achieve equilibrium was reported[13]. The sorptive floatation involves sequestering of heavy metals using adsorbents or bio sorbents and followed by floatation of metal bearing sorbents to favour separation from treated water[12]. Studies conducted by Zouboulis A. I reported recoveries of greater than 90 % for hydroxyl appetite and removal of 95% for heavy metal cadmium[16].

2.3 Coagulation- flocculation

Coagulation involves removal of dual electrically charged layer of the colloidal particles present in wastewater. Flocculation is phenomenon wherein polymers form links between the flocs generated by coagulation and bind particles to large lumps[17]. The commonly used coagulants are aluminium sulphate and ferric chloride and commonly used flocculants are poly aluminium chloride and poly ferric sulphate[7]. Coagulation/ flocculation is advantageous as it the capability to remove colloidal particle, soluble substances say metal ions and very small solid suspensions[18]. Removal of turbidity caused due to colloidal particle is critical as these solids provide attachment sites for micro -organisms and heavy metals. In addition to charge neutralization by the coagulants, the mechanism of sweep coagulation helps reduce turbidity[19].

Sakhi .D and co-workers recently demonstrated the use of ferric chloride as the coagulant for the removal lead, nickel, arsenic, cadmium and selenium. Their study focussed upon identification and optimization of key parameters that effect the coagulation/ flocculation. Dose of coagulant, flocculant and p^H were the parameters identified and were optimized using response surface methodology[18]. Optimized values of 0.64 g/l of the coagulant, 2.6/l of the flocculant and p^H of 8.1 were reported and high removal percentage of 81 was reported for arsenic.

The sludge generated by the use conventional coagulants is non- biodegradable and last traces of ferric and aluminium ions have been reported as the causes for neuro degenerative diseases and Alzheimer's disease, therefore Lugo. L and co-workers suggested an eco-friendly approach to remove copper, chromium and lead by the use modified acacia tannin as the coagulant. Tannin was modified by mannich reaction, removal percentages of 60 for copper, 87 for chromium and 50-80 were reported at pH of 10 and modified tannin dose of 375 ppm[17]. Its performance was comparable to conventional coagulants and unaffected by presence of organic matter. Mehdinejad. M and Bina. B identified that reaction of alum with water reduced pH and efficiency of coagulation and suggested the use of coagulant aid –moringa oleifera coagulant protein (MOCP) for the effective removal of iron, copper, zinc and manganese. Highest removal percentages were reported at maximum turbidity and during sequential addition of alum followed by MOCP[19]. The use of coagulant aid helped reduce the usage of alum.

Similar studies were carried out by Rodriguez. D.I and team, which used pectin with the inherent ability of chelation as a dual coagulating-flocculating agent to remove Zn^{2+}, Pb^{2+} and Ni^{2+} ions and optimization studies carried out reported an optimal dose of 0.019mg/ml with removal percentages greater than 99 for all metals[20]. It is clear from the above studies there is a transition from use of conventional to eco-friendly multi-functional coagulants.

2.4 Photo-catalysis

Photo-catalysis is advanced oxidation process which works with the aid of radiation from the electro- magnetic spectrum with the advantages of simultaneous removal of heavy metals, organic compounds, microorganisms and no usage of chemicals[6]. Once the photo-catalyst is added into the heavy metal laden wastewater, adsorption of ions takes place and followed by the action of light. When radiation of energy equal to the bandgap of the photo-catalyst is incident on the photo-catalyst, transfer of electrons from the valence band to the conduction band takes place which leads to the formation of electron hole pair, the reaction below shows this formation

$$PC + h\nu \longrightarrow h^+ + e^-$$

Once the electron hole pairs are formed simultaneous oxidation and reduction of the pollutants present in water leads to formation of intermediates and the final product is deposited on the surface of the photo-catalyst by the reaction shown below.

$M^{n+} + ne^- M \longrightarrow$

Metal oxides such as zinc oxide, titanium dioxide and zirconium dioxide have been used as photo-catalysts for treatment of waste water. Shukor. S. A. A and team [21] removed cadmium, chromium and copper by the synergetic effect of photo- catalysis and adsorption using TiO_2 nanoparticle and activated carbon[21]. In an attempt to develop a photo-catalyst which is functional under visible light, Shruthi .L and co –workers developed a zinc oxide/ selenium nanocomposite with reduced bandgap of 2.5 eV compared to 3.37 eV for zinc oxide. The composite was successful in removing copper, cadmium, zinc, nickel, chromium and lead at an optimal dosage of 0.5g/L and pH of 4 and also a reduction in COD level has been reported which confirms the multi functionality of the photo-catalysis technology[22].

Similar studies were carried out Rashed. M. N and team to simultaneously remove methyl orange and cadmium from pollutant stream by employing a composite of TiO_2 and activated bagasse fly ash. Degradation of methyl orange was reported to be maximum in the presence of UV irradiation and presence of H_2O_2 while removal of Cd^{2+} was maximum under dark condition, hence it can be inferred that main photo-catalysis and adsorption are the crucial operating mechanisms for the removal dye and metal ion respectively, based on this an optimal pH of 7, catalyst dose of 2g/L and contact time of 300 mins in the presence of UV light and H_2O_2 was reported for simultaneous removal of ions and dye[23]. Recombination of charge carriers is one limitation of photo-catalysis, in order to overcome this limitation Shahzad. K and co-workers doped $MoSe_2/BiVO_4$ composite with $CuCo_2S_4$. $CuCo_2S_4$ played a significant role in light reaction inspired Z scheme as it increased the donor concentration, specific surface area and generated a fermi level changing the energy band gap of the composite[24]. 1% doping of $CuCo_2S_4$ increased the efficiency of photo-catalysis process 40 times compared to pure composite.

2.5 Ion exchange

Ion exchange works on principle of reversible exchange of ions between the waste water and ion exchanger. This process has been widely used to treat waters having low concentrations of metal ions due to high effectiveness, selectivity, no sludge production and high selectivity[1]. An ion exchanger can be cationic or anionic, based on this an ion exchanger can remove soluble ions from wastewater and release ions of the same kind in an equivalent amount[2].Once the ion exchanger is saturated with heavy metal ions, these metal ions are recovered using an eluent. Generally ion exchange resins are used as ion exchangers. For the removal of metal ions from waste water cation ion exchangers based on strongly acidic sulfonic acid groups and weakly acidic carboxylic acid groups have been used[7]. These resins exchange hydrogen ions in an equivalent amount for the metal ions in waste waters. Temperature, p^H, initial metal concentration and contact time are important factors which determine the performance of ion exchange resins.

$nR\text{-}SO_3H + M^{n+} (r\text{-}SO3^-)_nM^{n+} + nH^+ \longrightarrow$

$nR\text{-}COOH + M^{n+} (r\text{-} COO^-)_nM^{n+} + nH^+ \longrightarrow$

Hagag. M. A and co –workers demonstrated the use of macro porous strong cation exchange resin for the removal of Cu^{2+} using a rotating fixed bed of ion exchange resin. A number variables were studied which included initial concentration of Cu^{2+}, pH, rotating speed and ratio of mass of the resin to liquid volume(s/l). Best removal was reported at p^H of 4-5 and a decrease in removal rate with a rise in initial concentration of Cu^{2+} and increase in removal rate with increase in pH, rotating speed and (s/l) ratio was reported[25].

Murray. A and Ormeci .B synthesized polymeric sub microscopic ion exchange resin to study the removal capacity for lead, copper, zinc and nickel in comparison to the natural organic matter(NOM) present in water bodies. Reports indicated that the removal capacity for ions was little or not affected due to the presence of NOM. Removal percentages of 86 ± 0.1 for lead, 38 ± 0.8 for copper, 28 ± 1 for zinc and 11 ± 1 were reported[26].

Besides the use of synthetic resins and some of the functionalized polymers, zeolites in their natural form have been used for the purpose of ion exchange. Erdem. E and team, demonstrated the use of clinoptilite to remove Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} under concentrations ranging from 100-400 mg/l[27]. It was reported that in addition to adsorption, ion exchange played a crucial rule in the elimination of heavy metal ions and selectivity was in the order of $Co^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$. Chitpong.M and Husson. M.S researched on the use of polymer grafted cellulose nanofiber mats for the removal of Cd^{2+}, Ni^{2+} and Ca^{2+} [28]. Poly acrylic acid and poly itonic acid grafted membranes prepared by them showed higher selectivity to Cd^{2+} and from the single component ion exchange isotherm it was concluded that, poly-itonic acid grafted membrane have maximum capacities which exceeds 220mg/L, thereby showed a similar performance to that of a conventional ion exchange resin and higher than functionalized microfiltration membranes. Similar studies were carried out by Martin .D.M and co- workers used functionalized, ion selective polyacrylonitrile nanofibers and reported adsorption capacities of 6.1 mmol/g, 8.8 mmol/g, and 7.2 mmol/g for Cu^{2+}, Pb^{2+} and Zn^{2+} respectively[29].

2.6 Electrochemical treatment

Electrochemical treatment has proven to be labour extensive, highly effective and maintenance free. Electro chemical treatment often involves three main mechanisms namely electro coagulation, electro floatation and electrodeposition. Electro coagulation and floatation processes often go hand in hand where in the electricity generated destabilizes the colloids in wastewater and resulting in the formation of flocs. The electrochemical treatment processes are often accompanied by the release of hydrogen due to the following electrode reactions

At anode: $M \rightarrow M^{n+} + ne^-$

At cathode: $nH_2O + ne^- \rightarrow nH_2 + OH^-$

The hydrogen generated induces the floatation of the formed flocs[30]. On the other electrodeposition involves transfer of metal ions present in wastewater to the cathode, where reduction of metal ions takes place to obtain metal in pure form, generally applied to recover valuable metals[6, 7] Most of the current studies on electrochemical treatment have served two purposes that is removal of heavy metal ions and reduction in the COD levels of waste water respectively. Ya.V and team removed zinc and nickel and reduced COD levels of water using iron as the sacrificial anode. Zinc was selectively removed before nickel due to higher reduction potential of zinc, but a reduction of 40 % in COD level was achieved under low current density of 24.2mA/cm^2. The removal percentage was improved to 67.1% using electrochemical fenton process[31]. Tran T.K and team carried out similar studies, optimized electrode material, pH, supply power and working time and established that electrochemical treatment has great potential to generate green energy due to the liberation of hydrogen during the process[30]. The difference in the reduction potential of metals explained the sequential recovery of metal using electrochemical treatment. Optimization of electrode material involved choosing the best material with superior electrochemical performance at high current densities[30]. Carbon cloth with conductive ink was used as the electrode material by T.K. Tran and team.

2.7 Adsorption on low cost adsorbents

Adsorption is a mass transfer phenomenon involves transfer solute from the bulk of the liquid phase to the surface of the solid. There are namely two kinds of adsorption physical where the interaction between the adsorbate and adsorbent is due to non- specific weak van der waals forces and chemical wherein the interaction is due to the development of ionic or covalent bonds[32]. Although the name indicates adsorption there are associated mechanisms like electrostatic attraction and ion exchange which are in operation and aid the removal of heavy metals[27, 33]. Adsorption is usually a reversible process where desorption in the reverse phenomenon accompanying adsorption[32]. There are wide a range of adsorbents ranging from agricultural wastes, industrial by products, natural and modified zeolites, carbon nanotubes, activated carbon, number of nanoparticles, plant biomass and a number of microorganisms[34-38]that have been reported in literature. But in the recent days low cost adsorbents are gaining attention due to their overall cost efficacy in comparison to, no necessity of regeneration as they are present in abundance and less toxic sludge produced[2]. An adsorbent can be termed low cost if the associated processing costs are low, available abundantly in nature or is an industrial by product. The adsorption on low cost adsorbents is highly dependent on factors like pH, temperature, adsorbent dosage, initial metal ion concentration and contact time[37] therefore in all the major studies these parameters were optimized.

The use of low cost adsorbents for heavy metal removal dates back to as early as 1993 where Y. Orhan and co-workers removed heavy metal using waste tea, Turkish coffee, exhausted coffee, nuts and walnuts for the removal of aluminium, chromium and cadmium, removal efficiencies comparable to that of activated carbon were achieved[35]. Furthermore use rice husk, fly ash, peanut husk charcoal were reported for the removal of heavy metals iron, lead, nickel, cadmium, copper and zinc[34, 37]. Bio adsorbents derived from animals like crustaceans, chickens have been experimented for heavy metal removal[36, 38]. Alkaline treated chicken feathers removed copper and zinc ions efficiently obeying the Freundlich adsorption isotherm. On the other hand egg shells and chitosan removed chromium, iron, nickel and mercury according to Langmuir adsorption isotherm. In order improvise the performance of these materials O.S Amuda and co-workers prepared an acid activated coconut shell- chitosan composite. The composite was successful in removing zinc ions from waster of a synthetic beverage industry and alkaline treatment of the exhausted adsorbent confirmed that ion exchange was the controlling mechanism of heavy metal removal[39].

Apart from agricultural wastes and adsorbents based on agricultural wastes, zeolites (natural and modified), clays and minerals in their inherent form have been used as adsorbents for heavy metal removal. Montomorillonite, kaolin, tobermite, magnetite, silica gel and alumina were successful in chemisorbing cadmium, chromium, copper and lead with proven advantage of regeneration[40]. E. Erdem and co-workers reported charge density and hydrated ion diameter are the parameters which determine the performance of zeolite (clinoptilolite)[27]. On the other hand bentonite clay was used for column studies and was reported to have superior performance than activated carbon for the removal of copper and cadmium ions[41].

Microscopic members of the environment like algae, bacteria and fungi have been used heavy metal removal as they possess specialized cell enclosures with functional groups like carboxyl, amine and hydroxyl and rich in substances like chitins, mannans and phospho mannans which aid heavy metal removal[42]. Live strains of microorganisms as well as dead biomass have been used for ion and organic matter removal from waste water. Micro-organisms reduce or oxidize the heavy metal ions into less soluble species and effect their removal. In addition to this, action of extracellular and intracellular enzymes aid heavy metal removal[4]. Microorganism immobilization has advantages such as easy reuse, recovery and maintenance of high biomass density[43].

Adsorbents derived from plant sources date palm (leaves, trunk, base and fibres), bio char, ulva seaweed are the alternatives under consideration for the replacement of activated carbon (AC) [44-46]. The performance of these adsorbents depend on the internal structure and particle size, hence the adsorbents are subjected to pre-treatments- alkali treatment in case of ulva seaweed and surface oxidation or reduction in case of bio char which helped modify the surface structure and improve the desorption capacity. Also the composition of these adsorbents as they should have the capability to bind to the heavy metal ions- date palm consists of 62% by weight of carbon hence can be considered to replace AC. The table below shows the adsorbents, metal ions removed and the corresponding optimized p^H values (Table 2).

Table 2: Adsorption of heavy metals on low cost adsorbents

SL. NO	Adsorbent	Metals removed	Optimum pH	References
1.	Zeolite(clinoptilolite)	Co^{2+}, Cu^{2+},Zn^{2+}, Mn^{2+}	6-8	27
2.	Montomorillonite, Kaolin, Tobermorite	Cd^{2+}, Cu^{2+}, Cr^{6+}, Pb^{2+}	4	40
3.	Alkali treated Chicken feathers	Zn^{2+}, Cu^{2+}	-	36
4.	Acid activated coconut shell carbon/ chitosan	Zn^{2+}	6	39
5.	Immobilized bentonite	Cu^{2+}, Cd^{2+}	4.5-6.9	41
6.	Peanut husk charcoal, fly ash, natural zeolite	Cu^{2+}, Zn^{2+}	6-8	37
7.	Rice husk(R.H) and fly ash (F.A)	Fe^{3+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}	6-7	34
8.	Seaweed, Chitosan, egg shell, saw dust	Cr^{6+}, Fe^{3+}, Ni^{2+} and Hg^{2+}	-	38
9.	Immobilized cells of aspergillus Niger	Cu^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pb^{2+} and Cd^{2+}	5.5-7.5	43
10.	Ulva seaweed	Cd^{2+}, Zn^{2+}, Cu^{2+}, Cr^{6+} and Ni^{2+}	8	44
11.	Waste Tea, Turkish coffee, Exhausted coffee, nuts, walnut	Al^{3+}, Cr^{6+}, Cd^{2+}	-	35

2.8 Membrane technology

Membrane technology has proven capability of removal of organic contaminants, inorganic contaminants like heavy metals and also micro-organisms. Based on the size of the pore in the membrane, the membrane technologies are classified as microfiltration, ultrafiltration, nano filtration and reverse osmosis[1]. The pore size, pore distribution, surface charge, degree of interaction with water and presence of functional groups are the important set of characteristics of the membrane to be taken into consideration prior to the selection of membranes. The elimination of contaminants can take place via three mechanisms size exclusion/ steric hindrance, donnan exclusion principle and adsorption. Microfiltration is seldom used for heavy metal removal as the size of the solubilized ions is 400-500 times smaller than the pore size of microfiltration, hence they easily pass through the pores[5]. The technologies currently under development are micellar enhanced ultrafiltration (MEUF), complexation enhanced ultrafiltration (CEUF), adsorptive ultrafiltration, nano filtration (NF) and reverse osmosis (RO).

Micellar enhanced ultrafiltration involves the use of surfactants at or higher than critical micellar concentration (CMC). The micelle formation occurs at concentration above CMC and the metal ions solubilize in the micelle due to electrostatic or Van der waals[47]. The micelle solution thus formed is then forced through a suitable ultrafiltration membrane with an appropriate molecular weight cut off. Usually surfactants having charge opposite to that of metal ion is used and the commonly used one is sodium dodecyl sulphate. CEUF is similar to MEUF, wherein a polymer with the inherent capability to chelating is added to wastewater. The working functional groups on the polymer allow the bonding of metal ions via electrostatic interaction[5]. M.A Barkat used carboxy methyl cellulose as the polymer in CEUF to remove copper nickel and chromium ions and optimization studies on p^H and metal to polymer ratio were carried out[47]. Adsorptive membranes are synthesized by attaching functional groups to the surface or pore wall of the polymer membranes thus combining adsorption effectively with filtration process. When the heavy metal laden stream passes through the membrane the functional groups present in association with the membrane interact with the heavy metal ions resulting in adsorptive filtration of heavy metals[48]. Several recent studies on MEUF, CEUF and adsorptive ultrafiltration have been summarized (Table 3)

Table 3: Removal of Heavy Metals using CEUF, MEUF and Adsorptive Filtration

Mechanism	Membrane	Polymer/Surfactant	Target ions	Efficiency	Reference
CEUF	Polyether sulfone	Carboxy methylcellulose	Cu^{2+}, Cr^{3+}, Ni^{2+}	>95%	47
CEUF	Ceramic	Poly(acrylic acid) sodium	Cu^{2+}	99.5%	7
CEUF	Poly-sulfone	Poly(ammonium acrylate)	Cd^{2+}	99%	7
MEUF	Poly-carbonate	Dodecyl benzene sulfonic acid	Ni^{2+}	98.6%	7
MEUF	Ceramic	Sodium lauryl ether sulfate	Pb^{2+}, AsO_4^-	99%, 19%	7
MEUF	Poly-sulfone	Sodium dodecyl sulfate	Cd^{2+}, Zn^{2+}	92-98%	51
Adsorptive Filtration	Polymeric	Polyacrylonitrile-polyvinyltetrazole	Pb^{2+}	-	52
Adsorptive Filtration	Mixed Matrix	ZnO- Polyvinyldiene flouride	Cu^{2+}	>90%	53
Adsorptive Filtration	Mixed Matrix	Graphene Oxide-PolySulfone	Cu^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}	>90%	54

Nano filtration has been effective for removing bi valent ions and has a lower operating pressure compared to reverse osmosis. Nano filtration is a membrane technology where pressure difference is the driving force. Substances with molecular weight less than 200D pass through the membrane while multivalent ions are completely rejected. Nano filtration is generally operated in cross flow to avoid membrane fouling. The nano-filtration membranes operate via steric hindrance or donnan exclusion mechanisms[49]. The various studies carried out using nano-filtration have been summarized below (Table 4).

Reverse osmosis technology bares the smallest pores in comparison to all other membrane technologies, generally used for desalination. It involves pressurising the solvent through a semi permeable membrane from region of high solute concentration to region of low solute concentration by applying a pressure in excess of the osmotic pressure. Due to the high operating pressures the process is seldom used[50]. H. A. Qdais and team compared the performance of R.O and N.F technologies in removing copper and cadmium ions. R.O was reported have achieved higher removal for both ions[3].

Table 4: Removal of Heavy Metals using Reverse Osmosis

Membrane	Membrane material	Target ions	Efficiency	References
Polymeric	Polypyyrole-polyaniline	Cr^{6+}, Zn^{2+}, Pb^{2+}	>90%	55
Polymeric	Polyamide	Cr^{6+}, Cd^{2+}	>98%	56
Polymeric-TFC	Polyamide-Polysulfone	Pb^{2+}	98%	49
Polymeric-TFC	Ag-Poly(PIP)-Polyethersulfone	Pb^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}	>99%	57
Metal oxide-Polymer	Alumina- Chitosan	Cu^{2+}	>95%	56
Carbon based-Polymer	MWCNT-Polyethersulfone	As^{5+}	-	58

3. Conclusions

There are a numerous technologies/ methods available for removal of heavy metal ions from wastewater, each one subjected to some advantages and limitations which are discussed below.

Chemical precipitation is the widely and most commonly adopted method to remove high concentrations of heavy metals from wastewater. But on the downside uses large amount of chemicals which results in the production of toxic sludge and additional costs involved in handling the sludge produced.

Floatation method offers several advantages like high selectivity, production of low volume high concentration sludge and high removal efficiency. Limitations include high maintenance and operating costs.

Coagulation flocculation technique is economic and simple to operate without the use of any sophisticated equipment. However the use of chemicals produces toxic sludge and the heavy metal removal is incomplete.

Photo catalysis is energy efficient utilizing visible light, brings about concurrent removal of heavy metals and organic matter present in wastewater but long treatment times, electron hole recombination and high cost of photo catalysts have limited its industrial use.

Ion exchange technique possesses some unique advantages like high separation efficiency and selectivity only until the ion exchange resins remain unsaturated. Secondary pollution resulting due to usage of large quantities of chemical to regenerate the ion exchange resins has limited its large scale application.

Electrochemical treatment is highly selective aiding sequential removal of valuable heavy metal and no use of chemicals, therefore no sludge production. High capital investment, operating and damage to electrodes at high current density are some disadvantages which is limiting its full-fledged application

Adsorption is simple, effective and cost efficient technique for wastewaters bearing low concentrations of heavy metals. Requirement of secondary treatment to recover adsorbents and additional costs involved in functionalization, pre-treatment of adsorbents are the limitations of this technique.

Membrane technology offers advantages like low space requirement, high separation efficiency and selectivity but due to reasons like fouling, high energy consumption, complexity associated when handling low concentrations of metals and low filtrate rate have limited its use for heavy metal removal.

Therefore an appropriate technology must be chosen after consideration of facts like cost, separation efficiency required, concentration of metal ions in waste water, space availability and requirement of multi functionality.

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