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A Review on Treatment Technologies for Heavy Metal Removal from Waste Water

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ABSTRACT: Environmentalists are primarily concerned with the presence of heavy metals due to their high toxicity and impact on human health and environment. The interest in the development of cost-effective methods for the removal and recovery of heavy metals from contaminated waters has greatly increased because of the ecological awareness of the role of heavy metals in the environment. There are various treatment technologies employed for efficient removal of toxic heavy metals from industrial waste waters. The conventional treatment technologies include chemical precipitation, ion-exchange, membrane processes, electrochemical treatment, coagulation, adsorption, etc. Adsorption has been found to be superior compared to the other techniques for water re-use in terms of initial cost, ease of operation, sensitivity to toxic pollutants, flexibility and simplicity of design. Adsorption also does not result in the formation of harmful substances.

Key Words: Heavy metals, chemical precipitation, ion-exchange, membrane processes, electrochemical treatment, coagulation, adsorption

INTRODUCTION

“Heavy metal” is a general collective term, it mainly includes the transition metals, some metalloids, lanthanides, and actinides having atomic density greater than 4000 kg m^{-3}, or 5 times more than water and they are natural components of the earth’s crust. Heavy metals occur naturally in the ecosystem with large variations in concentration. Although some of them are essential micro nutrients for living beings that is required in small quantities but a higher dose may lead to severe poisoning (Lenntech, 2004).

Metals such as lead, cadmium, copper, arsenic, nickel, chromium, zinc and mercury have been recognized as hazardous heavy metals. These are non-biodegradable and gets accumulated in living tissues, causing various diseases and disorders (Ahmaruzzaman, 2011) and can cause life-threatening illness including irreversible damage to vital body system (Malik, 2004). From the eco-toxicological point of view, the most dangerous metals are mercury, lead, cadmium and chromium (Ahluwalia *et al.,* 2007); therefore they must be removed from industrial effluents before discharge. The most toxic forms of these metals in their ionic species are the most stable oxidation states e.g. Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{+} and As^{3+} in which, they react with the body’s bio-molecules to form extremely stable biotoxic compounds which are difficult to dissociate (Duruibe *et al.,* 2007). Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

The most dangerous metals which should be removed are: Chromium in its hexavalent form, Cadmium (II), Copper (II), Nickel (II). The common industries discharging these heavy metals are mainly electroplating and Paint and pigment manufacturing industries.

As we know the accumulation of heavy metals causes irreparable damages to mankind, so it’s a perquisite requirement to treat the waste-water coming out of the industries before merging it into the aquatic systems. For removing metals or for decreasing their concentration upto the permissible limits in the water bodies many techniques have been employed.

Table 1: The major sources of heavy metals in the environment and the problems which arise due to their higher concentration. (www.lenntech.com).

Heavy metals	Sources	Effects
Chromium	Electroplating, alloy making, chrome plating, magnetic tape, leather manufacturing, paint, pigments, photography, wood preservation, metal finishing	Skin rashes, allergic reactions, stomach ulcers, respiratory problems, Weakened immune systems, kidney and liver damage, human carcinogen
Cadmium	Electroplating, making pigments and batteries, coating, stabilizers, smelting, mining and refining.	Damages lungs, affects kidney, bone, Reproductive failure, damage to CNS, psychological disorders also causes cancer.
Copper	Electroplating , metal cleaning and plating, paper board, printed circuit board, wood, pulp, fertilizer, paints and pigments	Reproductive failure , stomach upset and ulcer, mental retardation, liver and brain damage
Arsenic	Glass industry, wood preservative	irritation of the stomach and decreased production of red and white blood cells, skin cancer, lung cancer, liver cancer and lymphatic cancer, cause infertility, heart disruptions and brain damage, can damage DNA.
Mercury	As amalgams, detonator [$Hg(ONC)_2$], paints, poisons, disinfectants	Neurotoxin, impairment of pulmonary and kidney function, chromosomal damage, Negative reproductive effects and chest pain.
Nickel	Electroplating, batteries manufacturing, power plants, paint industries.	serious lung and kidney problems, gastrointestinal distress, pulmonary fibrosis and skin dermatitis
Lead	cables, solders, lead crystal glassware, ammunitions, bearings, car batteries, paint	Disruption of biosynthesis of haemoglobin and anaemia, Damages central nervous system, kidney, liver and reproductive system, basic cellular processes and brain functions.

Table 2: Permissible limits of ionic species in potable water. (http://hppcb.gov.in/EIAsorang/Spec.pdf)

Heavy Metals	Permissible limit for industrial effluent discharge (mg/L) (Indian Standards)	Permissible limit for potable water (mg/L) (Indian Standards)
Chromium (VI)	2	0.05
Arsenic	0.2	0.01
Zinc	5	5
Mercury	0.01	0.001
Lead	0.1	0.05
Cadmium	2	0.01
Nickel	3	0.02
Copper	3	1.5

TREATMENT TECHNOLOGIES

There are various treatment technologies employed for efficient removal of heavy metals from industrial effluents. Such techniques are Coagulation/flocculation, Membrane–filtration, Electrochemical treatment, Ion-exchange, Chemical precipitation, Adsorption.

Feasibility of the process depends upon the cost employed, availability of the raw material and treating reagents, composition of the effluents of a particular industry or area and finally the large scale application of the technique. Since the effluents contain several metals it is necessary to study the simultaneous sorption of two or more metal ions and also to quantify the interactive effect of one metal ion on the other.

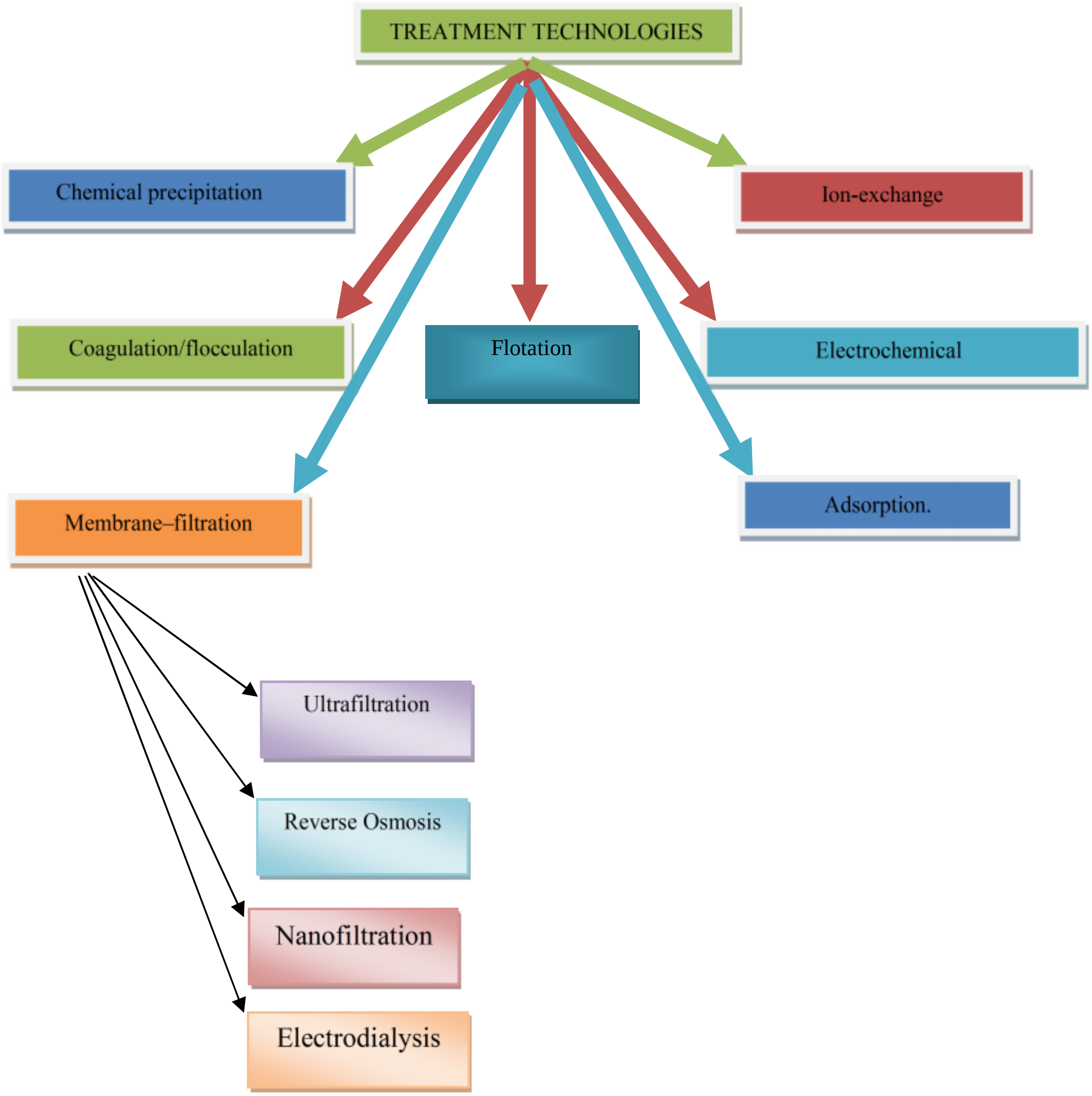

Fig. 1. Various treatment technologies for heavy metal removal from waste water.

A. Coagulation/flocculation

The coagulation-flocculation processes are used for separating suspended solids. Coagulation uses chemical reagent or coagulants for destabilization of colloidal particles. While in flocculation destabilised particles get agglomerated into flocs and adding flocculant aid may promote the formation of the floc. Along with the removal of heavy metals they work upon decreasing turbidity present in the water.

Factors influencing the processes are velocity gradient, the time, and the pH (prominent factor).

The inorganic salt aluminium sulphate (alum) is one of the most widely used coagulants in wastewater treatments. Alum is appreciated for its low cost, ease of use and availability. However, it produces abundant sludge that is difficult to dehydrate, its efficiency is entirely dependent on the pH and when formed in cold water alum flocs are not very mechanically resistant. In addition, possibility of toxicity is open. Since high aluminium concentrations in water may have human health implications, environmentally friendly coagulants will present an interesting alternative for the purification of wastewaters.

Commercial synthetic polymers show some of the advantages over alum: lower coagulant dose requirements, increase in the rate of separating the solid and water phases arising from larger agglomerate sizes, efficiency at low temperatures (hydrolysing metal coagulants perform less well at low temperatures), a smaller volume of sludge, a smaller increase in the ionic load of the treated water, a less pH-dependent process and a reduced level of aluminium in the treated water. Polymer-based products also improve settleability and increase the floc toughness. However, although synthetic water-soluble polymers find a wide range of applications as coagulants and flocculants, the potential problems associated with their use are high cost, lack of biodegradability and polymer toxicity.

In a work by Chang and Wang, 2007 coagulation was used for removing both soluble heavy metals and insoluble substances. They grafted sodium xanthogenate group to polyethyleneimine by reacting polyethyleneimine with carbon disulphide in presence of sodium hydroxide. This grafting was done with reference to the earlier work (Navarro *et al.,* 2003) which inferred that heavy metals xanthogenate are insoluble. Jar test was conducted on the synthesized samples at different pH and the supernatant was analyzed for Ni^{2+}, Cu^{2+}, Cr^{6+} and turbidity using diacetyldioxime spectrophotometry, diethyldithiocarbamate spectrophotometry and atomic absorption spectrophotometry. Floc formation was found to be faster than observed in chemical precipitation. The paper shows that Ni^{2+} and turbidity affect each other. Due to large turbidity large flocs form providing large surface area, thus more ions get removed by adsorption and sweep mechanism while Ni^{2+} neutralizes the negative charge of xanthogenate radical decreasing its repulsion with turbid molecules and thereby increases the flocculation. Experiment was further extended to electroplating factory waste water, at pH 5.5 percentage removal increased with the dose and reached 95% at 160 mg/L. Metal removal was seen at a higher pH while 99% turbidity was removed at a low dose and at low pH. This was good in relation to isoelectric point but aimed more towards turbidity.

But coagulation must be followed by some other units like adsorption, ion-exchange and membrane for increasing effective removal of heavy metals since coagulation alone aims towards turbidity.

Flocculation method has been traditionally used with inorganics but over a last decade chitosans are receiving high interest. Chitosan is a linear copolymer of d-glucosamine and *N*-acetyl-d-glucosamine produced by the deacetylation of chitin (second most abundant biopolymer) Chelating ability varies with degree of deacetylation and molecular weight. Chitosan has the advantage of being a non-toxic material, non corrosive and safe to handle well (non hazardous product, not irritating for skin and eyes. Native chitosans show limited ion exchange sites (Gamage and Shahidi, 2007) and looses efficiency at pH>7 thus they need to be chemically modified.

Bratskaya, 2009 applied polyampholyte chitosan derivatives – N-carboxyethylated chitosans (CEC) with deacetylation degree of 84% for removal of Cu^{2+}, Zn^{2+},Ni^{2+} at pH 7.5-9. At pH 8 Cu^{2+}, Zn^{2+} were removed efficiently but that of Ni^{2+} was below 60%. While at a pH 9 very slow sedimentation rate was reported and increasing pH adds up to the cost. They used varying degree of substitution on CEC and concluded that higher the pH and Degree of substitution of CEC derivative, the narrower was flocculation range and a strong negative effect hydroxides colloids restabilization on the efficiency was noticed.

In a work by Chang, 2009 mercaptoacetyl chitosan (MAC) was formed for Cu^{2+} and turbidity removal. Just chitosan addition was useless but the removal efficiency reached 59.26% by TGA (reacting chitosan with mercaptoacetic acid) efficiency was reported to be 88.89% by MAC but hyped to 96.3% in the presence of turbidity. As seen in earlier work heavy metal removal (Cu^{2+}) rate increases with increase in pH while contradictory to this, turbidity removal decreases with increasing pH.

Chitosan is only efficient over a limited pH range and when present in excess, has a negative effect on performance (overdosing can restabilize a dispersion and affect other process aspects); the coagulation/flocculation properties depend on the different sources of chitin/chitosan (the quality of commercial chitin available is not uniform). Such processes require addition of some coagulation aids (bentonite) or ultrasonic treatment to increase the efficiency and increase the settling rate. These techniques rather require simple equipments but involve high cost of chemical consumption and even produces large amount of sludge which leads to secondary pollution.

B. Membrane filtration

Membrane filtration is the most widely and commercially used technique available for water treatment due to the easy operability, high efficiency and less space requirement. The processes used under this technique for heavy metal removal operate through Ultrafiltration, Nanofiltration, Reverse osmosis and electrodialysis.

In Ultrafiltration the liquid is forced through a semi-permeable membrane under hydrostatic pressue, suspended solids and solutes of high molecular weight get retained, while water and low molecular weight solutes pass through the membrane. This works in the range of (10^3-10^6Da) particle size. To obtain high removal efficiency of metal ions, the micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) was proposed.

This separation technique is based on the addition of surfactants to wastewater. When the concentration of surfactants in aqueous solutions is beyond the critical micelle concentration (CMC), the surfactant molecules will aggregate into micelles that can bind metal ions to form large metal-surfactant structures. The micelles containing metal ions can be retained by a UF membrane with pore sizes smaller than micelle sizes, whereas the untrapped species readily pass through the UF membrane. To obtain the highest retentions, surfactants of electric charge opposite to that of the ions to be removed have to be used. Sodium dodecyl sulfate (SDS), an anionic surfactant, is often selected for the effective removal of heavy metal ions in MEUF.

Reverse osmosis is the process of forcing a solvent from a region of high solute concentration (Low Water Potential) through a semipermeable membrane to a region of low solute concentration (High Water Potential) by applying a pressure in excess of the osmotic pressure. The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. To be "selective," this membrane should not allow large molecules or ions through the pores (holes), but should allow smaller components of the solution (such as the solvent) to pass freely.

Nanofiltration is a recent development, used mostly with low total dissolved solids water with the purpose of softening. Its application is in food processing (dairy) for simultaneous concentration and partial (monovalent ion) demineralisation. The nominal pore size of the membrane is typically about 1 nanometre. Nanofilter membranes are typically rated by molecular weight cut-off (MWCO) rather than nominal pore size. The trans- membrane pressure (pressure drop across the membrane) required is lower (up to 3 MPa) than the one used for RO, reducing the operating cost significantly. However, NF membranes are still subject to scaling and fouling and often modifiers such as anti-scalants are required for use. Nanofiltration lies in between RO and UF.

Electrodialysis (ED) is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. This is done in a configuration called an electrodialysis cell. The cell consists of a feed (diluate) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes. In almost all practical electrodialysis processes, multiple electrodialysis cells are arranged into a configuration called an electrodialysis stack, with alternating anion and cation exchange membranes forming the multiple electrodialysis cells.

Micellar-enhanced ultrafiltration (MEUF) combines the high selectivity of RO and high flux of UF. Samper, 2009 used MEUF alongwith two anionic surfactants (SDS and LAS) for removing Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} . Effects of surfactant concentration, pH and conductivity on metal retention were studied. MEUF consumes less energy and provides high metal removal efficiency. As predicted ion retention increases with surfactant concentration. In the case of SDS concentration has to be above CMC (Critical micelle concentration) but LAS was found to be effective even below it. This was tested for a lower concentration of metal in solution. It was noticed that the retention of Ni^{2+} requires high amount of surfactant and the change in pH showed least variation. The problem which arises in membranes is the formation of gel layer which poses resistance.

As a hybrid approach Barakat and Schmidt, 2010 used water soluble metal binding polymers (Carboxymethyl cellulose) with UF membranes (Polyethersulfone polymer). This complexation provides high separation selectivity. Experiment was found to be pH dependent, and the separation increased with the increasing pH. Metal rejection efficiency was high at a low initial metal concentration for Cu(II), Cr(II), Ni(II), it worked upto a certain concentration. However again Ni(II) showed similar problem of low rejection efficiency in a solution containing several heavy metal ions than for an individual solution of Ni(II). Use of membrane and even with some polmer complexation results in high cost.

Cu^{2+} and Ni^{2+} ions were successfully removed by the RO process using spiral wound type membrane and the rejection efficiency of the two ions increased up to 99.5% by using Na_2EDTA (Mohsen-Nia *et al.,* 2007).

Dialynas and Diamadopoulos (2009) applied a pilot-scale membrane bioreactor system in combination with RO and they found heavy metal removal efficiencies were very high. Pb and Ni were removed completely, indicating that these two metals were in particulate form, while Cr and Cu were removed by 89% and 49%, respectively. The major drawback of RO is the high power consumption due to the pumping pressures, and the restoration of the membranes

Nataraj *et al.* (2007) performed a new working system to investigate the removal of hexavalent chromium ions using a built ED pilot plant comprising a set of ion-exchange membranes. Results were satisfactory in meeting the maximum contamination level of 0.1 mg/L for chromium.

This technique results in good and efficient removal but it employs costly membrane arrangements and generates concentrated sludge.

C. Electro-coagulation

Electrocoagulation offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions. The technology removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species. These species neutralize the electrostatic charges on suspended solids and oil droplets to facilitate agglomeration or coagulation and resultant separation from the aqueous phase. The treatment fastens the precipitation of certain metals and salts.

An electrocoagulation reactor is made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. The positive side undergoes anodic reactions while cathodic reactions are seen on negative side. Consumable metal plates, such as iron or aluminum, are usually used as sacrificial electrodes to continuously produce ions in the water. The released ions neutralize the charges of the particles and thereby initiate coagulation. Electrocoagulation cannot remove infinitely soluble matter. Therefore ions with molecular weights smaller than Ca^{+2} or Mg^{+2} cannot be dissociated from the aqueous medium.

This method involves electrodeposition or reduction of metal ions from an electrolyte. A current is passed between the electrodes and metal cations diffuse to the surface of the cathode, form a surface complex, receive electrons from the cathode and get reduced to the metallic state.

In a laboratory study by Heidmann and Calmano, 2008 electrocoagulation was used on water containing Zn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{2+}, $Cr_2O_7^{2-}$ ions. Removal technique behind the mechanism was precipitation of ions as hydroxides. Earlier precipitation was done using NaOH and coagulation with $FeSO_4$ or $Al_2(SO_4)_3$ with slow sedimentation. Effect of initial metal concentration, charge loading and current density were noticed. This technique requires no additional chemical thus produces reduced volume of sludge. They varied one parameter at a time keeping others constant. Concentration of Zn, Ni, Cu were found to decrease linearly with coagulation time but it was not effective in case of Ag and even did not follow linearity for Cr. At first the pH decreased but then increased to 10 while for Ag no decrease in pH value was noticed. Reason behind different behavior of chromate Cr (VI) is that rather than getting directly precipitated as hydroxides $Cr(OH_3)$, it has to first reduce to Cr(III).

With the variation of initial metal concentration it was seen that removal of Zn was least affected while that of Cr is strongly dependent. High coagulant dose means high current density and in addition if there are losses, process gets less efficient.

By studying the interaction of metals, it was proved that Zn and Cu follow the same mechanism. Removal rates of Zn, Cu, Ni were lowered by the presence of other metals because of the competition for the OH^- ions produced at the cathode. So this process does not suit multicomponent heavy metal removal.

For the treatment of water from metal plating containing Cu, Cr, Ni electrocoagulation was employed with different combinations of Fe-Al electrodes. Effect of various parameters like electrode material, current density, pH and conductivity were studied in a work by Akbal and Camcı, 2011. In this case also efficiency increases with current density (2.5-5 mA/cm^2) as seen earlier. Cu removal was found to be better with Fe-Fe and Fe-Al combinations because adsorption capacity of ferric oxides is higher than aluminium oxides. Out of various processes the % removal achieved through this work was quite high. But the drawback of metal recovery from dilute solutions is low current efficiency.

Chemical coagulation generates large volumes of sludge with high bound water content that can be slow to filter and difficult to dewater. These treatment processes also tend to increase the total dissolved solids (TDS) content of the effluent, making it unacceptable for reuse within industrial applications. An electrocoagulated flock tends to contain less bound water, is more shear resistant and is more readily filterable. This has proved to be rapid and effective for removal of certain heavy metals but consumes high energy.

D. Ion exchange

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins, or passing the treated solution through several different ion exchange materials. Examples of ions that can bind to ion exchangers are:

-H^+ (proton) and OH^- (hydroxide)
-Single-charged monatomic ions like Na^+, K^+, and Cl^-
-Double-charged monatomic ions like Ca^{2+} and Mg^{2+}
-Polyatomic inorganic ions like SO_4^{2-} and PO_4^{3-}
-Organic bases, usually molecules containing the amino functional group $-NR_2H^+$
-Organic acids, often molecules containing $-COO^-$ (carboxylic acid) functional groups
-Biomolecules that can be ionized: amino acids, peptides, proteins, etc.

Ion exchange is a reversible process and the ion exchanger can be regenerated or loaded with desirable ions by washing with an excess of these ions. Process has certain advantages such as high treatment capacity, high removal efficiency and fast kinetics.

Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyüz and Veli, 2009).

Factors affecting the removal are pH, temperature, initial metal concentration, contact time and ionic time. Zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions (Motsi *et al*., 2009) applied over acid mine drainage. Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attention due to its selectivity for heavy metals. It has good removal ability for wide range of heavy metals.

E. Chemical precipitation

Chemical precipitation is one of the most effective and mostly used process in industry because it is relatively simple and inexpensive to operate. Chemicals react with heavy metal ions to form insoluble precipitates which can be separated from the water by sedimentation or filtration. Treated water is decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation.

In a work by Mirbagheri, S.A., Hosseini, S.N., 2005 alkaline reagents such as $Ca(OH)_2$ (lime) and NaOH (caustic soda) in removing copper and chromium ions were evaluated. Maximum conversion occurred in the pH range of 2.0 and 2.3, adjusted by ferrous sulfate and sulfuric acid. . Lime was preferred due to economics and its high speed of precipitation.

There are certain limitations of hydroxide precipitation:

-Generation of large volume of sludge of low density which presents dewatering and disposal problems
-Some metal hydroxides are amphoteric, and the mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may put another metal back into solution.
-When complexing agents are in the wastewater, they will inhibit metal hydroxide precipitation.

In sulfide precipitation solubilities of the metal sulfide precipitates are dramatically lower than hydroxide precipitates and sulfide precipitates are not amphoteric. It works over a broad range of pH as compared to hydroxide precipitation. Metal sulfide sludges also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges.

Özverdi and Erdem (2006) investigated pyrite and synthetic iron sulfide to remove Cu^{2+}, Cd^{2+} and Pb^{2+}. The mechanism governing the metal removal processes was determined as chemical precipitation at low pH (<3) due to H_2S generation and adsorption at high pH (in the range 3-6).

F. Adsorption

Adsorption has proved to be a viable method due to its high efficiency, low investment, design flexibility and simplicity. Adsorbents used can also be regenerated and hence reused. Mostly used adsorbent is activated carbon, which shows good result for metal adsorption but is restricted due to its high cost of activation.

Nowadays work has been focussed on using efficient low cost adsorbents. Waste biomass, industrial waste, mineral wastes have been investigated and shown better adsorption capacities.

Certain inexpensive industrial wastes like fly ash, blast furnace sludge, red mud, coffee husks have already been utilised. Even the researchers have approached biomasses for the purpose. Peapod, cotton, mustard seed cakes, *Ocimum basilicum* seeds, waste tea, sugarcane bagasse, jatropha oil cake all have been investigated.

These can be applied either for a single metal sorption or for simultaneous removal for two or more metal ions from the aqueous solutions.

In order to reduce the Cr (VI) level to the acceptable limit Sarin and Pant, 2006 tested Eucalyptus bark for Cr (VI) removal in batch mode. Process was found to be spontaneous and feasible. Adsorption capacity was reported as 45 mg/g with maximum removal at pH 2. Laboratory scale experoment was extended to the effluent of metal finishing industry containing 200 mg/l of Cr (VI) concentration and the adsorbent proved to be effective. Freundlich isotherm satisfactorily suited the data.

Adsorption of Cr (VI) was studied on boiled and formaldehyde treated *Helianthus annuus* (sunflower) stem waste by Jain *et al.*, 2009. In both the cases maximum removal was found at a pH 2 while removal percent approached 81.7 % and 76.5 % respectively, at a dose of 4 g/L.

In a work by Bhattacharya *et al.*, 2008 several low cost adsorbents (Clarified sludge, rice husk ash, activated alumina, fuller's earth, fly ash, saw dust and neem bark) were investigated. Factors studied were pH, adsorbent type and concentration, initial metal concentration, contact time. Optimum pH was reported to be between 2 and 3. Among all Clarified sludge was foud to be the most effective one.

Sorption of Cr (VI) using formaldehyde treated saw dust (SD) and sulphuric acid treated saw dust (SDC) of Indian Rosewood was studied by Garg *et al.*, 2004. Equilibrium time reached at 60 min which is quite less in comparison to the work by other researchers. Most favorable pH was found to be at 3 with a high removal percentage shown by SDC.

In a similar approach by Baral *et al.*, 2006 formaldehyde treated saw dust of sal was used. At an initial metal concentration of 5 mg/l maximum removal was seen between pH 4.5 – 6.5. Process was exothermic in nature. Data well suited Lagrangian adsorption isotherm and pseudo second order reaction model.

Batch experiments were carried out by Gupta and Babu, 2009 for Cr (VI) removal using abundantly available biodegradable saw dust. pH 1 was the point of maximum adsorption with an adsorption capacity of 41.5 mg/g. Even the interference of other ions present in effluents of electroplating and tannery industries have been investigated.

Adsorption studies on hexavalent chromium removal were made by Gupta *et al.*, 2010 using fertilizer industry waste—carbon slurry, which was chemically treated and activated. At a temperature of 303 K maximum adsorption was achieved within 70 minutes at a pH of 2. With the initial metal concentration of 100mg /l, adsorption capacity was found to be 15.2 mg/g. In this work also the spontaneous process with exothermic nature was seen. Experiments were further extended to the column studies and the data fitted both the Lagrangian and Freundlich isotherms.

Adsorption is an effective technique, earlier activated carbon has potential of a good adsorbent but needed activation involving high cost. In replacement to this many industrial wastes (termed as low-cost adsorbents) have been used for this purpose.

Fly ash, a residue generated from combustion was employed as a low cost adsorbent. It comprises of silica (SiO_2), alumina (Al_2O_3), magnetite (Fe_2O_3), calcium oxide and some other constituents depending upon the source. Raw fly ash has low adsorption capacity while a chemical treatment (impregnation by Fe, Al) can increase the capacity. This has been applied for removing Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+} , Cr^{6+} by many researchers.

Sharma *et al.*, 2008 used fly ash from thermal power plants for Cr (VI) removal. They investigated the effect of various parameters like concentration, contact time, pH, ionic strength, adsorbent size on the removal. They extended their work to kinetic and equilibrium modeling. As removal is fast in initial stages and slow down with time it is essential to find out the time needed to reach the equilibrium in order to calculate the process efficiency. pH proved to be a strong factor, high metal separation was seen at pH 2.5 but decreased to25.4% at pH8. The best part of this research was that the fly ash was given no chemical treatment but it still resulted in a spontaneous process.

Poplar sawdust was used as an adsorbent by Marina *et al.*, 2007 on wastewater from electroplating industry, it proved to be effective in the removal of copper, zinc and cadmium. Batch adsorption experiments at constant temperature (23± 2ºC) and without pH adjustment was carried out by adding different amounts of wood sawdust. The sawdust adsorption efficiency increased with the increase in the amount of the sawdust.

After attainment of equilibrium the filtrate was analyzed. This could be used at a larger scale if a proper disposal is assured as it keeps COD within limits. Multilayer adsorption of Cu(II) was confirmed by BET model. Langmuir competition model showed that Zn(II) and Cd(II) are competing ions for Cu(II). Larous and Meniai 2012 used chemically activated saw dust for Cu (II) adsorption from synthetic waste water. They carried out batch wise experiments and found Langmuir adsorption i.e. monolayer coverage of ions on the saw dust. The used saw dust was supposed to be a source of fertilizer. Similarly, Liu *et al.*, 2013 prepared EDTA functionalized magnetic nano- particles for Cu (II) adsorption.

Langmuir model was found to be best suited and maximum adsorption capacity of 46.27 mg/g at pH 6.0 and 298K was obtained.

It is also necessary to draw attention towards the combined removal of ions as generally various species are present in the waste water. In a work by Srivastava *et al.,* 2008 rice husk ash (RHA) a waste obtained from the rice husk-fired furnaces , without any pretreatment was used as an adsorbent for the removal of cadmium Cd(II) and zinc Zn(II) ions in a batch treatment process. The adsorption of metal ions increases with an increase in initial pH. Maximum sorption for both Cd (II) and Zn(II) metal ions was found to occur at pH0 6.0. The affinity of RHA for Zn (II) ions was found to be greater than that for Cd(II), for both single component and the binary solutions under similar experimental conditions. The net interactive effect of Cd (II) and Zn (II) ions on the adsorption of Cd(II) ions by RHA was found to be antagonistic.

In a similar approach of combined adsorption of ions, Kapur and Mondal 2014 used coal dust collected from Northern Coal Fields Limited, Singrauli (MP), India, for adsorbing Cu (II) and Ni (II) ions from the aqueous solutions. Variations of different parameters viz., pH, Initial solution concentration, temperature were done in a set range to optimize the conditions. Adsorption was found to be spontaneous for both the metals. They even tested the feasibility of coal dust for ion adsorption on the industrial effluent collected from electroplating industry (Kapur and Mondal 2014).

Table 3: Comparison of various treatment methods for heavy metal removal.

Method	**Merits**	**Demerits**
Chemical precipitation	Process simplicity Low capital cost	Large amount of sludge containing metals Sludge disposal cost Ineffective when metal ion concentration is low
Ion exchange	High removal capacity Fast kinetics Metal selective Limited pH tolerance High regeneration, Good for wide range	High initial capital cost High maintenance cost Regeneration required for ion - exchanger Disposal causes serious secondary pollution
Coagulation/ flocculation	Economically feasible Bacterial inactivation capability Good sludge settling and dewatering characteristics	High sludge production and formation of large particles Chemical consumption Increased volume of sludge generated
Membrane filtration	Low solid waste generation Low chemical consumption Small space requirement Possible to be metal selective Good removal of heavy metals	High initial capital cost High maintenance and operation costs Membrane fouling Limited flow-rates Concentrated sludge production
Electrocoagulation	Engineered to tolerate suspended solids without chemical requirement Moderately metal selective Rapid process and effective for certain metal ions	High initial capital cost Production of H_2 in some processes Filtration process for floc separation High energy costs and formation of by-products
Flotation	Metal selective Low retention times Removal of small particles	High initial capital cost High maintenance and operation costs
Adsorption	Wide variety of target pollutants High capacity Fast kinetics Wide range of available adsorbents Flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Physical or chemical activation of adsorbent to improve its sorption capacity Adsorbents requires regeneration

CONCLUSION

Out of various processes studied and seen through the work done by different researchers it can be well inferred that the techniques involving chemicals are not in favor of environmental conditions and moreover adds upto the cost involved like coagulating and flocculating agents, surfactants and frothers. Using membrane is a cost ineffective issue and separation through electro-coagulation is a mere wastage of electricity. In addition to these drawbacks such processes produces large volume of sludge creating another problem of waste disposal. So the best way to find out the solution for the waste water treatment is by using a suitable low cost adsorbent and even if it is applied without any chemical modifications. The only problem which arises is of regeneration, which can be achieved by flushing it with acetic acid, HCl, H_2SO_4, and HNO_3.

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