Methods of Removing Heavy Metals from Industrial Wastewater

Gunatilake S.K.
Department of Natural Resources
Sabaragamuwa University of Sri Lanka
Belihuloya, Sri Lanka
e-mail: sksg@sab.ac.lk;sunethrasum@yahoo.com

***Abstract*—Methods for treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards. This article was focused on the recently developed and newly applicable various treatment processes for the removal of heavy metals from industrial wastewater. Physico-chemical removal processes such as; adsorption on new adsorbents, ion exchange, membrane filtration, electrodialysis, reverse osmosis, ultrafiltration and photocatalysis were discussed. Their advantages and drawbacks in application were evaluated.**

In the processes of biological treatments microorganisms play a role of settling solids in the solution. Activated sludge, trickling filters, stabilization ponds are widely used for treating industrial wastewater. Bioadsorption is a new biological method and various low cost bioadsorbents (agricultural waste, forest waste, industrial waste, algae etc.) are used for maximum removal of heavy metals from wastewater. Bioadsorption techniques are eco friendly best solutions for removing heavy metals from wastewater rather than physic-chemical methods. But chemical methods are most suitable treatments for toxic inorganic compounds produced from various industries which cannot removed from any biological and physical techniques.

Keywords—heavy metals; removal techniques; bioadsorption; physico-chemical treatments

I. Introduction

The environmental issues due to globalization and rapid industrialization are becoming more and more nuisance for human being. Therefore efficient and effective methods are needed especially for chemical industries. Heavy metals present in wastewater and industrial effluent is major concern of environmental pollution. Heavy metals are generally considered those whose density exceeds 5 g per cubic centimeter. Most of the elements falls into this category are highly water soluble, well-known toxics and carcinogenic agents. Heavy metals are considered to be the following elements: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese, and Aluminum. They represent serious threats to the human population and the fauna and flora of the receiving water bodies ([1]. They can be absorbed and accumulated in human body and caused serious health effects like cancer, organ damage, nervous system damage, and in extreme cases, death. Also it reduces growth and development. Industrial wastewater streams containing heavy metals are produced from different industries. Heavy metals such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium are generated in electroplating, electrolysis depositions, conversion-coating, and anodizing-cleaning, milling, and etching industries. Significant amount of heavy metals wastes like Tin, lead, and nickel result from printed circuit board (PCB) manufacturing. Wood processing industries where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments contain chromium compounds and cadmium sulfide; petroleum refining generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludge that can be categorized as hazardous wastes requiring extensive waste treatment [2]. As the low amounts of these metals are highly toxic, removal of heavy metals from wastewater has recently become the subject of considerable interest owing to strict legislations. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. These include limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The Maximum Contaminated Level (MCL) standards, for those heavy metals, established by USEPA [3] are summarized in Table 1. Therefore it is necessary to treat metal contaminated wastewater prior to its discharge to the environment.

Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes. Removal of heavy metals from industrial wastewaters can be accomplished through various treatment options, including such unit operations as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations. This paper describes these various treatment strategies and methodologies employed for heavy metal removal.

TABLE 1 The MCL standards for the most hazardous heavy metals (Babel and Kurniawan, 2003)

Heavy metal	Toxicities	MCL(mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogen	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nikel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and nervous system	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system and nervous system	0.00003

Chemical precipitations, conventional adsorption [4-8], ion exchange [9], membrane separation methods [10] and electro-remediation methods are used more commonly to treat industrial wastewater. Among these methods precipitation is most economical and hence widely used, but many industries still use chemical procedures for treatment of effluents due to economic factors [11, 12]. However due to complexing agents in wastewater, efficiency of the precipitation process can drastically be decreased [13] and this creates incomplete processing and production of toxic sludge. Therefore numerous novel approaches have been studied to develop cost effective and more efficient heavy metal adsorption techniques [14].

Biosorption is considered as a user-friendly, effective purification and separation method for the removal of heavy metals from industrial wastewater with the advantages of specific affinity, low cost and simple design [15, 16]. Therefore it has been widely used for treatment of wastewater. Sorption with sorbents made of agricultural or industrial by-products are used widely to remove heavy metals from aqueous solution due to their abundant availability, low cost, and favorable physical, chemical and surface characteristics [17]. Those methods and materials were widely discussed focusing their advantages.

II. HEAVY METAL REMOVAL METHODS

A. *Physico-chemical methods*

Following methods have been used by various researchers for removal of heavy metals. Physical separation techniques are primarily applicable to particulate forms of metals, discrete particles or metal-bearing particles [18]. Physical separation consists of mechanical screening, hydrodynamic classification, gravity concentration, flotation, magnetic separation, electrostatic separation, and attrition scrubbing, [18]. The efficiency of physical separation depends on various soil characteristics such as particle size distribution, particulate shape, clay content, moisture content, humic content, heterogeneity of soil matrix, density between soil matrix and metal contaminants, magnetic properties, and hydrophobic properties of particle surface [19, 20].

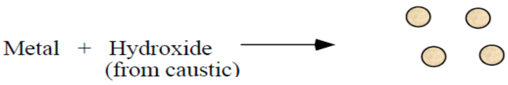
The conventional chemical processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition. Factors that may limit the applicability and effectiveness of the chemical process are high content of clay/silt, humic, calcite, Fe & Ca, heavy metals, anions, or high buffering capacity [21].

B. *Chemical Precipitation*

Chemical precipitation is one of the most widely used for heavy metal removal from inorganic effluent in industry due to its simple operation [22]. These conventional chemical precipitation processes produce insoluble precipitates of heavy metals as hydroxide, sulfide, carbonate and phosphate. The mechanism of this process is based on to produce insoluble metal precipitation by reacting dissolved metals in the solution and precipitant. In the precipitation process very fine particles are generated and chemical precipitants, coagulants, and flocculation processes are used to increase their particle size to remove them as sludge [21, 22]. Once the metals precipitate and form solids, they can easily be removed, and low metal concentrations, can be discharged. Removal percentage of metal ions in the solution may be improved to optimum by changing major parameters such as pH, temperature initial concentration, charge of the ions etc. The most commonly used precipitation technique is hydroxide treatment due to its relative simplicity, low cost of precipitant (lime), and ease of automatic pH control. The solubilities of the various metal hydroxides are minimized for pH in the range of 8.0 to 11.0.

C. *Coagulation and Flocculation*

The coagulation-flocculation mechanism is based on zeta potential (ζ) measurement as the criteria to define the electrostatic interaction between pollutants and coagulant-flocculant agents [23]. Coagulation



Metal Precipitation

process is reduced the net surface charge of the colloidal particles to stabilize by electrostatic repulsion process [24]. Flocculation process continually increases the particle size to discrete particles through additional collisions and interaction with inorganic polymers formed by the organic polymers added [25]. Once discrete particles are flocculated into larger particles, they can be removed or separated by filtration, straining or floatation. Production of sludge, application of chemicals and transfer of toxic compounds into solid phase are main drawbacks of this process.

D. Electrochemical Treatments

Electrolysis: Electrolytic recovery is one technology used to remove metals from wastewater streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Electricity can be generated by movements of electrons from one element to another. Electrochemical process to treat wastewater containing heavy metals is to precipitate the heavy metals in a weak acidic or neutralized catholyte as hydroxides. Electrochemical treatments of wastewater involve electro-deposition, electro-coagulation, electro-flotation and electro-oxidation [26].

Electrodestabilization of colloids is called coagulation and precipitation by hydroxide formation to acceptable levels. It is the most common heavy metal precipitation method forming coagulants by electrolytic oxidation and destabilizing contaminants to form folc [27]. The electro-coagulation process the coagulant is generated in situ by electrolytic oxidation of an appropriate anode material. In this process, charged ionic metal species are removed from wastewater by allowing it to react with anion in the effluent. This process is characterized by reduced sludge production, no requirement for chemical use, and ease of operation.

However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are huge sludge production, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [28]. It changes the aqueous pollution problem to a solid waste disposal problem without recovering the metal.

E. Ion Exchange

Ion exchange can attract soluble ions from the liquid phase to the solid phase, which is the most widely used method in water treatment industry. As a cost-effective method, ion exchange process normally involves low-cost materials and convenient operations, and it has been proved to be very effective for removing heavy metals from aqueous solutions, particular for treating water with low concentration of heavy metals [29, 30]. In this process cations or anions containing special ion exchanger is used to remove metal ions in the solution. Commonly used ion exchangers are synthetic organic ion exchange resins. It can be used only low concentrated metal solution and this method is highly sensitive with the pH of the aqueous phase.

Ion exchange resins are water-insoluble solid substances which can absorb positively or negatively charged ions from an electrolyte solution and release other ions with the same charges into the solution in an equivalent amount. The positively charged ions in cationic resins such as hydrogen and sodium ions are exchanged with positively charged ions, such as nickel, copper and zinc ions, in the solutions. Similarly, the negative ions in the resins such as hydroxyl and chloride ions can be replaced by the negatively charged ions such as chromate, sulfate, nitrate, cyanide and dissolved organic carbon (DOC).

F. Membrane Filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent. It is capable of removing suspended solid, organic compounds and inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal from wastewater.

Ultrafiltration (UF) utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000– 100,000 Da) [31]. Depending on the membrane characteristics, UF can achieve more than 90% of removal efficiency with a metal concentration ranging from 10 to 112 mg/L at pH ranging from 5 to 9.5 and at 2–5 bar of pressure. UF presents some advantages such as lower driving force and a smaller space requirement due to its high packing density.

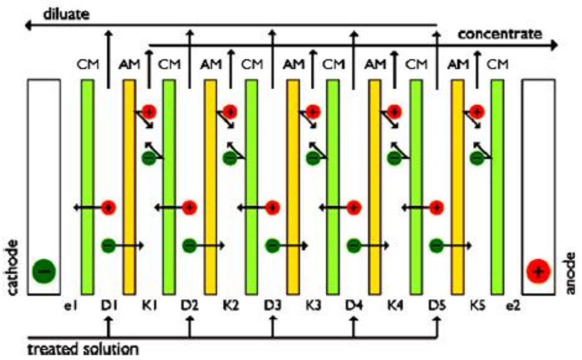
Polymer-supported ultrafiltration (PSU) technique adds water soluble polymeric ligands to bind metal ions and form macromolecular complexes by producing a free targeted metal ions effluent [32]. Advantages of the PSU technology are the low-energy requirements involved in ultrafiltration, the very fast reaction kinetics and higher selectivity of separation of selective bonding agents in aqueous solution.

Another similar technique, complexation–ultrafiltration, proves to be a promising alternative to technologies based on precipitation and ion exchange. The use of water-soluble metal-binding polymers in combination with ultrafiltration (UF) is a hybrid approach to concentrate selectively and to recover heavy metals in the solution. In the complexation – UF process cationic forms of heavy metals are first complexed by a macro-ligand in order to increase their molecular weight with a size larger than the pores of the selected membrane [33, 34]. The advantages of complexation–filtration process are the high separation selectivity due to the use of a selective binding and low-energy requirements involved in these processes. Water-soluble polymeric ligands have shown to be powerful substances to remove trace metals from aqueous solutions and industrial wastewater through membrane processes.

Reverse osmosis (RO) is a separation process that uses pressure to force a solution through a membrane that retains the solute on one side and allows the pure solvent to pass to the other side. The membrane here is semipermeable, meaning it allows the passage of solvent but not for metals. The membranes used for reverse osmosis have a dense barrier layer in the polymer matrix where most separation occurs. Reverse osmosis can remove many types of molecules and ions from solutions, including bacteria, and is used in both industrial processes. Reverse osmosis involves a diffusive mechanism, so that separation efficiency is dependent on solute concentration, pressure, and water flux rate [35].

G. Electrodialysis

Electrodialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation-exchange membranes [36]. A noticeable disadvantage is membranes replacement and the corrosion process [37]. Using membranes with higher ion exchange capacity resulted in better cell performance. Effects of flow rate, temperature and voltage at different concentrations using two types of commercial membranes, using a laboratory ED cell, on lead removal were studied [38].



.

Fig. 1 Electrodialysis principles (Chen, 2004) CM – cation exchange membrane, D-dialute chamber, e1 and e2-electrode chambers, AM-anion exchange membrane and K-concentrate chamber

Results show that increasing voltage and temperature improved cell performance and separation percentage decreased with an increasing flow rate. This offers advantages for the treatment of highly concentrated wastewater laden with heavy metals to recovery undesirable impurities from water.

H. Biological Methods

Biological removal of heavy metals in wastewater involves the use of biological techniques for the elimination of pollutants from wastewater. In this processes microorganisms play a role of settling solids in the solution. Activated sludge, trickling filters, stabilization ponds are widely used for treating wastewater. Activated sludge is the most common option uses microorganisms in the treatment process to break down organic material with aeration and agitation, and then allows solids to settle out. Bacteria-containing "activated sludge" is continually re-circulated back to the aeration basin to increase the rate of organic decomposition. Most of the research on heavy metals removal in biological systems has been directed towards the suspended growth activated sludge process. Trickling Filters which consist beds of coarse media (often stones or plastic) 3-10 ft. deep help to grow microorganisms. Wastewater is sprayed into the air (aeration), then allowed to trickle through the media and microorganisms break down organic materials in the wastewater. Trickling filters drain at the bottom and the wastewater is collected and then undergoes sedimentation. Stabilization ponds or lagoons are slow, cheap, and relatively inefficient, biological method that can be used for various types of wastewater. They rely on the interaction of sunlight, algae, microorganisms, and oxygen.

Biosorption is another method that can use to remove heavy metals from wastewater. Sorption process is transfer of ions from solution phase to the solid phase, actually describes a group of processes, which includes adsorption and precipitation reactions. Adsorption has become one of the alternative treatment techniques for wastewater. Basically, adsorption is a mass transfer process and substances bound by physical and or chemical interactions to solid surface [3]. Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated water. Use of activated carbon in water and wastewater treatment has been oriented towards organics removal [39]. Research efforts on inorganics removal by activated carbon, specifically metallic ions, have been markedly 1imited [39] Selective adsorption by red mud [40], coal [41], photocatalyst beads [42], nano-particles [43] fertilizer industrial waste [44], biomass [45], activated sludge biomass [46], algae [47, 48] etc. has generated increasing excitement.

Industrial by-products such as fly ash [49], waste iron, iron slags [50], hydrous titanium oxide [51, 52], can be chemically modified to enhance its removal performance for metal removal from wastewater.

Recently, research for the removal of heavy metals from industrial effluent has been focused on the use of agricultural by-products as adsorbents through biosorption process. New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk, rice straw, rice husk, coconut shell etc can be used as an adsorbent for heavy metal uptake after chemical modification or conversion by heating into activated carbon or biochar [3, 53]. They found that the maximum metal removal occurred by those biomass due to containing of cellulose, lignin, carbohydrate and silica in their adsorbent [54].

Biopolymers are posse a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake [55]. They are widely use in industrially as they are capable of lowering transition metal ion concentrations to sub-part per billion concentrations. New polysaccharide-based-materials are described as biopolymer adsorbents (derived from chitin, chitosan, and starch) for the removal of heavy metals from the wastewater. The sorption mechanisms of polysaccharide-based-materials are complicated and depend on pH [55]. Also hydrogels, which are cross linked hydrophilic polymers, are widely used in the purification of wastewater. The removal is basically governed by the water diffusion into the hydrogel, carrying the heavy metals inside especially in the absence of strongly binding sites. Maximum binding capacity increases with higher pH due to polymerization/cross linking reaction.

III. EVALUATION OF HEAVY METAL REMOVAL PROCESSES

Removal of heavy metals from the effluent is very important part of the research carried out in environmental field. Various methods tried by the researchers include physical, chemical and biological methods. Physico-chemical treatments offer various advantages such as rapid process, easy operation and control, various input loads etc. Whenever it is required, chemical plants can be modified. These treatment systems require a lower space and installation cost. Their benefits are outweighed by a number of drawbacks such as their high operational costs due to the chemicals used, high-energy consumption and handling costs for toxic sludge disposal. If the chemical costs are possible to reduce anyhow, physico-chemical treatments have been found as one of the most suitable treatments for inorganic compounds produced from various industries which cannot removed from any biological and physical techniques.

Studies on biological methods are very important area of research with huge potential for research and applicability for removal of heavy metals. Various biological methods include trickling filter, biosorption, activated sludge process can be used. Biological methods by using various low materials were found be very effective methods with higher percentage of removal. Although biological methods are low cost and environmental friendly techniques they need large areas and proper maintenance and operation.

IV. CONCLUSION

Biological treatments are eco friendly, best removal and low cost methods. Lot of bio adsorbents can be found in nature. Physical and other most common chemical methods are produced toxic sludge which is unable to settle within industries. Although chemical cost is high chemical treatments is one of the most suitable treatments for toxic inorganic compounds produced from various industries which cannot removed from any biological and physical techniques.

V. ACKNOWLEDGMENT

The financial support given by the Nation Research Council is highly appreciated.

VI. REFERENCES

1. Babel, S. and T.A. Kurniawan, *Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan.* Chemosphere, 2004. **54**(7): p. 951-967.
2. Sörme, L. and R. Lagerkvist, *Sources of heavy metals in urban wastewater in Stockholm.* Science of the Total Environment, 2002. **298**(1): p. 131-145.
3. Babel, S. and T.A. Kurniawan, *Low-cost adsorbents for heavy metals uptake from contaminated water: a review.* Journal of hazardous materials, 2003. **97**(1): p. 219-243.
4. Maity, H., et al., *Protein hydrogen exchange mechanism: local fluctuations.* Protein science, 2003. **12**(1): p. 153-160.
5. Amritphale, S., et al., *Adsorption behavior of lead ions on pyrophyllite surface.* Main group metal chemistry, 1999. **22**(9): p. 557-566.
6. Chandra Sekhar, K., et al., *Removal of heavy metals using a plant biomass with reference to environmental control.* International Journal of Mineral Processing, 2003. **68**(1): p. 37-45.
7. Prasad, B. and U. Pandey, *Separation and preconcentration of copper and cadmium ions from multielemental solutions using Nostoc muscorum-based biosorbents.* World Journal of Microbiology and Biotechnology, 2000. **16**(8-9): p. 819-827.
8. Ho, Y.-S. and G. McKay, *Pseudo-second order model for sorption processes.* Process Biochemistry, 1999. **34**(5): p. 451-465.
9. Vaca Mier, M., et al., *Heavy metal removal with Mexican clinoptilolite:: multi-component ionic exchange.* Water research, 2001. **35**(2): p. 373-378.
10. Reddad, Z., et al., *Adsorption of several metal ions onto a low-cost biosorbent: kinetic and*

equilibrium studies. Environmental science & technology, 2002. **36**(9): p. 2067-2073.

11. Zhou, W. and W. Zimmermann, *Decolorization of industrial effluents containing reactive dyes by actinomycetes.* FEMS microbiology letters, 1993. **107**(2): p. 157-161.
12. Sergeev, V., et al., *Groundwater protection against pollution by heavy metals at waste disposal sites.* Water Science and Technology, 1996. **34**(7): p. 383-387.
13. Salim, M. and B. Shaikh, *Distribution and availability of zinc in soil fractions to wheat on some alkaline calcareous soils.* Zeitschrift für Pflanzenernährung und Bodenkunde, 1988. **151**(6): p. 385-389.
14. Eccles, H., *Treatment of metal-contaminated wastes: why select a biological process?* Trends in biotechnology, 1999. **17**(12): p. 462-465.
15. Al-Asheh, S., et al., *Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data.* Chemosphere, 2000. **41**(5): p. 659-665.
16. Muhammad, S., M.T. Shah, and S. Khan, *Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan.* Microchemical Journal, 2011. **98**(2): p. 334-343.
17. Sawalha, M.F., et al., *Sorption of hazardous metals from single and multi-element solutions by saltbush biomass in batch and continuous mode: Interference of calcium and magnesium in batch mode.* Journal of environmental management, 2009. **90**(2): p. 1213-1218.
18. Dermont, G., et al., *Metal-contaminated soils: remediation practices and treatment technologies.* Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 2008. **12**(3): p. 188-209.
19. Smith, L., *Contaminants and remedial options at selected metal-contaminated sites. Technical resource report*, 1995, Battelle, Columbus, OH (United States).
20. Williford, C., R.M. Bricka, and I. Iskandar, *Physical separation of metal-contaminated soils*2000: CRC Press LLC, Boca Raton.
21. Fu, F. and Q. Wang, *Removal of heavy metal ions from wastewaters: a review.* Journal of Environmental Management, 2011. **92**(3): p. 407-418.
22. Ku, Y. and I.-L. Jung, *Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide.* Water Research, 2001. **35**(1): p. 135-142.
23. López-Maldonado, E., et al., *Coagulation–flocculation mechanisms in wastewater treatment plants through zeta potential measurements.* Journal of hazardous materials, 2014. **279**: p. 1-10.
24. Benefield, L.D., J.F. Judkins, and B.L. Weand, *Process chemistry for water and wastewater treatment*1982: Prentice Hall Inc.
25. Tripathy, T. and B.R. De, *Flocculation: a new way to treat the waste water.* 2006.
26. Shim, H.Y., et al., *Application of Electrocoagulation and Electrolysis on the Precipitation of Heavy Metals and Particulate Solids in Washwater from the Soil Washing.* Journal of Agricultural Chemistry and Environment, 2014. **3**(04): p. 130.
27. Mollah, M.Y.A., et al., *Electrocoagulation (EC)—science and applications.* Journal of hazardous materials, 2001. **84**(1): p. 29-41.
28. Aziz, H.A., M.N. Adlan, and K.S. Ariffin, *Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III)) removal from water in Malaysia: Post treatment by high quality limestone.* Bioresource Technology, 2008. **99**(6): p. 1578-1583.
29. Dizge, N., B. Keskinler, and H. Barlas, *Sorption of Ni (II) ions from aqueous solution by Lewatit cation-exchange resin.* Journal of hazardous materials, 2009. **167**(1): p. 915-926.
30. Hamdaoui, O., *Removal of copper (II) from aqueous phase by Purolite C100-MB cation exchange resin in fixed bed columns: Modeling.* Journal of hazardous materials, 2009. **161**(2): p. 737-746.
31. Vigneswaran, R., et al., *Cerebral palsy and placental infection: a case-cohort study.* BMC pregnancy and childbirth, 2004. **4**(1): p. 1.
32. Rether, A. and M. Schuster, *Selective separation and recovery of heavy metal ions using water-soluble N-benzoylthiourea modified PAMAM polymers.* Reactive and Functional Polymers, 2003. **57**(1): p. 13-21.
33. Petrov, S. and V. Nenov, *Removal and recovery of copper from wastewater by a complexation-ultrafiltration process.* Desalination, 2004. **162**: p. 201-209.
34. Trivunac, K. and S. Stevanovic, *Removal of heavy metal ions from water by complexation-assisted ultrafiltration.* Chemosphere, 2006. **64**(3): p. 486-491.
35. Crittenden, J.C., et al., *Understanding and Improving Process Performance of Advanced Oxidation Processes (AOPs).*
36. CHEN, L. and Q. CHEN, *Industrial application of UF membrane in the pretreatment for RO system [J].* Membrane Science and Technology, 2003. **4**: p. 009.
37. Kurniawan, T.A., et al., *Physico–chemical treatment techniques for wastewater laden with heavy metals.* Chemical engineering journal, 2006. **118**(1): p. 83-98.
38. Mohammadi, B. and O. Pironneau, *Shape optimization in fluid mechanics.* Annu. Rev. Fluid Mech., 2004. **36**: p. 255-279.

39. Gomez-Serrano, V., et al., *Adsorption of mercury, cadmium and lead from aqueous solution on heat-treated and sulphurized activated carbon.* Water Research, 1998. **32**(1): p. 1-4.
40. Gupta, V.K., M. Gupta, and S. Sharma, *Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste.* Water Research, 2001. **35**(5): p. 1125-1134.
41. Lakatos, T., *Jensen et al.* 2002.
42. Idris, A., et al., *Photocatalytic magnetic separable beads for chromium (VI) reduction.* Water Research, 2010. **44**(6): p. 1683-1688.
43. Liu, K., et al., *Step-growth polymerization of inorganic nanoparticles.* science, 2010. **329**(5988): p. 197-200.
44. Gupta, V.K., A. Rastogi, and A. Nayak, *Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material.* Journal of Colloid and Interface Science, 2010. **342**(1): p. 135-141.
45. Sharma, A.K., *Experimental study on 75kW th downdraft (biomass) gasifier system.* Renewable Energy, 2009. **34**(7): p. 1726-1733.
46. Wu, J., et al., *Cr (VI) removal from aqueous solution by dried activated sludge biomass.* Journal of hazardous materials, 2010. **176**(1): p. 697-703.
47. Mane, P., et al., *Bioadsorption of selenium by pretreated algal biomass.* Adv. Appl. Sci. Res, 2011. **2**(2): p. 202-207.
48. Moustafa, M. and G. Idris, *Biological removal of heavy metals from wastewater.* Alexandria Engineering Journal, 2003. **42**(6): p. 767-771.
49. Alinnor, I., *Adsorption of heavy metal ions from aqueous solution by fly ash.* Fuel, 2007. **86**(5): p. 853-857.
50. Deliyanni, E., E. Peleka, and K. Matis, *Removal of zinc ion from water by sorption onto iron-based nanoadsorbent.* Journal of hazardous materials, 2007. **141**(1): p. 176-184.
51. Ghosh, U.C., et al., *Studies on Management of Chromium (VI)–Contaminated Industrial Waste Effluent using Hydrous Titanium Oxide (HTO).* Water, Air, and Soil Pollution, 2003. **143**(1-4): p. 245-256.
52. Barakat, M., *Adsorption behavior of copper and cyanide ions at TiO 2–solution interface.* Journal of Colloid and Interface Science, 2005. **291**(2): p. 345-352.
53. Bansode, R., et al., *Adsorption of metal ions by pecan shell-based granular activated carbons.* Bioresource Technology, 2003. **89**(2): p. 115-119.
54. Tang, D.-S., et al., *Extraction and purification of solanesol from tobacco:(I). Extraction and silica gel column chromatography separation of solanesol.* Separation and purification technology, 2007. **56**(3): p. 291-295.
55. Crini, G., *Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment.* Progress in polymer science, 2005. **30**(1): p. 38-70.