Comparative Study of Traditional and Advanced Techniques for Heavy Metal Removal from Electroplating Wastewater

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ABSTRACT

The main goal today is to adopt appropriate measures and develop suitable techniques for removing heavy metals from waste water released from industrial operations. The major constituents in the waste water being generated from the metal finishing processes are cyanides, various metal ions [Fe, Cu, Ni, Ag, Mn, Pb, Zn and Cr(VI)] oils and greases, organic solvents, acids and alkalies. The characteristics of the waste stream from electroplating industries are so toxic and corrosive due to the presence of these heavy metals. The present paper reveals the electroplating industry operations which involve use of heavy metals and toxic chemicals and finally result in increased contamination and load of these metals in their waste stream discharges. The paper focuses on various easily available methods as chemical precipitation, low cost novel adsorption through coconut shell, mango seed and shell, bagasse, waste tea leaves, wood barks and usar soil, membrane processes, which are capable of 90% -100% removal of these metals, bioremoval methods, removal by minerals and removal by newer technique as semiconductor photo catalysis technology.

KEYWORDS: Heavy Metal, Electroplating, Waste water, Removal Techniques.

INTRODUCTION

Heavy Metal term refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Heavy metals are natural components of the earth's crust. They cannot be degraded or destroyed. They are dangerous because they tend to bioaccumulate which is an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment [1, 2].

For many years, attention has been devoted to the development of methods for removing heavy metals from wastewater arising from industrial operations. The most common methods for removing heavy metals have involved chemical precipitation, ultra filtration, solvent extraction, electrodeposition, biological treatment, ion exchange and adsorption. Waste water from industries like electroplating, dye, textile, metal, engineering and pesticides etc contain higher concentration of heavy metal. Plating waste water contains heavy metal at levels that might be considered hazardous to environment and could pose risks to public health.

The main purpose of electroplating which is transformed in to a process of science and technology since 1930 is to altar the surface properties of metal or non metal in order to achieve improved appearance (decoration), improved resistance to corrosion(surface protection). Improved frictional and galling behavior and Increased hardness at lower cost. The type of plating required is determined on the basis of the appearance desired, the intended use of the finished article and nature of base material to be plated. Cr, Ni, Ag, Au, Cu and Rd are the most widely used metals for decorative plating. The base metals and alloys that are the most commonly subjected to electroplating are steel, brass, copper, nickel, silver, white metal alloys of lead, zinc, tin and aluminium. Chrome plating is most commonly used for decorative purposes because of its durability and resistance to chemical attack, abration and tarnish. Steel is most commonly used for construction material which must be protected from corrosion and chemical attack. The protective coating of zinc, cadmium, and tin is preferred as it not only protects steel but also does not contaminate the food. Many metals, particularly iron and steel, undergo some "finishing" before commercial use. This finishing often consists of a coating of some other, corrosion resistant-metal such as zinc, copper, chrome or nickel. Metal coatings can be applied in several ways. The most common of these finishing methods, not only for galvanizing but for the application of all metal coatings, is electroplating which involves-

Pretreatment- Involves degreasing with soaps, alkaline cleaning, acid dipping, and/or "Desmutting" to remove fine particles of base metal, particularly aluminium.Alkaline cleaners generally contain sodium compounds such as sodium hydroxide, sodium phosphate, sodium carbonate, sodium silicate and sodium metal silicate and also a wetting agent such as kerylbenzene sulfonate. Their prolonged use for aluminium cleaning may lead to the formation of aluminium oxides precipitates. To increase the quality of the precipitate, citrates, tartrates, or gluconates may be added. The waste water from the pretreatment stage thus contains dissolved metals plus some of these cleaning agents.

Plating- The constituents of the waste water from plating operation will depend of course on the metals being plated and on the nature of the plating bath. Metals that are commonly plated include copper, nickel, chromium, zinc, cadmium, lead, tin, gold and iron. Each of these can be plated from several types of baths.
Post treatment- This treatment steps include processes such as chromating, phosphating and colouring. Chromate coatings are applied to a number of metals for protection. The solutions contain chromic acid or its sodium or potassium salts, nitric acid and some other organic or inorganic acids that function as activators or catalysts. Phosphate coatings provide a good base for paints and other organic coatings. They also help resist corrosion or provide a good base for rust preventing waxes and oils [3, 4].
Generally these solutions contain metal phosphates dissolved in phosphoric acid with added nitrates, nitrites, chlorates or peroxides as catalysts. Colouring is caused by conversion of the metal surface to an oxide or other compound. The pollutants can be any of a wide variety, but frequently include arsenic, antimony,, mercury, molybate and permanganate. Copious amounts of waste water are generated through these steps, plating waste water contains heavy metals at levels that might be considered hazardous to the environment and could pose risks to public health. Heavy metals in particular are of great concern due to their toxicity [5, 6].

Composition of electroplating bath

The electroplating bath composition for nickel (watts) and nickel-acid fluoride plating is nickel sulphate, nickel chloride, nickel fluoroborate, boric acid, phosphoric acid, phosphorous acid, "Stress reducing additives" and nickel chloride, hydrofluoric acid, citric acid, sodium lauryl sulphate (wetting agent) respectively. For black nickel plating the bath composition is nickel ammonium sulphate, nickel sulphate, ammonium sulphate, zinc sulphate and sodium thiocyanate[7].
Cyanide is produced on a large scale for use in electroplating and the waste water generated by these industries contains cyanide complexed with heavy metals (Cu, Ni, Zn, Cd, Cr, Ag and Au etc) of variable stability and toxicity [9]. High concentration of heavy metals in raw water is generally associated with industrial discharges. Waste water containing heavy metals such as Pb, Cu, Mn, Zn, Fe, Cd, Ni and Cr were analyzed by flame atomic absorption spectrophotometer [9]. The extensive use of Chromium containing compounds in plating industrial processes releases Cr (VI) resulting in the contamination of surface water and soil. Though Cr is essential nutrient for plant and animal metabolism, however when accumulated at higher concentration it causes serious disorders and diseases and it can ultimately become lethal [10].

Adverse Health effect of heavy metal

Heavy metal pollutants are toxic both to the humans and other living beings due to their presence beyond certain limits [11,12]. The heavy metals are the most harmful and insidious pollutant because of their non-biodegradable nature. The reason for higher values of these parameters may be ascribed to the disposal of sewage estates, wastes from metal processing industries and house hold refuses [13]. Exposure of human beings to the chrome bearing dust for longer period will cause skin irritation and corrosion of skin, ulcer formation, lever damage, respiratory tract infection, nausea, vomiting, severe diarrhea, epigastric pain and hemorrhage [14,15]. Heavy metal pollutants cause direct toxicity both to humans and other living beings, due to their presence beyond specified limits. Several of these metals are bioaccumulative and detrimental to human health.

Removal of Heavy metals

a. Removal of heavy metals by chemical methods

Results of a study conducted on the application of sulphide precipitation technique on the removal of lead, cadmium and silver when they are present together are reported. The results indicate that the sulphide precipitation technique is effective in simultaneous removal of three or more metals[16]. Theoritical hydroxide precipitation curves normally found in plating baths indicates that there is no one ideal pH for a multiple-metal system. [17]. Heavy metal ions can be removed by precipitation method [18].All these "conventional" technologies such as filtration, chemical precipitation and solvent extraction have raised issues of efficacy when faced with low metal concentrations, high start-up or operating costs and low metal selectivity. Conversely, the most commonly adopted method for the treatment of cyanide contaminated effluent is alkaline chlorination oxidation process. It is not effective for nickel and silver cyanide complexes due to slow reaction rates [19]. Other physico-chemical methods, such as copper catalyzed hydrogen peroxide, oxidation, azonation, electrolytic decomposition etc are used for treatment of metal cyanides [20].

Four naturally derived chitinuous materials, commercial cryogenically milled carapace (CCMC), mechanically milled carapace (MMC), chitin and chitosan, were assessed for their ability to remove a range of transition and heavy metals from aqueous media in flow through column trials. In general chitin was the least efficient material for removal of transition and heavy metals (~35 %) while chitosan was most effective (>99%), CCMC and MMC both removed >90 % of transition and heavy metals tested from solution[21]. A thiol-functionalized layered magnesium phylloslicate material (called Mg-MTMS), prepared by a direct and cost effective co-condensation synthesis, has been investigated as a high capacity adsorbent for heavy metal ions [22].

Physico- chemical methods, such as chemical precipitation, chemical oxidation, or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies have been widely used to remove heavy metal ions from industrial waste water. These processes may be ineffective or expensive specially when the heavy metal ions are in solution containing in the order of 1- 100 mg dissolved heavy metal ions/l [23, 24].

The metal finishing industry presents one of the most critical industrial waste problems. There is, therefore, growing interest in developing methods for reclaiming metals from plating waste stream and recovery of water using membrane technology. The application of reverse osmosis (RO) to the global effluent from the electroplating industry has been studied and the results show 75-95% recovery of water and nearby total removal of metals in the permeate[25].

The successful treatment of heavy metals in electroplating waste water is done using cellulose acetate micro filtration membrane and polysulphone ultra filtration membrane for the removal Cr, Cu, Ni and Zn present in this waste water [26]. K.E. Bouhidel and M. Rumeau [27] investigated electro dialysis membrane fouling (EDMF) by boric acid during nickel salts electro dialysis(ED).This process is used in the nickel electroplating industry to concentrate and reuse nickel salts and to recycle treated rinse waters. To reduce rinse water treatment costs, increased emphasis is being placed in metal plating shops on recycling process, low cost metal recovery and pollution prevention, a technology is designed which is a combination of electrowinning and electrodialysis unit, that recovers nickel metal while generating a mixed inorganic acid solution that can be reused in plating shop pickling baths [28].

b. Cheap and natural available Adsorbents for heavy metals removal

A number of low cost novel adsorbents have been tried by several investigators such as fly Ash, bituminous coal, blast furnace slag, coconut shell, mango seed and shell, bagasse, used waste tea leaves and wood barks[29-38].The characteristic properties will help in understanding the nature and selectivity of the adsorbent. Usar soil was used as absorbent to remove the heavy toxic metals such as Pb, Cr, Ni, Cu and Zn from electroplating waste and contaminated water. Results of usar soil as absorbent show 100% removal of the heavy metals from electroplating waste and contaminated water [39]. Natural and activated clays have been investigated as adsorbent for the removal of Ni from waste water [40]. Batch adsorption experiments of Pb, Cu and Zn ions on to waste fluidized catalytic cracking (F.C.C) catalyst were performed.Adsorption data for each ion were well described by the Freundlich and Langmuir adsorption models. The removal of Pb, Cu and Zn ions attained values of 97.0 %, 90.5% and 91.5% respectively [41]. Several workers studied the removal of lead and copper from aqueous solutions by using low cost adsorbent like bagasse and fly ash[42].

P.Kumar and S.S. Dara [43] studied the removal of lead from aqueous solution using red onion skin. The chemically activated sugar cane Baggasse carbon (CASBC) adsorbent prepared from a waste material from the sugar industry was converted in to a sorbent, which exhibit good sorption for both the metals. Sorption of Cu is higher than Pb[44]. Neem leaf powder was found to be an effective adsorbent for removal of Cr(VI) from aqueous solution and could be used for treatment of waste water contaminated with heavy metals like chromium [45].

lbizEa lebbeck pods were used for the treatment of chromium from industrial waste waters in laboratory.

The optimum pH for adsorption was found to be 2.0. The metal removal efficiency was 94-99 %. The phenomenon of adsorption by biosorbent can be attributed to various mechanisms such as electrostatic attraction and repulsion, chemical interaction and ion exchange [46].There are reports of removal of Cr from waste water by adsorption using low cost adsorbents such as fly ash, baggsse, wheat, straw dust and coconut coir [47]. Use of dhaoda tree bark for the removal and recovery of cadmium ions from industrial waste water is discussed. The dried and powdered bark is contacted with acidified formaldehyde and the resin product so obtained is highly efficient in removing Cd^{2+} ions from the solution. The metal ion uptake increases with increasing pH values. It is also observed that more than 99% of Cd^{2+} ions is removed by substrate from solution instantaneously [48].

Agricultural wastes materials can be used to remove toxic heavy metals from waste water as they are capable of binding heavy metals by adsorption, chelation and ion exchange. The exchange properties of these wastes can be attributed to the presence of carboxylic, phenolic, hydroxylic groups [49].The technical feasibility of coconut shell charcoal (CSC) and commercial activated carbon (CAC) for Cr (VI) removal is investigated in batch studies using synthetic electroplating waste water. Both granular adsorbents are made up of coconut shell (Cocos nucifera L.), an agricultural waste from local coconut industries [50].

The aquatic plants can concentrate heavy metals 1000-20,000 times their concentration in water. Some of the plants used for the purpose are Cerato phylum, Lemna, Spirodela, Pistia, Elodea etc but the most outstanding and promising plant has been water hyacinth [51].

The use of palsa (Butea monosperma) bark substrate for the retrieval of Cu^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+} from industrial waste streams is discussed. The dried and powdered palsa bark in contact with acidified formaldehyde and the resinous product so obtained was found highly efficient for removing Cu^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+}, from solution

[52]. The removal of heavy metals from plating factory waste water with economical materials was investigated by the column method . Montmorillonite, Kaoolin, tobermorite, magnetite, silica gel and alumina were used as the economical adsorbents to wastewater containing Cd (II), Cr(VI), Cu(II) and Pb(II). Since economical adsorbents used can be obtained commercially because they are easily synthesized the waste water treatment system developed is rapid, simple and cheap for the removal of heavy metals [53]. The potential of a lignocellulosic fibre, jute, was assessed for adsorption of heavy metal ions like Cu (II), Ni (II) and Zn (II) from their aqueous solutions. The fibre was also used as an adsorbent after chemically modifying it by two different techniques viz, loading of a dye with specific structure, and oxidizing with hydrogen peroxide. Both the modified jute fibres gave higher metal ion adsorption [54].

c. Bioremoval of heavy metals

Existing industrial techniques for the purification of waste water are expensive. Cheaper alternative may be 'bioremoval', i.e. concentration of pollutants from aqueous solution using biological material. Adsorption of Cu, Zn and Cd using two dried seaweeds Ecklonia maxima and Laminaria pallida(order Lamnariales) and Kelpak waste(also made from Ecklonia maxima), a byproduct from manufacture of seaweed concentrate. Kelpak, were investigated under lab conditions to determine some factors affecting heavy metal adsorption. Optimum adsorption occurred at pH 3 and pH 7, Kelpak waste had equal or superior adsorption ability to dried Ecklonia maxima and Laminaria pallida particularly for Cu, optimum adsorption occurred at 20^0 C and 30^0 C, heavy metal adsorption trends by individual seaweed biosorbent remains constant regardless of the species of anion present[55].

Biological methods such as biosorption/bio accumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods [56].

Most studies of biosorption for metal removal have evolved the use of either laboratory grown microorganism or biomass generated by the pharmacology and food processing industries or waste water treatment units [57-60]. Many aquatic microorganisms, such as bacteria, yeast and algae can take up dissolved metal from their surrounding on to their bodies and can be used for removing heavy metal ions successfully [61].

Biosorption of metals cations have been studied extensively by several researchers [62].Biosorption and biodegradation processes can be used to remove copper cyanide and from plating waste water[63]. Experimental studies showed that brown marine algae, Sargassum vulgaris and Padina pavonia, can be used to develop an efficient biosorbent for heavy metal removal from aqueous solutions [64].

Removal of nickel from the effluent of an electroplating industry by Saccharomyces cerevisae was studied, the maximum removal was found to be at 2.5 g of biomass within five hours of treatment. The bound metal was recovered by 0.1 NHCl and the biomass was charged to be reusable. In the regeneration cycle, the efficiency was not affected in first two cycles. However, it decreased insignificantly in the third cycle [65]. Micro organism uptake metal either actively (bioaccumulation) and / or passively (biosorptuion)[66-68].

Feasibility studies for large scale application demonstrated that biosorptive process are more applicable than bioaccumulative process because living system(active uptake) often require the addition of nutrients and hence increase biological oxygen demand(BOD) or chemical oxygen demand (COD) in the effluent. In addition, maintenance of healthy microbial population is difficult due to metal toxicity and other unsuitable environmental factors. In addition, potential for desorptive metal recovery is restricted since metal may be intercellularly bound, metabolic product may form complexes with metals to retain them in solution and mathematical modeling of a non defined system is difficult [69-71]. The use of adsorbent of biological origin has emerged in a last decade as one of the most promising alternative to conventional heavy metal management strategies[72-75]. Efficient removal of dissolved Ni is observed in biologically active moving-bed 'Meresafin' sand filter treating rinse water from an electroless nickel plating plant. Analysis of the nickel containing biosludge using chemical , electron microscopical and X-ray spectroscopic technique confirmed crystallization of Ni phosphate as arupite ($Ni_3(PO_4)_2.8H_2O$), together with hydroxyapatite with in the bacterial biofilm on the filter sand grains [76]. A consortium of bacteria(S.R) isolated from electroplating sludge has high capacity to reduce Cr(VI), to Cr(III), Zn(II), Cu(II), Ni(II), ,Cd(II) and other metal ions were accumulated by the SR biomass. The heavy metals in sludge can be recovered with microbiological or chemical method and the effluent can be reused. This process has strong adaptation to the changes of waste water characters. Advantages of the use of SR are:

1. Reduces Cr (VI) quickly.
2. No reagents are used.
3. There is no secondary pollution.
4. Less sludge generated.
5. Complete recovery of Cr, Zn, Cu, Ni, Cd, Pb and Sn.
6. Reuse of purification waste water.
7. Treatment processes are easy to be constructed.
8. Low maintenance and low operation cost.

There are numerous reports documenting the capability of pure cultures of bacteria [77, 78], algae[79, 80]. and fungi [81-84] to remove heavy metal ions from waste water multispecies communities of bacteria removed silver equal 32% of the dry cell weight[66]. Metal removal using biological processes is becoming more widely accepted ,initial studies have shown that the sulphate-reducing bacterial bioreactor coupled with a membrane can remove up to 90% of the metal ions present in an aqueous solution [85].

d. Removal of heavy metals by Minerals

The adsorption by different silicate minerals of some heavy metals present in industrial waste water has been studied. Sepiolite (orera, spain) has an adsorption capacity of 8.26 mg g^{-1} for Cd^{2+} the metal adsorbed is in the order: $Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$ .This mineral shows the highest sorption capacity relative to the other minerals studied[86].

Kyanite a commercial mineral has been utilized as an adsorbent for the removal of heavy metals , such as Ni(II), Cu(II), Zn(II) and Cr(VI) from electroplating waste water .The adsorbed metal ions from electroplating waste water were recovered by batch as well as column operation using dilute hydrochloric solution [87].

The sorbent behaviour of (natural and exfoliated) vermiculite minerals was studied with respect to metal cations (Ni, Cu, and Cd) commonly present in waste water of the metal finishing industry .Column studies performed with this mineral show that a large volume of metal solutions with similar concentration to those usually present in waste water can be purified down to the legal limit of waste. These positive results validate the use of this mineral as a cost effective treatment to purify such waste water [88]. Chemically activated saw dust is found to possess greater adsorption efficiency for all metals than rice husk under identical experimental conditions [89].

e. New techniques

Reduction by semiconductor photo catalysis technology is relatively new technique for the removal or recovery of dissolved metal ions in waste water. The process couples low-energy ultraviolet light with semiconductor particles acting as catalyst and is based on the reduction by the photo generated electrons (90). Waste waters from industries like electroplating, dye, textile, metal and engineering etc. contain high concentration of heavy metals. The electroplating waste water has been used to assess the applicability of ecotechnological treatment-soil scape process. The applicability was tested through lab scale, pilot scale, and field scale studies. The removal efficiency was observed for COD about 80 %, for BOD 74 % and metallic contaminants 98% at large scale application [91]. The extraction of hexavalent chromium from aqueous solution by cocobetaine in a mixture of kerosene and benzene is investigated. The results indicate that in acidic solution the extraction efficiency of chromium (VI) is excellent. Experimental results show that dichromate ion ($Cr_2O_7^{2-}$) is the major extractable species of Cr (VI) at lower pH [92].

CONCLUSION

There has been an increasing ecological and global public health concern associated with environmental contamination by heavy metals but as exposure to them is unavoidable due their use in several industrial, agricultural, domestic and technological applications they present inescapable recovery and removal requirement. Heavy metal recovery techniques from waste streams generated from electroplating industry has gain importance and is equally significant as their detection in industrial effluents. The present paper has reviewed various removal techniques which are cost effective as material used for the purpose are easily available and their use in heavy metal removal has not been explored on large scale and in larger interest. These techniques have the future prospect of strong foundation of green chemistry revolution in India.

REFERENCES

[1] J.M. Bubb and J.N Lester; The impact of heavy metals on low land rivers and the implications for man and the environment. The science of total environment; 100, 207 – 233 (1991).

[2] V.S. Tare and S. Chaudhari; Heavy metal pollution: Origin, Impact, and Remedies in Encyclopedia of pollution and control. Edited by R.K. Trivedy, Enviromedia, Karad; 1, 386-411 (1995).

[3] H.Silman; Reclamation of materials from waste water emanating from metal finishing processes. J. Inst. Metal Finishing; 52, 163-168 (1984).

[4] S. Corinne, B. Pierre and N. Eric; Scheduling issues for environmentally responsible manufacturing: The case of hoist scheduling in an electroplating line. International Journal of Production Economics; 85, 137-146 (2004).

[5] A.K. Rai, S.N. Upadhyay, S. Kumar and Y.D Upadhyay; Heavy metal pollution and its control through a cheaper method: A review. J.IAEM; 25, 22-51(1998).

[6] N. Muthukumaran, N.Balasubrahmanian and T.V. Rama; Removal and recovery of lead and cadmium from plating wastes. Journal IAEM; 22, 136-141 (1995).

[7] APHA-AWWA-WPCF.1995.Standard Methods: For the examination of water and waste water. American Public Health Association and water pollution control federation 19th edition .
[8] H.M.Azab, H.M.Elshora and H.A. Mohammed; Biosorption of cyanide from industrial waste water. Bull Sci; 6, 311-332 (1995).
[9] A .S. Nafde, V.K. Kondawra and M.Z; Hasan. Precision and accuracy control in the determination of heavy metals in sediment and water by atomic absorption spectrophotometry. J.AEM; 25, 85-91 (1998).
[10] S. Bhalke, R.M. Tripathi, S. Mahapatra and V.N. Sastry; Up take of heavy metals by sun flower plant dry powder. Research for chemistry and environment; 3, 9-12 (1999).
[11] V.S. Tare and S. Chaudhari; Heavy metal pollution: Origin, Impact, and Remedies in Encyclopedia of pollution and control. Edited by R.K. Trivedy, Enviromedia, Karad; 1, 386-411 (1995).
[12] A.K. Rai, S.N. Upadhyay, S. Kumar and Y.D Upadhyay; Heavy metal pollution and its control through a cheaper method: A review. J.IAEM; 25, 22-51(1998).
[13] R.S. Lokhande and N. Kelkar; Studies on heavy metals in water of Vasai Greek, Maharastra. J.Environ.Protec, 20, 441-446 (2001).
[14] G.N. Manju and T .S. Anirudhan; Use of coconut fibre pith based pseudo activated carbon for chromium (VI) removal. Indian J.Environ.Health; 32, 289-291 (1990).
[15] N. Narayana and A. Krishnaiah ; A study on removal of chromium by adsorption on bituminous coal from synthetic effluents. Indian J.Environ.Health; 31, 304-306 (1989).
[16] P. Kamaraj, S. Jacob, N. Sathyamurthy and D. Srinivasan; Sulphide precipitation technique in the removal of heavy metals. Indian J.Environ.Health; 33, 208-212 (1991).
[17] R. Kanluen and S.I. Amer,; Treating Plating Waste water. Desalination; 163, 115-119 (2000).
[18] B.Wen, S.I. Ishikawa and K Suyama; Recovery and refining of gold by gold-cyanide ion biosorption using animal fibrous proteins. Application.Biochem Biotechnol; 70, 719-729 (1999).
[19] W.W. Eckenfelder; Industrial water pollution control. New York: Mc Graw Hill. (1989).
[20] Y.B Patil and K.M Paknikar; Removal and recovery of metal cyanide using a combination of biosorption and bio degeration processes. Biotechnology letters; 21, 913- 919 (1999).
[21] I. B .Rae and S.W. Gibb; Removal of metals from aqueous solutions using natural chitinous materials. Water Science Technology; 47, 189- 196 (2003).
[22] L. Lagadic, K. Molly, P. Mitchell and D. Bryan; Highly Effective Adsorption of heavy metal ions by a Thiol-Functionalized Magnesium Phyllosilicate Clay. Environ.Sci.Technol; 35, 984-990 (2001).
[23] B. Volesky; Biosorption and biosorbents. In: Biosorption of heavy metals. Boston, USA, CRC press; 3-5 (1990a).
[24] B. Volesky; Removal and recovery of heavy metals by biosorption.In: Biosorption of heavy metals. Boston, USA, CRC press; 7-43 (1990b).
[25] Y. Benito and M.L Ruiz; Reverse osmosis applied to metal finishing waste water. Desalination; 142, 229-234 (2002).
[26] G. Srisuwan and P. Thongchai; Removal of heavy metals from electroplating waste water by membrane. J.Sci.Technol; 24, 965-976 (2002).
[27] K.E. Bouhidel and M. Rumeau; Ion exchange membrane fouling by boric acid in the electrodialysis of nickel electroplating rinsing waters: generalization of our results. Desalination; 167, 301-310 (2004).
[28] T. Bolger and C. Szlag; Electrochemical treatment and reuse of nickel plating rinse waters. Environmental progress; 21, 203-208 (2002).
[29] P. Khanna and S.K. Malhotra; Kinetics and mechanism of phenol adsorption on fly ash. Indian J.Env.Hlth; 19, 224-237 (1977).
[30] D. Singh and N.S. Rawat; Sorption of Pb (II) on activated bituminous coal. Journal of the IPHE; 4, 15-22 (1993 a).
[31] D. Singh and N.S. Rawat; Adsorption of Cu (II) on treated and untreated bituminous coal dust. Journal of the IPHE; 2, 33-40 (1993 b).
[32] S.K. Srivastava, V.K .Gupta and D. Mohan; Removal of lead and chromium from activated slag a blast furnace waste. J.Envir.Engrg.ASCE; 123, 461-468 (1997 b).
[33] K. Joseph and V.Rajenthiran; Activated carbon from acidic sludge of a petrochemical industry. Indian J.Env.Hlth; 37, 172-178 (1995).
[34] N. Muthukumaran, N.Balasubrahmanian and T.V. Rama; Removal and recovery of lead and cadmium from plating wastes. Journal IAEM; 22, 136-141 (1995).
[35] A. Mohammad, R .Yousuf and A Ahmed; Adsorption behaviour of cadmium, zinc, nickel and lead from aqueous solutions by mangifera indica seed shell. Indian J. Environ. Health; 40, 15-26 (1998).
[36] S.Chand, V. K. Agrawal and P. Kumar; Removal of hexavalent chromium from waste water by adsorption. Indian J.Environ.Health; 36, 151-158 (1994).

[37] D.K. Singh, D.P. Tiwari and D.N. Saksena; Removal of lead from aqueous solutions by chemically treated used tea leaves. Indian J.Env.Hlth; 35, 169-177 (1993).
[38] P. Kumar and S.S. Dara; Modified barks for scavenging toxic heavy metal ions. Indian. J.Env.Hlth; 22, 196-202 (1980).
[39] S.P.S. Jadon; Removal of heavy toxic metals from electroplating waste and contaminated water by the use of usar soil as absorbent. Poll Res; 24, 209-212 (2005).
[40] S Hawash, J.Y. Farah and M.S. Geundi; Investigation of nickel ion removal by means of activated clay. Adsorp.Sci.Technol; 7, 114-117 (1993).
[41] Y. Tang, F.Chen and H. Zhang; Adsorption of lead, copper and zinc ions on to waste fluidized catalytic cracking (FCC) catalyst. Adsorp.Sci.Technol; 16, 24-26 (1998).
[42] M .Rao and A.G Bhole; Chromium removal by adsorption using fly ash and bagasse. Journal of Indian Water Works Association; 33, 97-100 (2001).
[43] P. Kumar and S.S. Dara; Modified barks for scavenging toxic heavy metal ions. Indian. J.Env.Hlth; 22, 196-202 (1980).
[44] S. Dahiya, D.G. Mishra, R. Karpe, A.G. Hedge and R. Gurg; Removal of lead and copper from aqueous solution using chemically activated sugarcane baggasse carbon. Proceeding of XII National symposium on environment; 400-406 (2003).
[45] A. Sharma and G. Bhattacharya; Removal of hexavalent chromium from waste water using a low cost adsorbent made of neem leaves. Proceeding of XII National symposium on environment; 477-484 (2003).
[46] N. Verma and R. Rehal; Removal of chromium by albizia lebbeck pods from industrial waste water. J.Ind Polln Contl; 12, 55-59 (1996).
[47] A.Y. Talokar and N.W. Ingole; Studies on removal of chromium from waste water by adsorption using low cost adsorbents. RAWM; 23, 297-303 (2001).
[48] P.P. Rampure and P.V. Patil; Use of modified dhaoda bark for scavenging cadmium ions from industrial waste water. J. Ind. Polln Contl; 12, 35-39 (1996).
[49] S Babel; Removal of heavy metals from aqueous solution/sludge using agriculture waste materials. Waste management and research; 23, 260-269 (2005).
[50] S. Babel and T. Kurniawan; Chromium (VI) removal from synthetic waste water using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and chitosan. Chemosphere; 951-967 (2004).
[51] R .K. Trivadi and G.A. Joag; Treatment of industrial waste water by water hyacinth application. J. Pollution management in industries; 10, 295-313 (2000).
[52] P.R. Rampure and P.V. Patil; Use of palsa bark substrate for the recovery of copper, lead, zinc and nickel from waste waters. Cheml Environ Res; 4, 105-109 (1995).
[53] H .Katasumata , S. Kaneco, K. Inomata, K. Itoh, K. Funasaka, K. Masuyama and K. Suzuki; Removal of heavy metals in rinsing waste water from plating factory by adsorption with economical viable materials. J. Environ. Management; 69, 187-191 (2003).
[54] S.R .Shukla and R.S. Pai; Adsorption of Cu (II), Ni (II) and Zn (II) on modified jute fibres. Biosource Technology; 96, 1430-1438. (2005).
[55] S.A. Nigro, W.A. Stirk and J. Van; Optimizing heavy metal adsorbance by dried sea weeds. South African journal of botany; 68, 333-341 (2002).
[56] A. Kapoor and T Viraraghavan; Fungal biosorption-an alternative treatment option for heavy metal bearing waste water: a review. Biosource Technology; 53, 195-206 (1995).
[57] M. Tsezos and B. Volesky; Biosorption of uranium and thorium. Biotechnology and Bioengineering; 24, 385-401(1981).
[58] C.C Townsley, I.S. Ross and A .S. Atkins; Biorecovery of metallic residues from various industrial effluents using filamentous fungi. Process Metallurgy; 4, 279-289 (1986).
[59] L. Rome and G.M Gadd; Copper adsorption by Rhizopus arrhizus Cladospoium resinae and Penicillium italicum. Applied Microbiology and Biotechnology; 26, 84-90 (1987).
[60] L.E. Macaskie; An immobilized cell bioprocess for removal of heavy metals from aqueous flows. Journal of chemical Technology and Biotechnology; 49, 330-334 (1990).
[61] Z. Asku, T. Kutsal, S.Gun, N. Haciosmanoglu and M.Gholminejad; Investigation of bisorption of Cu(II), Ni(II), and Cr(VI) ions to activated sludge bacteria. Environmental Technology; 12, 915-921 (1991).
[62] F.Veglio and F.Beolchini; Removal of metals by biosorptiona review. Hydrometallurgy; 44, 301-316 (1997).
[63] Y.B Patil and K.M Paknikar; Removal and recovery of metal cyanide using a combination of biosorption and bio degeration processes. Biotechnology letters; 21, 913- 919 (1999).

[64] R.Ofer, A.Yerachmiel and Y. Shmuel; Marine Macroalgae as biosorbents for cadmium and nickel in water. Water Environment Research; 75, 246-253 (2003).
[65] R. K. Gill, V. Jindal, S.S. Gill and S.S Marwaha; Studies on the biosorption of nickel from industrial effluent. Polln Res; 15, 303-306 (1996).
[66] S.E. Shumate and G.W. Strandberg; Accumulation of metals by microbial cells, in comprehensive biotechnology. Ed. By Moo-Young M, perganon press, New York; 20:153-156 (1985).
[67] M.Y. Andres and C.J. Hubert; Bacterial biosorption and retention of thorium and uranyl cations by mycobacterium smegmatis. Journal of radio analyses nuclear letter; 166, 431-440 (1992).
[68] E. Fourest and C.J Roux; Heavy metal biosorption by fungal mycilial by-products: mechanisms and influence of pH. Applied Microbiology and Biotechnology; 37, 399- 403 (1992).
[69] H .Hussein, S. Farag and H. Moawad; Isolation and characterization of Pseudomonas resistant to heavy metals contaminants. Arab journal of biotechnology; 7, 13-22 (2003).
[70] M. J. Brown and J.N. Lester; Role of bacterial extracellular polymers in metal uptake in pure bacterial culture and activated sludge. Water Research; 16, 1539- 1548 (1982).
[71] M. Ajmal, A.K. Rafaqat and A.S. Bilquees; Studies on removal and recovery of chromium (VI) from electroplating waste. Water Research; 30, 1478-1482 (1996).
[72] S.E. Shumate and G.W. Strandberg; Accumulation of metals by microbial cells, in comprehensive biotechnology. Ed. By Moo-Young M, perganon press, New York; 20:153-156 (1985).
[73] H. Eccles; Biosorption of heavy metals: a scientist's dream or a commercial reality. Journal of Chemical Technology and biotechnology; 49, 330-334 (1990).
[74] L.E. Macaskie; An immobilized cell bioprocess for removal of heavy metals from aqueous flows. Journal of chemical Technology and Biotechnology; 49, 330-334
[75] M.Tsezos and A.A. Deutschmann; The use of mathematical model for the study of important parameters in immobilized biomass biosorption. Journal of chemical Technology and biotechnology; 53, 1-12 (1992).
[76] T. Pumpel, L. E .Mackaskie, J .A. Finlay and L. Diels; Nickel removal from nickel plating waste water using a biologically active moving - bed sand filter.Bio metals; 16, 567-581 (2003).
[77] A.B. Norberg and H.Persson. Accumulation of heavy metal ions by zoogloea vamigeva. Biotechno Bioeng, 26, 239-246 (1984).
[78] P. Yong and L. E Macaskie. Removal of lanthanum, uranium and thorium from the citrate complexes by immobilized cells of curobacter sps. in a flow through reactor: Implications for the decontamination of solutions containing plutonium. Biotechnol Lett; 19, 251-255 (1997).
[79] D. Kratochvil, E. Fourest and B. Volesky; Biosorption of copper by sargassion fluitans biomass in fixed BOD column; Biotechnol Lett, 17, 777-782 (1995).
[80] A. Leush, Z.R. Holun and B.Volesky; Biosorption of heavy metal (Cd, Cu, Ni, Pb, Zn) by chemically-reinforced biomasses marine algae. J.Chem technol.Biotechnol; 62, 279-288 (1995).
[81] N.M.D. Akthar, S.K. Sastry and M.P. Mohan.; Biosorption of silver ions by processed aspergillus niger biomass. Bitechnol Lett; 17, 551-556 (1993).
[82] G .I. Kararaiko, A.S. Kareva, Z.A. Avakian, V.I. Zakharova and A.A. Korenevsky; Biosorption of scandium and yttrium from solutions. Biotechnol Lett; 18, 1291-1296 (1996).
[83] Y. Sag and T. Kutsal; The selective biosorption of chromium (VI) and copper (II) ions from binary metal mixtures by R.Arrhizus, Process. Biochemistry; 31, 561- 572 (1996).
[84] J.H. Suh, D.S. Kim, J.W. Yun and S.K. Song; Process of lead ions accumulation in saccharomyces cervisiae. Biotechnol Lett; 20, 153-156 (1998).
[85] J .E. Burgess, C. Mack and J.R. Duncan; Membrane bioreactors for metal recovery from waste water: A Review. Water SA; 30, 521-526 (2004).
[86] A.G. Sanchez, E.A. Ayuso and O.J.D. Blas; Sorption of heavy metals from industrial waste water by low cost mineral silicates. Clay minerals; 34, 469-469 (1999).
[87] M. Ajmal, R.A. Rao, R. Ahmed, J. Ahmed and L.A. Rao; Removal and recovery of heavy metals from electroplating waste water by using kyanite as an adsorbent. J.Hazard Matter; 87, 127-137 (2001).
[88] E. Alvarez and A. Garcia; Removal of heavy metals from waste water by natural and sodium exchanged bentonites. Clay and clay minerals; 51, 475-480 (2003).
[89] R. Savavanane, T .Sundara and S. Sivamurthy; Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from waste water. Indian J.Environ.Health; 44, 78-87 (2002).
[90] D. Chen and K. Ray; Removal of toxic metal ions from waste water by semiconductor photo catalysis. Chemical Engineering Science; 56, 1561-1570 (2001).
[91] S. Joshi; Ecotechnological Treatment for the Industrial Waste water Containing Heavy Metals. J.IAEM; 27, 98-102 (2000).
[92] D. K. Singh, R.K. Bharadwaj, B. Srivastava and A .Sahu; Extraction of Hexavalent

Chromium from Aqueous Solution by Emulsion Liquid Membrane. Journal of Scientific and industrial research; 61, 538-422 (2002).

[93] S.Verghese, P and M.singh; Physico-Chemical characteristic and heavy metal concentration in waste water from gold-silver plating sites of Agra city, A case study Indian j. Environ. Prot; 26, 1112—1117(2006).

[94] M. Singh and S. Verghese. P; Physico-chemical investigation of waste water from electroplating industry at Agra and Technologies for metal removal and recovery of water". Proc. of 22nd national conference of Engineers and Seminar on rain water harvesting and waste management, Nagpur; 397-401(2007).

[95] M. Singh, S.Saxena and A.P.Singh; Analysis of Copper from Electroplating Industry Waste Water and Its Reuse as Fungicide, International Journal of Scientific Engineering and Technology; 3, 43-46(2014).

[96] M. Singh, N. Mantha and S. Verghese. P; Techniques for Recovery and Reuse of Heavy Metals From Industry Effluents, Global Journal for Research Analysis; 5 ,2277-8160(2016).