International Research Journal of Environment Sciences E-ISSN 2319–1414
Vol. **5(10),** 61-66, October **(2016)** *Int. Res. J. Environment Sci.*

Review Paper

A Review on Methods available for Removal of Cadmium: with Special Reference to Electroplating Industrial Waste Water

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Available online at: www.isca.in, www.isca.me
Received 24th Feburary 2016, revised 25th August 2016, accepted 15th September 2016

Abstract

Electroplating industrial waste contains considerable concentration of some potentially toxic heavy metal wastes. These wastes have toxic effect on environmental flora and fauna. One of the potentially toxic content is the cadmium present in toxic waste. This paper aims to compile the toxic effects of electroplating processing waste and available methods for the removal of cadmium. This paper reviews about the different removal methods available for cadmium and the research studies associated with the topic. The studies of toxic effect of cadmium on different environmental segments are also described.

Keywords: Electroplating Industry, Toxic metals, Removal methods, Adsorption, Cadmium, Biosorption.

Introduction

The development and growth of metal manufacturing industries is highly influenced by electroplating and metal finishing industries. After World War II the electroplating operations became an integral and essential part of engineering industries. The electroplating industries have economic and environmental advantages over other industries, as these industries uses less water and produce lesser volume of wastes. Nevertheless the toxicity of waste water is always a cause of concern due to the presence of some toxic metals and cyanides. The tolerable limits of such metals and other constituents in water and land environment are in general considerably lower than that of organic type of pollution. Although the methods of removal of these toxic constituents from waste waters are well established now, the problem of pollution of water courses, and particularly of disposal of untreated electroplating waste waters into municipal sewers, in many countries of South East Asia is yet to be solved.

The accumulation of toxic metals in the municipal sewage from electroplating waste causes problem and make these waste unfit for further solid waste utilization. A sewage treatment report from Chandigarh, India reveals that if different metal finishing industries from Chandigarh, Ludhiana and Punjab areas would dispose toxic metals in their waste water to municipal sewers, the sludge from treatment plant will contain considerable amount of toxic metals and will be totally unfit to use as manure on agricultural land[1]. It would appear, therefore, that the problem of treatment and disposal of waste waters from a large number of small-scale electroplating industries in South East Asian countries is unique in nature and is different from that of large engineering industries using electroplating as an integral part of their production processes. Nevertheless, the information which has been compiled on the methods and costs of pollution control in electroplating industries and which is incorporated in this report may assist the industries and the concerned regulatory agencies in the affected regions in organizing appropriate pollution control programs for this important industry. The types of plating generally employed in an electroplating industry are chromium, cadmium, zinc, silver, gold etc. The plating operations are carried out in liquid state and then metal surfaces are cleaned to remove greases rust and scales present.

Cleaning: Greases are generally present on metals due to stamping, polishing etc. activities, which can be of two type organic and inorganic greases and can be removed by saponification or emulsification.

Stripping: Stripping as a substitute of pickling, removal of rust and scale using concentrated acid solutions is used due to its rapid action. Stripping includes two steps. In the first step the material to be plated is made anode and then in second step metal surface cleaning is done by using hydrofluoric acid.

Plating: Plating also includes some toxic metals and acids to the waste water. The plating metal generally made anode and is generally done in acidic solution. The concentration of chemicals normally used in some of the common plating baths is shown below[2].

Rinsing: After plating has been done, the plated objects are rinsed with water. They are first dipped in stationary water baths, which are allowed to drain and then dipped in running water baths to remove the adhering plating solution. Bath and rinse concentration are shown Table-1.

Metal wastes from Plating Baths: They include rinse waters from copper, zinc, nickel, cadmium and lead vats. All these metals seldom occur together because the baths are never used all at a time and the operations are staggered to meet the demand. However, a combination of these baths is practiced occasionally resulting in the appearance of several of these metals at a time in the mixed rinses. The metals are present in soluble ionic form and most of them are extremely toxic Table-2 is showing general characteristics of waste water from plating baths like waste flow, basicity, cyanides, COD, solids etc.

Potential Environmental Problems from Electroplating Process

The different activities of electroplating industries generates waste waters which are low in volume and contains highly toxic materials like Cyanides, Cadmium, Chromium etc. The electroplating effluents have different environmental effects like: i. Toxicity to aquatic flora and fauna, ii. Sewage toxicity, iii. Effects on biological sewage treatment processes, iv. Pollution on ground water and surface waters.

Toxicity to fish and other aquatic life: The aquatic flora and fauna get affected by the presence of acids, alkalies and toxic substances in waste waters. The extent of toxicity is decided by the size, age and species of the aquatic life and also by the general physiochemical characteristics of receiving water. The type and quantity of aquatic flora and fauna in water reservoir, the possibility of pollution extent from other polluting source of that area, presence of other toxic compound in water also decides the toxicity effect on aquatic life.

Effects on sewers: In electroplating industries, presence of acids makes the waste water acidic. They attack metal and concrete structures, especially the concrete sewers, in which the waste waters are discharged. Further, the acids hydrolyze the soaps present in sewage, liberating fatty acids, which may form floating scum, because the floating objects to stick together and clog the sewers. Alkaline wastes are also corrosive but they are not as aggressive as acid wastes to most of the construction materials.

Effects on sewage treatment: Electroplating wastes have a deleterious effect on biological sewage treatment processes due to the presence of acids, alkalis and toxic metallic ions such as Cr (VI), Cu (II), Zn (II), etc. These compounds inhibit or kill the micro-organisms that take part in the purification of sewage. Although presence of small concentrations of the heavy metals in sewage may not affect its biological purification, most of these metals are precipitated during the process and get accumulated in sludge, rendering it unfit for use as manure. Although cyanides exert direct toxicity to fish and other higher forms of life, they can be oxidized by acclimatized bacterial flora in a sewage treatment plant.

Therefore, the presence of cyanides in sewage within certain limits may not inhibit the sewage purification process once the system is acclimatized to cyanides. It has been found that hexavalent chromium and nickel ions even at small concentrations (1 to 10 mg/l) affect nitrification and the general performance of the sewage treatment plant. Sodium and potassium cyanides also inhibit nitrification initially but have no effect after a few days. Carbon oxidation is also affected by sudden discharges of cyanide but is not affected if the sludge is acclimatized. Higher concentrations of copper, iron, nickel and cyanide affect gas production in anaerobic sludge digestion. Cyanides could be tolerated much easier than the metals after a period of acclimatization. Toxicity of plating wastes constituents to fish and fish food is shown in Table-3.

Pollution of ground and surface waters: Discharge of untreated electroplating waste waters on land may pose a problem of ground-water contamination with toxic metals and may render it unfit for drinking purposes. While some of the metallic ions may be retained in the soil during the passage of the waste water through the soil and as a result the ultimate quantum of the toxic metals reaching the sub-soil water table may be much lower than those present in the raw waste water, the concentration of the toxic metals in a surface water receiving the waste waters would be dependent solely on the dilution available in the surface water. The U.S. Public Health Service Drinking Water Standard (USPHS 1962) states that the presence of the hexavalent chromium in excess of 0.05 mg/l shall constitute grounds for rejection of the supply. However, nickel is considered to be relatively non-toxic to man and a limit for nickel is not included in the U.S. EPA National Interim Primary Drinking Water Regulations, 40 FR 59566, December 24,1975[3].

Waste Treatment

Generally electroplating wastes are low pH and rich in toxic metals. Removal of these toxic metals requires coagulation, flocculation and sedimentation etc[4].

The toxic metals which are present in electroplating waste water cannot be removed easily. The recovery can be done by converting these toxic metals to their hydroxides then precipitating and removing them as sludge. But there will always be sludge fixation problem. Another treatment technique which is available is ion exchange technique in which both recoveries of toxic metals as well as reuse of waste water is possible. Alternatively electrolytic decomposition, single and multistage evaporation can also be applied but these methods requires high initial and operating cost and time. Technically it is possible to have zero waste discharge from these industries but due to high cost these techniques are not feasible and cause unknown hazards to environment.

Table-1
Bath and Rinse Concentration for different Bath Formulae

Bath formulae	Bath concentration	Rinse concentration
Cadmium Cadmium cyanide,25g/1 Sodium cyanide, 30g/1	Cd - 19000 mg/l CN - 22000 mg/l pH 9.2	Cd - 1.2 mg/l pH - 8.3
Copper (cyanide) Cuprous cyanide, 22.5 g/l Sodium cyanide, 30 g/l Sodium carbonate, 10 g/1	CN - 20 5000 mg/l Cu - 10 4000 mg/l pH - 10.9	CN - 8.6 mg/l Cu - 1.34 mg/l pH - 8.2
Copper (acid) Copper sulphate, Copper sulphate,120 g/l Sulphuric acid 80 g/1	Cu - 49 000 mg/l pH - 0.2	Cu - 2.3 mg/l pH - 6.3
Chromium Chromic acid, 300 g/1 Sulphuric acid, 3 g/l	Cr - 140 000 mg/l pH - 1.2	Cr - 30 mg/l pH - 7.3
Nickel Nickel sulplate 210 g/l Nickel chloride 60 g/l Nickel citrate, 30 g/l	Ni - 93 000 mg/l pH - 5.5	Ni - 6.3 mg/l pH 7.8 Ni - 6.3 mg/l
Silver Silver cyanide, 25 g/l Sodium cyanide, 25 g/1	Ag - 24 600 mg/l CN - 21 800 mg/l	Ag - 51 mg/l CN - 45 mg/l
Zinc Zinc cyanide, 50 g/l Sodium cyanide 60 g/l Sodium hydroxide	Zn - 38 000 mg/l CN - 59 000 mg/l pH- 11	Zn - 6.2 mg/l CN - 7.0 mg/l pH - 9.4 mg/l

Various Methods used for Cadmium Removal

Several methods are reported for the removal of cadmium present in industrial waste water. A. Adsorption method B. Biological Method C. Electro coagulation and Electro dialysis D. Floatation process etc.

Adsorption Method: Different adsorption studies were reported for the removal of cadmium in waste water. The study on cadmium removal by using fly ash was carried out by Visa and Duta[5]. They studied the kinetics and thermodynamics of the process; they studied the proper contact time of adsorbent and adsorbate, wastewater volume, adsorbent mass ratio and ions concentration etc. Boparai et.al has studied the adsorption of cadmium ions on the nano zerovalent iron particles and concluded that removal is effective in the concentration range of 25-480 mg/l of cadmium and is sensitive towards temperature of medium[6]. Ulmanu et.al have used different low cost waste materials and found that bentonite a type of soil removes cadmium with 99 % efficiency with no copper interference[7]. The removal of cadmium is also reported by using barley hull and barley hull ash and reported that removal efficiency increases with increasing pH with maximum removal of 95.8% and 99.2 % using barley hull and barey hull ash respectively and results best fitted with Langmuir isotherm[8].

Biological Methods: Some biological methods are also reported for the removal of cadmium. In these methods different types of bacteria are used in which cadmium was precipitated on the cell surface of bacteria this necessitates the development of more environmentally relevant organism.

Electro coagulation and Electro dialysis: The electro coagulation is also very effective method for the removal of cadmium. The use of cadmium electrode for electro coagulation process of cadmium is reported where removal tank was filled with different synthetic cadmium concentration water at different pH range of 3, 7, and 10 and electrode potential of 20, 30, and 40 volts, their study reveals that removal efficiency is dependent on initial cadmium concentration, electrode potential and reaction time.

Floatation: Floatation is also reported for the removal of cadmium from waste water. Using adsorbing particle floatation for removal of cadmium is reported on bentonite and catholic surfactant where removal efficiency increases with addition of polyacryl amide and it is also possible to remove different metals separately by selecting the proper operating conditions.

Table-2
General characteristics of waste water from plating baths

Waste	Flow	pH	Basicity	Cyanides	COD	Perman Other items Ether	Total solids	Suspended solids	Ether extra tables	Other items
Cleaning solution (rinse waters)	450-680	7.8-8.4	300-650	0	290-350	14-22	960-1120	610-720	73-120	Fe:2.3-3.1
Cy**n**ide concentrates (rinse waters)	-do-	9.2-9.9	800-1700	0.3-21.2	25-42	4-7	430-600	23-35	15-21	Cu:2.8-9.7 Ca:0.3-0.8 Zn:1.8-2.4
Acid pickling rinse waters	900	4.5-5.5	28-43	-	-	-	450-590	76-141	-	Fe:80-110
Spent alkali rinse waters	2700-2650	8.8-9.8	180-410	-	300-550	24-44	800-1350	-	520-910	Cr (VI)3-3
Chromate rinse waters	1360-2270	5.5-6.8	31-562	-	-	-	460-750	-	-	Pb:0.1-0.7
Copper (cynide) rinse waters	450-680	-	10-340	7.3-11.6	-	-	-	-	-	Cu:1.1-1.4
Copper (acid) rinse waters	-do-	6.1	97-110	-	-	-	-	-	-	Cu:1.8-3.1
Nickel rinse waters	-do-	7.4-8.3	187-299	-	-	-	-	-	-	Ni:48-8.7
Cadmium rinse waters	-do-	8.0-8.8	191-320	3.2-4.6	-	-	-	-	-	Cd:1.8-3.1
Zinc rinse waters	-do-	8.9-9.8	210-405	5.4-9.0	-	-	-	-	-	Zn:5.4-7.3
Floor wash waters	-do-	7.6-8.0	170-230	0.1-0.3	-	-	350-480	65-79	25-27	Cu:0.05-01 Zn:0.3-0.5 Cd:0.1-0.2 Ni:0.1

Table-3
Toxicity of Plating Wastes Constituents to Fish and Fish Food

Substance	Concentration mg/l	Test Organism	Effect
Chromic acid	0.3 (as Cr)	Daphnia magna*	Toxic
Hydrochloric acid	60 (as HC1)	Daphnia magna*	Toxic
Nitric acid	107 (as HNO,)	Daphnia magna*	Toxic
Sulphuric acid	83 (as H,SO,)	Daphnia magna	Toxic
Strong acids	To pH 5.0	Fish	Toxic
Cadmium chloride	0.01 (as Cd)	Goldfish	Kills in 8-18 hrs.
Cadmium sulphate	5 13 (as Cd)	Minnows	Kills in 3 hrs.
Copper sulphate	0.04 (as Cu)	Daphnia magna*	Toxic
Copper sulphate	0.8 (as Cu)	Goldfish	Kills in 24 hrs.
Sodium chromate	0.1 (as Cr)	Daphnia magna*	Toxic
Potassium dichromate	36 (as Cr)	Goldfish	No effect in 108 hrs.
Potassium dichromate	180 (as Cr)	Goldfish	Kills in 3 days
Chromate (ion)	20 (as Cr)	Trout and minnows	Kills in 8 days
Chromate (ion)	50 (as Cr)	Sunfish, bluegills	Not toxic in a month
Chromate (ion)	0.01 (as Cr)	Micro-flora	Toxic
Ferric chloride	24 (as Fe)	Goldfish	Kills in 1-15 hrs.
Ferrous sulphate	37 (as Fe)	Goldfish	No effect in 100 hrs.
Ferrous sulphate	368 (as Fe)	Goldfish	Kills in 2-10 hrs.

Adsorption Method for Cadmium Removal

From all methods reported for removal of cadmium this paper reviews the adsorption methods. Adsorption is basically a physio-chemical phenomenon through which and gaseous or liquid solutions can be separated. This method is feasible due to its low cost of operation. Various non-conventional adsorbents, like saw dust, baggase pith, rice husk ash, activated coconut shell powder controlled burnt wood charcoal , flyash, peat, wood , jute fibers , have been tried for cadmium removal by many researchers. In this review, the research on adsorption of cadmium on various low cost adsorbent by various researchers is summarized with their findings.

Adsorbents for Cadmium Removal

Various adsorbents are reported for the removal of cadmium which are cost effective. The different adsorbents reported are sugarcane bagasse, bagasse flyash, peanut shells activated carbon, rice husk, rice husk activated carbon, waste wood activated carbon, barley hull, barley hull ash, coconut shell activated carbon, cashew nut shell activated carbon, carboxylated chitosan, tamarind seeds activated carbon, nano zerovalent iron particles and calcite. A comparative of different adsorbents reported for the removal of cadmium is shown in Table-4.

Conclusion

Cadmium toxicity from electroplating industrial waste water is one of the major threats to environment. Many anthropogenic activities also include cadmium to the environment on continuous basis. The wastes from electroplating industries contain many toxic substances and are very dangerous to environmental flora and fauna. The uses of different biological materials for the effective removal of cadmium from waste water are reported. These bio adsorbents remove cadmium (85 % to 99 %) from toxic waste following the Langmuir and freundlich adsorption isotherm. Due to high cost of chemical removal methods available the future aspect is in using some bioadsorbents for the removal of cadmium.

Table-4
Removal Percentage of Different Material Used

S.no.	Material	Adsorbent dose	Initial concentration	Time containing	pH	Isotherm	% of removal
1	Bagasse Flyash[10]	10g/l	-	90min	6	-	90%
		20g/l	-	60min	-	-	85%
2	Rice Husk[11]		20mg/l	180min	6		97.2%
3	Peanut shell[13]			40min	8	Langmuir isotherm	40.10mg/g
4	Barley Hull and Barley Hull ash[8]		30mg/l	180min	9	Freundlich adsorption	95.8%
5	Coconut shell[14]	0.5g		30min	6	Langmuir and freundlich isotherm	3.34mg/g
6	Cashew nut shell[15]					Langmuir isotherm	98.87%
7	Nanozerovalent iron particles[6]	25-480 mg/l				Ferundlich and Temkin isotherm	
8	Compost, Cellulose Pulp Waste[7]						99%
9	Nettle ash[19]				6	Langmuir isotherm	142.8mg/g

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