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Techniques for Recovery and Reuse of Heavy Metals From Industry Effluents

Dr.Monika Singh Associate professor, Mangalayatan University, Aligarh, U.P .India

Dr. Nagaraj Mantha Professor, Mangalayatan Univesity, Aligarh, U.P. India

Dr. Susan Verghese.P Associate Professor, School Of Chemical Sciences, St. John's College, Agra, U.P.India

ABSTRACT *Water is one of the most precious needs for life on earth. Scarcity of water can be handled if proper planning is set for wastewater treatment before its discharge in to aquatic resources as well as its reuse. The present paper deals with the heavy metals generated in the waste stream of electroplating industry and draws attention towards different available cost effective natural and newer techniques for the removal of these metals from the stream. Analysis and reuse of heavy metal iron and manganese as pesticide formula has also been detailed. Iron metal concentration was recorded highest(16.70 mg/l) in site 2 of electroplating industry during winter season and Mangnese concentration was highest up to 56.80 mg/l in site 4 of electroplating unit during winterseason. These metals when synthesized as carbamate pesticide effectively cured fungal disease of rose, brinjal and okra plants.*

KEYWORDS : waste water, removal of heavy metal, reuse of heavy metal, pesticide

Introduction

The increase in population has resulted in unplanned habitations giving rise to cuttings of forests, waste water discharge without any treatment in to the rivers/streams, downgrading the quality of natural waters causing water pollution. Similarly the growth of industries, planned/unplanned with industrial discharge of toxic /non toxic chemicals/ metals has also added to pollution of natural waters.

Out of all waste water discharges effluents from industries such as electroplating, oils, paints, textiles etc pose a threat as these waste water is usually dumped in to natural water resources like rivers, lakes, ponds etc and makes the same unfit for human, animal, plant consumption as well as for industrial use [1].

The metal finishing industry is classified under the Federal Registry 40 CFR as a categorical industry and falls under the direct jurisdiction of the USEPA or the State regulatory agency, if the state has primacy with the USEPA and on down to the local Publicly Owned Treatment Works (POTW) if the system discharges directly into the sewer system. A typical SIC code for this type operation will be 3471, which deals with the metal finishing in the automotive industry. This includes all industries that perform various types of plating, anodizing, coloring, forming, and finishing of metals. The metal finishing industry functions and processes are often directly related to other industries. The relationship of the metal finishing industry is often an integral part of larger production items such as automobiles, electrical components, major appliances and aircraft [2].

In a typical electroplating process, the pieces to be plated are carried on conveyor or racks, which are then dipped in to various solutions. After the desired amount of plating has occurred these are dipped in to a series of rinse tanks. The water in these tanks flows counter current to the progress of the plated pieces, hence the rinse water in each of the successive rinse tank is cleaner. The water that is in the first rinse tank is the most contaminated. For chrome plating up to 90% of the chrome plating metals originally in the plating solution may end up to in the rinse water in this tank. This is the water that forms a good share of the effluent [3,4,5]. Highly acidic waste water which is used in the process contains inorganic solution of various acids, used mainly are hydrochloric acid, nitric acid and hydrogen fluoride etc. which are highly toxic and dangerous to aquatic life, if not treated efficiently. This acid discharged into the streams without neutralization decreases the pH of stream water and results in mass mortality of aquatic culture [6].

Water in electroplating industry is used to clean, strip, pickle and rinse the metal before and after the plating process. Rinse water makes up majority of the waste water flow and usually provides a continuous stream of waste water. Another major concern is the intermittent batch dumping of spent acids and cleaning solutions. Batch discharges causes shock loads on the system when come from concentrated baths and require pretreatment to discharge. 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 metals which are termed as heavy metals [6, 7, 8]. These metals have extremely detrimental effect on the human body and aquatic life. They become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults. Ingestion is the most common route of exposure in children [7, 8].

Water Re-use and Recovery Practices

The largest amount of water used in the metal finishing process is from the use of rinse waters. Several new techniques have proven successful in reducing the amount of fresh makeup water required to complete the rinsing process. The use of new cleaners and counter-flow rinsing can reduce the need for stagnant rinse. It has been reported that a reduction of up to 90% can be achieved. Recovery processes are also available for cleaners, heavy metals, acids and alkaline products. These processes are extremely expensive and the capital outlay can only be recovered in very large processes [9,10].

Wastewater Treatment

The most prevalent pollution control problem in the metal finishing industry is dissolved heavy metals in the waste stream. The neutralization process causes the heavy metals such as iron, zinc, copper, cadmium, and chromium to precipitate and settle out. The first step in this process is adjustment of the pH of the waste stream. Insoluble metal hydroxides are formed by the reaction of the basic chemical with the metal at a pH range of 6.0 - 9.0. The heavy metals can successfully be removed using the neutralization and destabilization processes. Ninety-nine percent removals is easily obtained and the processes are not easily upset, making it one of the most effective methods in reducing heavy metal concentrations to meet pretreatment ordinances. Silver, nickel and copper plating wastes contain cyanide in the form of silver cyanide, nickel cyanide and copper cyanide.

Cyanide limits the removal of metals by precipitation. Hence, cyanide has to be removed first by alkaline chlorination by additions of sodium hypo-chlorite. Thereafter, these metals are removed/reduced by precipitation[11]. Removal of pollutants especially from waste water, through the commercial activated carbon is costly[12] . Hence there is a need to develop novel and cheaper adsorbents.

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.[13-24].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[25].

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[26].

Metal	Wave length λ (nm)	Slit (nm)	Characteristic concentration (mg/l)	Fuel/ Oxidant	Flame
Fe	248.3	0.2	0.11	2:4	Air/Acetylene
Mn	279.5	0.2	0.052	2:4	Air/Acetylene

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[27].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[28].

Heavy metals from waste water can be recycled by precipitating metals (Cu, Fe, Mn, Ni, Pb and Zn) present in electroplating waste water with sodium diethyldithio carbamate and thus in the process forming respective metal diethyldithiocarbamte which works as fungicide in controlling diseases of vegetables and ornamentals[29-30]

Experimental

Collection of samples:

Grab samples of waste water from electroplating sites before their mixing in to the drainage system were collected from the five sites in plastic bottles of 1 litre capacity for specific parameters.

Labelling of samples:

Sample from each site was labelled with

1. Site name
2. Date of collection
3. Time
4. Sample No:

Colour and odour are noted at the time of collection. Conductivity and pH within 2 hours from collection upon lab arrival.

Preliminary digestion of metals

5 ml concentrated nitric acid was added to a beaker containing 50-100 ml sample and evaporated on a hot plate and the volume was reduced to about 50-20 ml . Heating and adding concentrated nitric acid continued until a clear light coloured solution was obtained. Filtrate was cooled, diluted to 100ml and mixed thoroughly .This was used for metal determination.

Analysis of heavy metals

The metal analysis was performed on an Atomic Absorption Spectrometer (Perkin-Elmer A. Analyst 100), following the condition of operation for the instrument. The standard solution of each metal iron(Fe) and manganese(Mn)was prepared using analytical grade reagents for calibration purpose. Samples were filtered and digested with nitric acid.

The wave length, slit, characteristic concentration, fuel/oxidant ratio and flame for particular metals are given below:

Synthesis of Iron and Manganese diethyldithiocarbamate in laboratory:

Reagents:

1) Metal (Fe & Mn) carbonate.
2) Sodium diethyldithiocarbamate.
3) Double distilled water.

Procedure:

i) 0.1 N metal carbonate solution is prepared.
ii) 0.1 N sodium diethyldithiocarbamate is prepared.
iii) Metal carbonate solution is added to sodium diethyldithiocarbamate solution with continuous stirring.
iv) Precipitate is filtered and washed with double distilled water.
v) Precipitate is then thoroughly dried by keeping it in air oven at 125 ° C.

Preparation of Metal diethyldithiocarbamate

i) Prepared 0.01 N (Fe and Mn) diethyldithiocarbamate solution in a mixture of ethyl alcohol and water (7:3 V/V).
ii) pH of each carbamate solution is measured with the help of pH meter.
iii) The pH lies between 9-9.2.

Result and Discussion

The concentration of Iron and Manganese metal recorded from five electroplating sites has been listed in Table 1(Fig 1) and Table 2 (Fig 2). Iron which cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts off which result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. Inhalation of iron may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens was found to be in decreasing order as follows during different seasons from five electroplating sites:

Mar-June

Site 2 > Site 4 > Site 3 > Site 5 > Site 1

Jul-Oct

Site 5 > Site 4 > Site 2 > Site 3 > Site1

Nov-Feb

Site 2 > Site 3 > Site 5 > Site 4 > Site 1

Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. When people do not live up to the recommended daily allowances their health will decrease. But when the uptake is too high health problems will also occur. Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson, lung embolism and bronchitis. When men are exposed to manganese for a longer period of time they may become impotent. Manganese metal was found to be in decreasing order of concentration as follows during different seasons from five electroplating sites:

Mar-Jun

Site 4 > Site 3 > Site 5 > Site > AB-1

Jul-Oct
Site 5 > Site4 > Site 3 > Site 2 > Site 1

Nov-Feb
Site 4 > Site 3 > Site 5 > Site 2 > Site 1 (N.D)

Concentration of iron and manganese metal(Table 1 & 2) in many electroplating sites were found above the limits prescribed by I:S [2490-1974], EPA[1987] and CPCB[2000] for discharge of industrial effluents in to inland surface waters which is 3mg/L for iron and 2 mg/L for manganese. These metals when converted to their diethyldithiocarbamate solution form for spraying to cure disease proned plants of rose, brinjal and okra, it was found that black spot disease of rose was cured successfully by iron diethyldithiocarbamate and manganese diethyldithiocarbamate effectively cured Phomopsis Blight disease of brinjal, damping off disease of okra and rust disease of rose flower plant. These Carbamate pesticides are less dangerous with regard to human exposure than organophosphorus pesticides. The ratio between the dose required to produce death and the dose required to produce minimum symptoms of poisoning is substantially larger for carbamate compounds than organophosphorus compounds. Because of their chemical structure carbamates do not cause delayed neuropathy.

Table 1: Iron metal concentration in mg/l

S.No.	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	Site 1	0.07	0.01	0.08
2	Site 2	12.56	0.09	16.70
3	Site 3	0.39	0.03	0.44
4	Site 4	2.60	1.24	0.28
5	Site 5	0.29	2.74	0.32

Table 2: Manganese metal concentration in mg/l

S.No.	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	Site 1	1.8	0.02	N.D
2	Site 2	3.14	2.08	3.18
3	Site 3	8.6	2.24	24.10
4	Site 4	12.0	3.92	56.80
5	Site 5	3.57	12.51	4.20

Concentration of Iron in different Sites

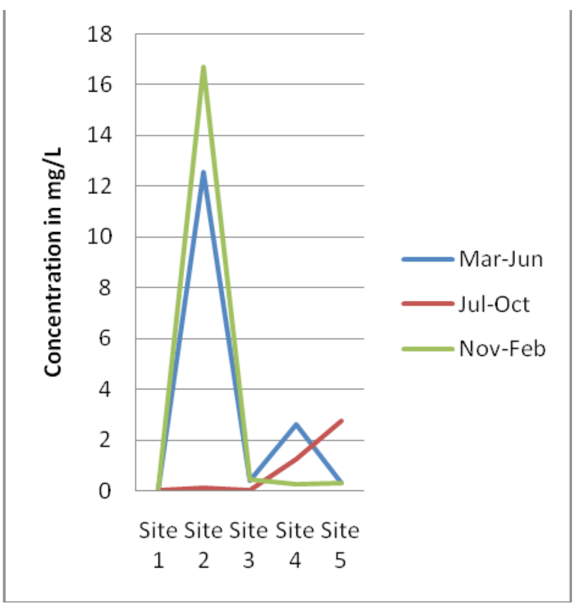

Figure 1

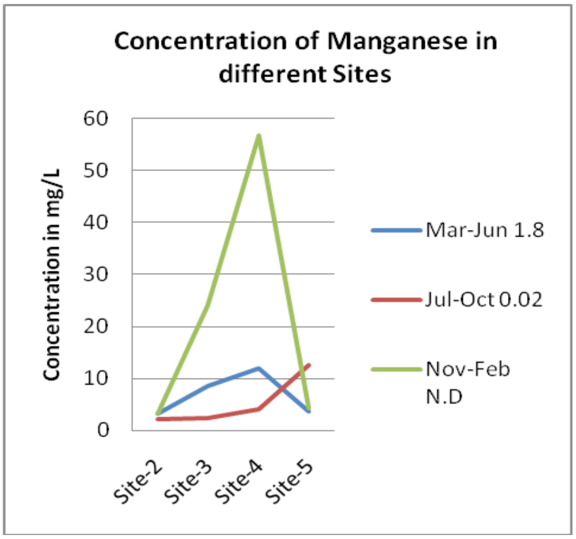

Figure 2

Conclusion

Electroplating industry effluents loaded with heavy metal can be treated by low cost adsorbents with 99% removal and also their bioremoval is also possible this will help in conserving natural reservoirs likes rivers and ponds from metal pollution which cause health hazard to very large extent to the people consuming and depending on such resources for their domestic need and also to the aquatic culture. Besides conservation of natural resource reuse of retrieved heavy metal as pesticide formulation in control of disease of ornamentals and vegetables of great market value has emerged as advanced technology as it discourages the fresh heavy metal consumption for synthesis of pesticides available in the market.

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