



Research Article

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## Characterization and treatment of electroplating industry wastewater using Fenton's reagent

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### ABSTRACT

*With the rapid increase in population, developmental works and industries, the environment is bound to get polluted, if timely steps are not taken for proper treatment of the pollutants, before allowing their mixing in the raw form with the main components of the environment i.e. air, food and water, earth, forests etc. which are the life sustaining resources available in the environment. The need of the hour is to adopt necessary steps for proper treatment of all types of wastes that are generated in the society due to our own day to day activities. The electroplating of a metallic product is done to prevent it from corrosion and to give a decorative and smooth finish. This paper deals with Characterization, quantification and treatment of electroplating Industry wastewater. The wastewater was treated with Fenton's reagent for the removal of heavy metals. The results indicated an increase in the percentage reduction of heavy metals with an increasing dose of Fenton's reagent. Hydrogen peroxide alone was not effective in the removal of heavy metals. However, hydrogen peroxide in combination with ferrous Sulphate (Fenton's reagent) was effective in the removal of heavy metals.*

**Keywords:** Characterization, treatment, electroplating, heavy metals, sustainable environment.

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### INTRODUCTION

The human activities development in different fields has given rise to pollution in such fields. The increase in vehicles/ transport based on age old technology of conventional petrol/ diesel engines with their smoke emissions have downgraded the quality of air, causing Air Pollution and Noise Pollution. The increase in population has resulted in unplanned habitations giving rise to cuttings of forests, waste water discharge without any treatment into the rivers/ streams downgrading the quality of natural waters causing water pollution. Similarly the growth of industries, especially in an unplanned manner with industrial discharge of toxic/ non toxic chemicals/ metals has also added to the pollution of natural waters. The equilibrium between earth's life forms and the environment that was existing since last so many years has been endangered with above human activities and this has become health hazard for the human beings themselves. Therefore, the need of the hour is to adopt necessary steps for proper treatment of all types of wastes that are generated in our society due to our own day to day activities. We generate all types of wastes viz in the form of solid, liquid, gaseous etc. These could be further categorized based on localized domestic/ commercial/ medical/ industrial activities. The wastes pollute our earth, air, water, plants and are hazardous to our health if not treated and disposed properly. Electroplating is usually carried out with Ni, Zn and

Cu. The most common type of electroplating is by using Ni (Nickel plating). The cell specifications for nickel plating are as follows:

Electrolyte:  $\text{NiSO}_4$  or  $\text{NiCl}_2$  dissolved in demineralised water (DMW).

Anode (+ve) : Ni

Cathode (-ve) : Cu

The Ni anode is stored in titanium bags to prevent the falling of anodic sludge. In the electrolyte solution, Boric acid ( $\text{H}_3\text{BO}_3$ ) is added in the electrolyte to ensure smooth electroplating[1].

### **Applications of Electroplating**

**(a) Electroplating** is used for Decoration or Better Appearance. In order to increase commercial as well as decorative value, base metals such as iron, brass, copper, aluminum alloys etc are electroplated with gold, silver, nickel chromium, palladium, platinum, rhodium and copper etc. For special decorative effects tin, cadmium, lead, platinum etc are also used. One metal may be electroplated over the base metal or an alloy may be electroplated over the base metal or several metals may be plated one over other on the base metal[2].

### **(b) Plating for protection**

Electroplating has widely been used for depositing protective coatings on iron and steel articles to protect them from corrosion, rusting and chemical attack. Protecting metals applied on iron and steel articles are zinc, cadmium, nickel, chromium, tin and copper etc.[3] Copper and chromium provide protection against rusting and chemical attack, while chromium plating gives shine and clean metal appearance and corrosion protection too. The three coating electroplating has widely been used in automobile industry, followed by lock. For the sake of protection, the galvanic effect of the metal couple formed by electroplating should also be considered. A galvanic couple, formed by the plated metal with the base metal should not be such that it may increase the corrosion of the base metal instead of preventing it[4].

### **(c) Plating for Special Surfaces**

There are plants, one part of which can be easily fabricated with an alloy and has got the required mechanical strength too, but is readily corroded when subjected to atmosphere of working or working conditions. In such cases, the part requiring corrosion resistance is exclusively electroplated with a corrosion resistant metal and it serves the purpose in an excellent manner. For example, in internal combustion engines, an electroplated chromium coating not only avoids the wear, but also improves the running performance[7].

### **(d) Electroplating for Engineering Effect**

In engineering, electroplating is employed for temporary use in metal treatment. Thus before carburizing, the steel parts are copper plated, in order to avoid carburizing at undesired portions. Similarly, portions of steel are protected from nitriding in hardening process by electroplating tin or copper-tin alloys on steel portions[5].

### **(e) Electroplating on Non-metallics**

Non-metallics such as glass, cloth, porcelain, leather, wood, dried leaves etc. are also electroplated for decoration, for preservation, for obtaining a conductive surface, for increasing their strength and for obtaining light weight parts with the properties of metal surfaces. For example, radar antenna masts made of hard wood or of synthetic resins are electroplated with copper, Electroforming as well as electrotyping both are examples of electroplating of the non-metallics[6].

### **(f) Electroforming**

Formation of articles by electro-deposition of metals is called electroforming, in which the layer of plated metal is quite thick. For example, many parts used in air craft, radio, radar, automobile industries are electroforming products.

### **Sources and Characteristics of Plating Waste**

#### **Cleaning**

These operations contribute to alkali waste containing NaOH, carbonates, silicates, wetting agents and emulsifiers. Whenever cleaning is performed with organic solvents, the effluent from this operation consists of the solvents such as benzene, toluene, petrol etc. as well as emulsifiers[8].

**Stripping or Pickling**

These effluents contain unused acids (e.g., HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) and ferrous sulfate.

**Electroplating**

All the constituents of the plating baths contribute to the wastewater stream either through part drag-out, batch dump or floor spill. Electroplating baths may contain Cu, Ni, Ag, Zn, Cd, Cr, Sn, Pb, Fe, ammonia, etc. The anionic components likely to be present include borate, cyanide, fluoride, tartrate, phosphate, chloride, sulfide, sulfate, sulfamate, nitrate, etc. Further, many other additives to induce grain refining, deposit brightening, surface leveling, etc. are also added to the plating baths. These include Mo, Se, As, Co, saccharin, aldehydes, etc., all of which contribute to the waste streams. Apart from these, contaminants like oil, grease, biodegradable mass, suspended solids, etc. may also be present in the wastewaters[10].

**Effects of the waste**

(i) Plating effluents are highly toxic and corrosive.

(ii) Cyanide, chromic acid, chromates, salts of heavy metals, e.g., Cd, Pb, Ni, Zn and Cu present are toxic to aquatic life. Their toxicity to micro-organisms inhibits self-purification property of the streams.

(iii) Fe, Sn etc. impart color to the receiving stream.

(iv) Phosphates and nitrates present in the effluent help in excessive algal growth which is undesirable.

(v) Colloidal and suspended impurities impart unaesthetic appearance to the stream

(vi) Owing to the toxic nature of the effluents, they are not disposed into the rivers or water courses. They are generally discharged into sewers. If cyanide is not completely removed, the HCN gas formed may affect the workers in the sewage treatment plant and sewer system. The organic solvents may cause explosion in the sewer system. Oils and greases present may interfere with the biological treatment of the sewage. Acidic or alkaline plating effluents may corrode the concrete structures. Suspended impurities present may clog the municipal sewer system[11].

**(vii) Arsenic (As)**

As is highly toxic, it is a chronic, cumulative poison and may cause eruptions on the skin and is said to be a causative agent of some forms of cancer.

**(viii) Cadmium (Cd)**

Cd affects metabolism and may substitute for Ca<sup>2+</sup> in the bone structure. In fact Cd result in the "Itai-Itai" disease, a seriously crippling effect, observed in Japan, is a result of Cd replacing Ca in the bone structure.

**(ix) Cyanide (CN<sup>-</sup>)**

Cyanide combined with H<sup>+</sup> forms deadly HCN, which boils at 26°C and is very dangerous.

**(x) Iron (Fe)**

High concentrations of Fe may stain laundry and fixtures, etc.

**(xi) Lead (Pb)**

Lead is known as cumulative poison and has been known to cause a disease called "Plumbism".

**(xii) Hexavalent Chromium (Cr<sup>+6</sup>)**

The harmful effects of water borne diseases are associated with hexavalent chromium. Cr<sup>+6</sup> of 10 mg/kg of body weight will result in necrosis and nephritis in human body. Low dose causes irritation of the gastrointestinal mucosa, while Cr<sup>+6</sup> in high doses have been reported to be the cause of digestive tract cancer, lung cancer and maxillary sinus cancer. Most commonly electroplated metals are Zinc, Nickel, Chromium, Aluminium, Copper, Cadmium etc. Out of these, chromium plating is one of the most widely used forms of electroplating and constitutes an important source of toxic heavy metal discharges. [4]

**Quality of the Electroplating Waste**

The sample test results of waste before and after treatment in the industry, in two such units are given below:

Sl.No.	Parameters	Before Treatment	After treatment
1.	pH	5.60	6.98
2.	T.S.S.	100.00 mg/l	50.00 mg/l
3.	Oil & Grease	8.00 mg/l	4.00 mg/l
4.	Temperature	25°C	26°C
5.	Total Chromium	0.19 mg/l	0.08 mg/l
6.	Hexavalent Chromium	0.07 mg/l	N.T.
7.	Nickel	5.82mg/l	1.75 mg/l
8.	Copper	12.94mg/l	1.46 mg/l
9.	Cadmium	0.03mg/l	0.01 mg/l
10.	Total Residual Chlorine	15.58 mg/l	N.T.
11.	Total Metal	19.03 mg/l	3.30 mg/l

From the sample test results, it could be seen that the generated raw waste contain pollutants in the form of heavy metals, suspended solids and PH and must be given suitable treatment to bring up to the permissible limits before discharging in open drain/ public sewer. One instance of Nickel could be taken. The raw waste is found to contain 5.82 mg/l of Nickel against permissible limit of 3 mg/l and total metal have been found 19.03 mg/l against permissible limit of 10 mg/l. Copper have been found as 12.94 mg/l against permissible limit of 3 mg/l. Hence, a treatment of raw waste is required.

**EXPERIMENTAL SECTION****Source of Waste Water for analysis**

The Waste water was obtained from M/s Sigma Electroplating Industry, Anoopshahr Road, Aligarh (U.P.), India which is a sister concern of M/s Link Locks (P) Ltd, Industrial Estate, Aligarh (U.P.). The Wastewater samples were analyzed in the Environmental Engineering Labs at Aligarh Muslim University, Aligarh(U.P.)

**pH adjustment**

The initial pH of the waste water was maintained at 4.0 by using 1N H<sub>2</sub>SO<sub>4</sub> and/or NaOH solution as at this pH maximum efficiency in the performance of Fenton's reagent was observed. Also at this pH iron ions are stable in the divalent state and the precipitation of ferric hydroxide is avoided.

**Addition of Fenton's reagent**

In this step the Fenton's reagent was added in four different amounts in the Wastewater (kept in four jars of the jar test apparatus). The mixing of the reagent was done by the stirring device, at an agitation rate of 300 rpm for 5 minutes.

**Instrument used for analysis of heavy metals**

The concentrations of Chromium, Copper and Nickel in the samples were analyzed by Atomic Absorption method using Atomic Absorption Spectrometer according to the methods specified by the "Standard Methods": 1985, 16th edition.

**RESULTS AND DISCUSSION**

The effect of various doses of Fenton's reagent on the removal of Cr, Cu and Ni without adjusting the pH of the wastewater is presented in Table 1, Table 2 and Table 3 respectively. The results indicate an increase in the Cr, Cu and Ni removal with an increasing Fenton's reagent dose. A 53.15 % removal of Cr, 48.53 % removal of Cu and 26.46 % removal of Ni is observed at the Fenton's reagent dose containing 20 ml of H<sub>2</sub>O<sub>2</sub>. This is due to the increase in the production of hydroxyl radicals at higher doses of hydrogen peroxide. The effect of various doses of Fenton's reagent on Cr, Cu and Ni removal with pH adjustment is presented in Table 4, Table 5 and Table 6 respectively. The results indicate an increase in the percentage reduction of heavy metals with an increasing dose of Fenton's reagent .A 60.00 % reduction of Cr is observed at a Fenton's reagent dose containing 20 ml of hydrogen peroxide with 1.0 g of ferrous sulphate.A 59.81 % reduction of Cu is observed at a Fenton's reagent dose containing 20 ml of hydrogen peroxide with 1.0 g of ferrous sulphate and a 48.79 % reduction of Ni is observed at the same dose of Fenton's reagent as in case of Cu. It is also observed that for each dose of the Fenton's reagent the

percentage reduction efficiency which is obtained after the pH adjustment is higher than that without adjusting the pH. This might be due to the generation of  $\text{Fe}(\text{OH})^{2+}$ , which is generating the OH radicals in the pH of 4.0.

Table 1: Chromium Removal Results without pH change

Sample No.	Initial Conc. of Cr. (mg/l)	Dose of Fenton's Reagent		Reaction Time (h)	Res. Cr. Conc. (mg/l)	Cr Reduction (%)
		H <sub>2</sub> O <sub>2</sub> (ml)	FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)			
1.	0.190	5.00	1.00	24	0.110	42.10
2.	0.190	10.00	1.00	24	0.102	46.31
3.	0.190	15.00	1.00	24	0.098	48.42
4.	0.190	20.00	1.00	24	0.089	53.15

Table 2: Copper Removal Results without pH change

Sample No.	Initial Conc. of Cu. (mg/l)	Dose of Fenton's Reagent		Reaction Time (h)	Res. Cu. Conc. (mg/l)	Cu. Reduction (%)
		H <sub>2</sub> O <sub>2</sub> (ml)	FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)			
1.	12.94	5.00	1.00	24	7.84	39.41
2.	12.94	10.00	1.00	24	7.24	44.04
3.	12.94	15.00	1.00	24	6.89	46.75
4.	12.94	20.00	1.00	24	6.66	48.53

Table 3: Nickel Removal Results without pH change

Sample No.	Initial Conc. of Ni (mg/l)	Dose of Fenton's Reagent		Reaction Time (h)	Res. Ni Conc. (mg/l)	Ni Reduction (%)
		H <sub>2</sub> O <sub>2</sub> (ml)	FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)			
1.	5.82	5.00	1.00	24	4.46	23.36
2.	5.82	10.00	1.00	24	4.42	24.05
3.	5.82	15.00	1.00	24	4.36	25.08
4.	5.82	20.00	1.00	24	4.28	26.46

Table 4: Chromium Removal Results at pH = 4.0

Sample No.	Initial Conc. of Cr. (mg/l)	Dose of Fenton's Reagent		Reaction Time (h)	Res. Cr. Conc. (mg/l)	Cr. Reduction (%)
		H <sub>2</sub> O <sub>2</sub> (ml)	FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)			
1.	0.190	5.00	1.00	24	0.091	52.10
2.	0.190	10.00	1.00	24	0.085	55.26
3.	0.190	15.00	1.00	24	0.081	57.36
4.	0.190	20.00	1.00	24	0.076	60.00

Table 5: Copper Removal Results at pH = 4.0

Sample No.	Initial Conc. of Cu. (mg/l)	Dose of Fenton's Reagent		Reaction Time (h)	Res. Cu. Conc. (mg/l)	Cu. Reduction (%)
		H <sub>2</sub> O <sub>2</sub> (ml)	FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)			
1.	12.94	5.00	1.00	24	5.76	55.48
2.	12.94	10.00	1.00	24	5.61	56.64
3.	12.94	15.00	1.00	24	5.41	58.19
4.	12.94	20.00	1.00	24	5.20	59.81

Table 6: Nickel Removal Results at pH = 4.0

Sample No.	Initial Conc. of Ni (mg/l)	Dose of Fenton's Reagent		Reaction Time (h)	Res. Ni Conc. (mg/l)	Ni Reduction (%)
		H <sub>2</sub> O <sub>2</sub> (ml)	FeSO <sub>4</sub> .7H <sub>2</sub> O (g)			
1.	5.82	5.00	1.00	24	3.92	32.64
2.	5.82	10.00	1.00	24	3.61	37.97
3.	5.82	15.00	1.00	24	3.31	43.12
4.	5.82	20.00	1.00	24	2.98	48.79

### CONCLUSION

The following conclusions were drawn from the present investigation on the treatment of electroplating waste water by advanced oxidation process using Fenton's reagent:

- Hydrogen peroxide alone was not effective in the removal of heavy metals.
- However, hydrogen peroxide in combination with ferrous Sulphate (Fenton's reagent) was effective in the removal of heavy metals the removal efficiency increases with increase in hydrogen peroxide concentration.
- The removal efficiency of heavy metals increases by adjusting the pH of the solution to 4.0.
- The results show that about 60% of Cr, 60% Cu and 50% of Ni can be removed from an electroplating effluent by advanced oxidation process using Fenton's reagent at acidic pH of 4.0.

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