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# Treatment of electroplating wastes

Dr Joo-Hwa Tay


## ABSTRACT

The electroplating industry has been playing a momentus role in the development and growth of engineering industries. Wastewater from the electroplating process contains high concentration of heavy metals, are harmful to aquatic life in the receiving waters. Physical - chemical method is commonly used for the treatment of electroplating wastes. The installation costs of treatment plants are 7% and 15% of the total capital investments for the small-and large scale-plants respectively. The unit treatment costs for electroplating wastes are US$1.46/$m^3$ and US$0.33/$m^3$ of wastewater treated for small and large plants respectively.


## INTRODUCTION

With the rapid economical and industrial development in South East Asia in the last decade, the search for clean water for national development calls for stringent measures for pollution control. Recently, the increased demand of consumer items has resulted in the set up of many small-to medium-scale plants engaging in electroplating work. In comparison with other industries, the electroplating industry uses relatively less water. Therefore, the volume of the waste water produces are also comparatively smaller. However, the waste waters are highly toxic in nature because of the presence of metals such as copper, zinc, nickel, cadmium, chromium, cyanide and other pollutants.

In the recent ESCAP (UN Economic and Social Commission for Asia and the Pacific) Expert Group Meeting in Bangkok, it was reported (1) that there are about 280 electroplating industries in Thailand, and most of them are located in Bangkok. These metal finishing industries discharge annually about 12 tonnes of heavy metals into the water courses. In Malaysia, it was estimated that there are as many as 100 operating electroplating shops in Klang Valley. In Hong Kong, there are presently about 770 registered electroplating industries. There are also a large number of unregistered small electroplating workshops in the area. There are about 87 factories or workshops that carry out electroplating activities in Singapore (2). Most of these electroplating plants in this region has no or inadequate treatment facilities.

Heavy metals bearing wastes are harmful to aquatic life in the receiving waters. In Singapore, electroplating wastes are not allowed to discharge before pretreatment. The allowable discharge limits for most heavy metals bearing wastes are stringent, not exceeding 5 mg/l into the sewer and 0.5 mg/l into the controlled watercourse. Although the methods of removal of these toxic constituents from wastewaters are well established (3 - 11), 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. One of the major problem is that the electroplating industries find it difficult to meet the effluent guideline without having to spend a large sum for treatment facilities. This paper presents the treatment methods that currently used for the electroplating wastes, and the costs of capital investment and operations for the treatment of wastewater.

## SOURCES AND CHARACTERISTICS OF ELECTROPLATING WASTES

Metals used in the electroplating industries are copper, chromium, nickel, cadmium, zinc, silver and gold. The plating operations are preceded by cleaning to remove grease, rust and scale from the metal surface. After plating has been done, the plated objects are washed with water.

The two major sources of wastewater is electroplating operation are batch solutions and rinse waters, they are distinctly different in volume and characteristics. Batch solutions from vats are highly concentrated and are discharged intermittently. Rinsed waters are more dilute but form the bulk of the wastewater of the electroplating industries.

The metal bearing wastes include rinse water from chromium, cyanide, cadmium, copper, lead, nickel and zinc vats. These metals are presents in soluble ionic form and most of them are extremely toxic. The ranges of concentration of these metals in the wastewaters (11,12) are

| | | |
|---|---|---|
| Chromium | : | 3 mg/l to 80 mg/l |
| Cyanide | : | 0.3 mg/l to 256 mg/l |
| Cadmium | : | 7 mg/l to 240 mg/l |
| Copper | : | 2 mg/l to 88 mg/l |
| Lead | : | 2 mg/l to 140 mg/l |
| Nickel | : | 3 mg/l to 900 mg/l |
| Zinc | : | 2 mg/l to 350 mg/l |

The volume and characteristics of various wastewater streams vary considerably from one plating plant to the other and within the same plant from day to day. Table 1 summarised the characteristics of wastewater from the plating operations (1,12). Generally, the drains inside the manufacturing plants are interconnected, mainly due to facility layout of the plant and partly to ignorance of the consequences. The composite plating wastes may be acidic or alkaline depending on the type of both used. Typical analysis of composite wastewater for a few electroplating industries in Indian (1,12) is shown in Table 2.

**METHODS OF ELECTROPLATING WASTES TREATMENT**

Cyanide Treatment

Several methods of treating cyanide wastes are currently use. The most popular method is cyanide destruction by chorination under the alkaline condition, or referred to as 'alkaline chlorination'. Another cyanide destruction process, electrolytic decomposition, is applicable where cyanide concentration are very high. Ozonation of cyanide wastes has been employed with some success. Other cyanide treatment processes include evaporative recovery, reversed osmosis, ion exchange and catalytic oxidation.

Destruction of cyanide by alkaline chlorination method may be accomplished by direct addition of gaseous chlorine or chlorine dioxide in presence of caustic soda, or sodium hypochlorite, or bleaching powder. When chlorine is added to the wastewater containing free cyanide and sufficient alkali is added to raise the pH to 10 or higher, the free cyanide is oxidized to cyanate with cyanogen choride as a intermediate product. This reaction is normally instantaneous or takes not more than 10 minutes. With excess chlorine, cyanate could be further slowly oxidized to carbon dioxide and nitrogen. This second stage of reaction takes 30 minutes to an hour. The averall reaction with excess chloride in presence of NaOH for complete conversion of cyanide to carbon dioxide and nitrogen gas is

$$2NaCN + 5Cl_2 + 12NaOH \longrightarrow 10NaCl + 2Na_2CO_3 + N_2 + 6H_2O$$

Theoretically, 2.73 parts of chlorine and 3.08 parts of alkali (NaOH) are required to oxidise each part of cyanide to cyanate. Additional 4.09 parts of chlorine and 3.08 parts of alkali for each part of cyanide are required to convert cyanate into carbon dioxide and nitrogen gas. However, the chlorine required in practice for the complete destruction of cyanide is higher than 6.82 parts and the alkali is lower than 6.16 parts per part of cyanide.

Chromium Treatment

The most effective and economical ways of chromium treatment is to reduce hexavalent chromium, Cr(VI) to trivalent state, Cr(III) in the acidic condition, and subsequent precipitation with an alkali. Ferrous sulphate along with sulphuric acid is commonly used for this purpose, other reducing agents used are sulphur dioxide and sodium bisulphite. Maximum reduction occurs in the pH range of 2.0 to 2.5. The reduction takes about an hour. The reduced trivalent chromium is precipitated by the addition of an alkali, line or caustic soda. Lime is commonly used, since it is cheaper than caustic soda. The step-wise reaction for precipitation by hexavalent chromium with ferrous sulphate and lime are:

$$H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Cr(OH)_3 + 3CaSO_4$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Fe(OH)_3 + 3CaSO_4$$

Theoretically, 16.03 parts of copperas ($FeSO_4.7H_2$), 6.01 parts of sulphuric acid and 9.48 parts of lime (90%) are required for the complete removal of 1 part of chromium. Other processes used for chromium removal are ion exchange, carbon adsorption, electrochemical reduction and evaporation recovery.

Treatment of other metal bearing wastes

The most common method of treating cadmium, copper, lead, nickel or zinc wastewaters, is chemical precipitation. Almost all the metals precipitate completely in the pH range of 9.5 to 10.5. Other treatment processes are ion exchange, carbon adsorption, reverse osmosis and evaporative recovery.

**TABLE 1 : CHARACTERISTICS OF ELECTROPLATING WASTEWATERS**

| Waste | Flow 1/hr | pH | Cyanides mg/l | COD mg/l | Total solids mg/l | Suspended solids mg/l |
|---|---|---|---|---|---|---|
| Cleaning solution (rinse waters) | 450-680 | 7.8-8.4 | 0 | 290-350 | 960-1120 | 610-720 |
| Cyanide concentrates (rinse water) | 450-680 | 9.2-9.9 | 0.3-21.2 | 25-42 | 430-600 | 23-35 |
| Acid pickling rinse waters | 900 | 4.5-5.5 | - | - | 450-590 | 76-141 |
| Spent alkali rinse waters | 2700-2650 | 8.8-9.8 | - | 300-350 | 800-1350 | - |
| Chromate rinse | 1360-2270 | 5.5-6.8 | - | - | 460-750 | - |
| Copper (cyanide) rinse waters | 450-680 | - | 7.3-11.6 | - | - | - |
| Copper (acid) rinse waters | 450-680 | 6.1 | - | - | - | - |
| Nickel rinse waters | 450-680 | 7.4-8.3 | - | - | - | - |
| Cadmium rinse waters | 450-680 | 8.0-8.8 | 3.2-4.6 | - | - | - |
| Zinc rinse waters | 450-680 | 8.9-9.8 | 5.4-9.0 | - | - | - |
| Floor wash waters | 450-680 | 7.6-8.0 | 0.1-0.3 | - | 350-480 | 65-79 |

**TABLE 2 : ANALYSIS OF COMPOSITED ELECTROPLATING WASTES**

| Plating shop | pH | Total solids | Suspended solids | Cr(VI) | CN | Cu | Zn | Cd | Ni | Ag |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 8.70 | 5200 | 800 | - | 3.80 | - | - | - | - | - |
| 1 | 7.50 | 2100 | 250 | - | 0.31 | - | - | - | - | - |
| 2 | 7.00 | 1400 | 260 | 1.85 | 0.62 | - | - | - | - | - |
| 3 | 7.90 | 1360 | 80 | 0.62 | 1.25 | 1.34 | - | - | - | 0.01 |
| 4 | 7.15 | 4450 | 350 | - | 9.20 | - | - | - | - | - |
| 5 | 6.50 | 2630 | 910 | 4.80 | 0.75 | 16.7 | - | - | 6.7 | - |
| 6 | 6.30 | 1850 | 270 | 2.90 | 0.60 | 6.0 | - | - | 21.5 | - |
| 6 | 6.40 | 1600 | 170 | 1.90 | 2.30 | 3.4 | 0.2 | 0.1 | 3.4 | - |
| 6 | 6.80 | 1900 | 90 | 1.20 | 2.50 | 1.9 | 0.1 | 0.1 | 1.2 | - |
| 7 | 7.00 | 1250 | 80 | 3.00 | 0.50 | 0.4 | 1.2 | - | - | - |
| 8 | 2.3 | - | - | 25 | - | 15 | 20 | 5 | 93 | - |

All results except pH are expressed in mg/l

## COSTS OF ELECTROPLATING WATER TREATMENT

The main items of a wastewater treatment plant for an electroplating industry are mixing, flocculation, reaction and settling tanks, pumps, floculators and chemicals. The major operating costs is the chemicals for the removal of heavy metals in the wastewater.

Information on the costs of capital investment and operating of wastewater facilities for electroplating industry are limited, particularly in the South East Asia region. One of the major reasons would be the wide variation in the flow and characteristics of the wastewater. Wastewater treatment plants of the engineering industries which have electroplating section are designed to handle the combined wastewater from all the manufacturing processes. Costs of installation and operation of such treatment platns are not representative. Other reason would be the electroplating industries which located as the urban area discharged their wastewaters into the public sewer after some minor pretreatment, therefore representative data cannot be obtained.

Table 3 compares the costs of the capital investment of manufacturing equipment and machinery with the installation costs of treatment plant facilities in Singapore. The data indicates that cost in installation for the small electroplating shops in Singapore (shops #1 to #3 in Table 3) range from US$2,500 to US$4,000 which is about 5% to 10% the cost of capital investment. Electroplating plant #4 is a large scale metal and plastic processing plant. The treatment plant consists of cyanide oxidation, chromium reduction, nickel precipitation and pH neutralization. The cost of treatment plant is US$450,000 or about 13% of the total capital investment. A bicycle parts manufacturer has a large electroplating plant mainly for nickel plating. The treatment plant includes coagulating-floculation, sedimentation and ion exchange units (Plant #5). The treated effluent is reused in the electroplating plant. The cost of treatment plant is US$1,000,000 or 16.7% of the capital investment. From these data, it shows that the installation costs of the treatment plant for the large scale electroplating shops is twice higher than the small plants.

Table 4 shows the operating costs for the treatment plants of some electroplating plants in Singapore. The unit costs of treatment for the small electroplating shops range from US$0.91/$m^3$ to US$2.27/$m^3$ with an average of US$1.46/$m^3$ of wastewater treated. However, the unit cost of treatment for the large-scale electroplating plants is only US$0.33/$m^3$ of wastewater treatment. It is quite evident that the unit treatment costs for small electroplating shops are in the order of 4 to 5 times the unit treatment costs for comparable large-scale plants.

## SUMMARY

The electroplating industry has been playing a momentus role in the development and growth of engineering industries. Wastewater from the electroplating process contains high concentration of heavy metals. Heavy metal bearing wastewaters are harmful to aquatic life in the receiving water. In Singapore, electroplating wastes are not allowed to

**TABLE 3 : INSTALLATION COSTS FOR ELECTROPLATING INDUSTRIES IN SINGAPORE**

| | Cost of Capital Investment (US$) | Cost of Treatment Plant (US$) | Percent | Reference |
|---|---|---|---|---|
| #1 | 50,000 | 2,500 | 5 | 13 |
| #2 | 40,000 | 4,000 | 10 | 13 |
| #3 | 45,000 | 3,000 | 6.7 | 13 |
| #4 | 3,500,000 | 450,000 | 13 | 14 |
| #5 | 6,000,000 | 1,000,000 | 16.7 | - |

**TABLE 4 : OPERATING COST FOR TREATMENT PLANTS OF ELECTROPLATING INDUSTRIES IN SINGAPORE**

| | Operating Cost (US$/month) | Volume of Wastewater ($m^3$/month) | Unit Cost (US$/$m^3$) | Ref. |
|---|---|---|---|---|
| #1 | 300 | 180 | 1.67 | 13 |
| #2 | 250 | 110 | 2.27 | 13 |
| #3 | 400 | 440 | 0.91 | 13 |
| #4 | 300 | 300 | 1.00 | 2 |
| #5 | 4500 | 14000 | 0.32 | 14 |
| #6 | 5000 | 15000 | 0.34 | 3 |

discharge before pretreatment. Physical-chemical method is commonly used for the treatment of electroplating wastes. Complete destruction of cyanide can be accomplished by the alkaline chorination process. Reduction of hexavalent chromium to trivalent state and subsequent hydroxide precipitation of the trivalent chromium is the most common method of hexavalent chromium disposal. Other metal-bearing wastes could be removed by chemical precipitation at high pH.

The installation costs of the small-scale treatment plants is about 7% of the capital investment of manufacturing facilities. However, the installation costs for the large-scale plants is twice higher than the small plants. The installation cost is about 15% of the total capital investiment. The unit treatment cost for the small electroplating shop is US$1.46/$m^3$ of wastewater treated, which is 4 to 5 times higher than the large scale electroplating plants. The unit costs of the treatment for large plants is US$0.33/$m^3$ of wastewater treated.

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