

SOLUTION FOR WASTEWATER PROBLEM RELATED TO ELECTROPLATING INDUSTRY : AN OVERVIEW

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Key words : Chlorination, Ozonation, Ion-exchange resin, Electrolytic decomposition,

ABSTRACT

Electroplating wastewater contains highly toxic cyanide, cyanide complexes and metal ions that makes treatment a complex problem. As the electroplating industries are located in tiny and unorganized sectors in India the problem becomes more grave. Due to lack of technology, Automation and process control, there is considerable change in the effluent coming from these industries. Therefore the effluent exerts variable characteristics. It is observed that effluent has high BOD/COD, SS, DS, TS, Colour, and Turbidity and there is depletion of oxygen. Proper treatment has to be provided for the safe discharge of electroplating effluent. The paper deals with the study of different processes for the reduction of pollution load related to this industry. Basically the paper covers all the different methods that have been used for the treatment of this waste along with the recent development of treatment. The benefits and limitations of the process has been discussed. The paper will be helpful in the selection of effective treatment method based on the quantity and characteristic of the effluent generated. It will help in further optimizing the process parameters.

INTRODUCTION

Metal finishing has now come to be known as surface engineering. Electroplating and metal finishing continue to have great potential in the development of technologies in various fields. Electroplating itself is a big industry.

Electroplating industry in India is mainly represented by small scale units having distinct features such as tiny, family owned jobber units, practices old and obsolete technologies, having unskilled or semiskilled power, located in unplanned and unauthorized areas with lack of industrial infrastructure facilities, working in small shop area most of the unit operates in an operating area of 10-25 sqm. Analytical facilities not easily accessible to the units resulting in lack of control on process parameter and improper documentation of production details.

Electroplating industry consumes and discharge large volumes of wastewater. Use of various chemicals and metal salt creates pollution problems. Major pollution caused by rinse water, spray losses and solution dumping and leakages. Valuable metals and cyanide along with different chemicals used are lost in wastewater. The amount may be 2-20% of the chemicals used. Therefore greater efforts shall be required to reduce the pollution problems. The effluent concentration depends on various factors such as surface area, shape of article, thickness of solution, speed of removal, drain time etc. The most important constituents of these wastes are acids used for pickling and cleaning, alkaline cleaners etc. This effluent is supposed to be most hazardous containing heavy metallic ions such as nickel, chromium, zinc, lead, silver, cadmium, mercury etc. as well as cyanides, hydrogen sulphides, ammonia, chloramines which are toxic but valuable. Electroplating wastewater is variable in character and alkaline in nature. It gives rise to obnoxious smell. The color imparts visible pollution, which persist for long distance in river stream decreases recreation capacity of stream impairing self-purification, disturbed penetration of sun rays which in turn retard photosynthesis activity. Most of the unit's practices dilution technique but dilution alone will not solve the problem. The Toxic character of waste water shows that one hundred gallon of chromium plating solution even though diluted by 200,000,000 gallons of stream water would provide enough chromate to kill most of aquatic species. Rapid industrialization and urbanization causes damage to ecosystem has crossed the bearing capacity of ecosystem. Serious attention has to be provided and no longer be overlooked. Hence complete detoxification should be achieved before the effluent is discharged in river stream. Many physico-chemical processes are employed for the removal of impurities and to reduce pollution load.

HISTORICAL SURVEY

Till 1947 the industrial waste were generally discharged without preliminary treatment. It was thought that dilution in sewer on natural water was sufficient to eliminate the dangerous effect.

In 1950s The first process for wastewater treatment were developed and used in industries. Electroplating wastewater has high BOD/COD, SS, DS, TS, Turbidity, Colour and depletion of oxygen along with metal ions. The toxicity due to heavy metals has also derived serious attention.

COAGULATION AND PRECIPITATION

The studies on the precipitation in the form of insoluble compounds started

to reduce the pollution load. Methods have been developed which allowed the removal of metals from the effluent to very low values. Treatment with different chemicals started with ferrous sulphate, with sulphur dioxide, with acids etc. At one time the precipitation method was supposed to be feasible, but detailed analysis showed that problems could not be solved by these methods. The addition of different chemicals alters the physical state of DS, SS and TS and facilitates their removal by sedimentation or precipitation. The degree of clarification depends on the quantity of chemical used. The theory of chemical precipitation reaction is complex one. The reaction may be often incomplete and numerous side reactions may occur.

Treatment with ferrous sulphate

Treatment with ferrous sulphate is one of the oldest method for removal of cyanides, chromium etc. followed by neutralization with lime to precipitate various heavy metals. With dilute solution the reaction is rather slow. Reduction of cyanide up to 85% can be achieved under ideal condition. This method has the advantage that the reagents used are cheap. When ferrous sulphate is added to the wastewater, insoluble complex cyanides of iron are formed. Maximum precipitate occurred at 10.5 pH. It is difficult to reduce the concentration of cyanide below limiting value. This process requires control and intelligent chemical control. In general the residual cyanide content is too high for safe disposal of waste to river stream. Numerous substances have been suggested in 1950s. Use of different chemicals including sulphide of sodium, calcium, barium, sulphur dioxide, sodium sulphite and bisulphate, Zinc dust etc were suggested. With barium sulphite the reaction with chromate were found to be complex. It was desirable to add ferrous sulphate in addition to barium sulphite.

Treatment with sulphur dioxide

Treatment with sulphur dioxide to high concentration of Cr and Cu under controlled condition and using sodium (carbonate to precipitate Cr) gives hydrated chromium oxide of high purity. The addition of sulphur dioxide to the wastewater shows a considerable decrease in impurities. Only 1.9 parts of SO₂ are required to reduce one part of hexavalent chromium as contrasted with 16 parts of copper but the effluent contained sulphites and would not be suitable for discharge without further treatment.

Treatment with sulphuric acid

Another method is the treatment of wastewater with the addition of sulphuric acid and simultaneous aeration. The disadvantages lie in the evolution of hydrogen cyanide, which is highly toxic in nature. Copper plating solution containing 15,200-ppm cyanide as NaCN can be treated with sulphuric acid and air is blown through perforated pipes for 16 hrs. There was substantial decrease in cyanide content. It is not generally satisfactory. Approximately nine days are required for removal of cyanide from wastewater by this process. The process is poor one and should only be employed if other methods are not possible. In practice this type of treatment is not recommended. Similarly the

acidic behaviour of the solution generates the dangerous hydrogen cyanide gas that creates air pollution problem.

Treatment with barium chromate

Another method of treatment is the addition of barium chromate. The wastewater is treated with barium chloride and sodium carbonate is added to raise the pH (alkaline) and then excess barium carbonates added to precipitate excess barium. This method of treatment is capable of removing chromate efficiently and of precipitating metals of which carbonates are insoluble. This method has the disadvantage that the reagents used are costly and barium salts are toxic in nature. The high cost and danger connected with the disposal of liquid sludge aided the development of newer methods of treatment. Coagulation and precipitation merely transform the nature of pollutant and convert it in solid waste.

The sludge disposal is a big problem; coarse solids in the effluent are troublesome and need special attention. These are chemical precipitates and consist largely of hydroxides and salt of metal from acid dips or plating baths. These hydroxides exist in different degree of hydration.

In the sixteen we could think the effluent treatment can be achieved to a fair degree but the recovery of heavy metals and their use was still not possible and economical. Work carried out for proper re-use of wastewater and recovery of valuable metals. The opportunity was provided by the development of organic exchanger resins.

Ion exchange method

One method, which may offer promise for the future in the treatment of plating waste and recovery of valuable constituents, is the use of ion exchange material. This technology has the advantage that wastewater can be reused instead of using fresh water. The use of ion exchanger in wastewater technology required high cost. The ion exchange has made possible to reuse 90 % of water and thus reduces the effluent volume to 5-10 % of the earlier practice. Studies have indicated that the regenerated solution from this process may be concentrated to about 2,000 ppm of copper and 2,000 ppm of Zn. By proper choice of ion exchange material and regenerator the regeneration of chromate ions can be achieved. It should be noted that ion-exchange material merely serves to concentrate the waste and do not dispose them off. The treatment of chromate containing wastewater can be achieved by passing through a column of acid absorbing artificial resin Deminrolit B. chromate was completely absorbed until the resin was exhausted but on treatment with 5% solution of ammonium hydroxide only a small portion of chromate was recovered as ammonium chromate. This method of treatment is at present in experimental stage but has great promise as a method of recovery of valuable metals from industrial waste. The disadvantage of this method is that it absorbs and store all dissolved salts and toxic chemicals but these substances are not destroyed. The second disadvantage is the formation of large quantities of salt that have to be discarded with wastewater. By direct precipitation of an equivalent

of heavy metal one equivalent of salt is produced. Ion exchanger produces double quantity of salt compared with direct precipitation.

Alkaline chlorination treatment

Treatment with chlorine and chlorine compounds started with the extensive work carried out by Eddy and Metcalf. The alkaline chlorination treatment of cyanide wastewater is apparently the most generally satisfactory method so far devised. Chlorine is a powerful disinfectant and has long residual time. Chlorination at high pH is the standard treatment process for cyanide containing wastewater. This process is successfully applied when the cyanide concentration in waste stream is less than 1000 mg/L. The reactive oxidant in alkaline is hypochlorite ion. In alkaline chlorination the cyanide concentration in the treated effluent is reduced to less than 0.1 mg/L, but if iron and other heavy metals are present they produce complex metal cyanide and are not oxidized. The addition of excess chlorine increases total cyanide content of wastewater and leaves high chlorine residual which are toxic to aqueous life. When cyanide is treated with chlorine it first forms cyanogens chloride, which in alkaline solution is converted to relative non toxic cyanate under suitable condition the cyanate is decomposed to ammonium carbonate. No details of method of control or composition of treated wastewater are published.

Electrolytic decomposition method

Another method that has got promising application is electrolytic decomposition of cyanide containing wastewater. In this process the cyanide wastes is subjected to electrolysis at high temperature at 95°C for several days. Initial cyanide is completely broken down to CO₂ and ammonia with cyanate as intermediate. As the process continues the waste electrolyte may not go to final completion, some residual cyanide and cyanate remains which require further treatment. By this method high concentration cyanide can be safely decomposed to concentration less than 1 mg/L.

Evaporation

Single stage and multistage evaporation have been used to recover the process water and plating chemicals. Evaporation of wastewater has been carried out to find out the economics of the process. Because of the high cost of equipment this method is not normally applied to all rinsing operations.

Oxidants other than chlorine can also be used to destroy cyanide. Hydrogen peroxide and potassium permanganate have been used to oxidize cyanide-containing wastewater (Renzo De 1981). The residual cyanide is less than one ppm. Operating costs are high and sludge disposal problems are there.

Treatment with ozone

In the last decades the most talked advances in the treatment of wastewater has been the use of ozone. The use of ozone is becoming more popular in wastewater treatment. The development in technology of producing ozone

and reaction kinetics has made the process reliable and feasible. Ozone is known to be highly selective oxidant. The disinfectant efficiency is 3125 times faster than chlorine. Wastewater with significant properties of industrial waste needed higher dosage in the range of 10-15 mg/L. Tertiary treatment plants have used ozone to reduce BOD/COD, cyanide and phenol. Ozone is suitable oxidant for cyanide. Broadly speaking ozone oxidizes these heavy metals to metallic oxides or hydroxides. Ozonation has become the most important innovation for ultimate treatment of all types of organic/inorganic impurities in wastewater by oxidation process. Sometimes complete Ozonation may not be achieved. Ozone molecule ruptures the target molecule and produces by products that are easily degradable.

There are large number of application in wastewater treatment Roth (1947) reported that ozone could be used to oxidize phenols in aqueous solution. Tyler *et al.* (1951) showed that Ozonation process could be used to destroy cyanide in bubble column. It was observed that a strong dependency exist on the pH of the solution and mass transfer controls cyanide oxidation rate in gas phase. The cyanate oxidation rate is approximately five times slower than that of cyanide oxidation under comparable conditions. In (1992) Balenskii *et al.* conducted experiments on Ozonation of unbuffered cyanide solution and reported that cyanate oxidation did not start before the cyanide conversion was almost complete. Cyanide disappearance curve was found to follow first order kinetic with respect to cyanide concentration.

Rowley and Otto (1980) carried out mass transfer studies related to Ozonation of sodium cyanide in stirred Dankwert cell and reported that reaction mechanics lies in transition of fast to instantaneous reaction regime. Gurol studied the decomposition of cyanide wastewater obtained from metal finishing in 1985 and reported that ozone reacts primarily with cyanide ion very fast reaction is first order with respect to ozone.

CONCLUSION

The electroplating industry effluent contains metal ions of Cu, Zn, Cr, Ni, Cd etc for which treatment and recovery is not possible from economic point of view. There are number of problems related to the treatment of electroplating wastewater by conventional method such as metals are precipitated as their hydroxides and removed as sludge. The sludge is difficult to handle and dispose. Expensive filtration equipment are required for dewatering sludge. There is sludge fixation problem. The use of Ion-exchange technique is effective for the recovery of valuable metals at the same time provides reuse of wastewater. The cost of treatment is high. Treatment with chlorine is an effective method when cyanide concentration is less than 1000 ppm but creates problems when applied to actual wastewater. It forms complexes with other metals that hinder the reduction of pollution load. No details of control and treated wastewater are published. The Electrolytic decomposition method is effective method but the operating cost is high and final completion is not achieved. The time required for treatment is very large (in days). Single

and multistage evaporation can be applied to the treatment of electroplating wastewater; it requires high initial and operating cost, which limits the application of this method.

The applicability of all these techniques depends on the type and scale of operation. All these methods of recovery are directly related to economy of the system in certain cases it is economical to treat the effluent rather than try to recover the metal. A complete survey of any individual plant and wastewater obtained should be made before selection of method of treatment. The direction for metal finishing wastewater control will come in near future will be guided by economics and influenced by legal pressure. The strongest pressure for change will be result of water supply problem and population. As water become scarce there will be increasing trend towards reuse of water or improved method and procedure. The future of wastewater treatment seems to be a combination of various process and advanced treatment methods. It is technically possible to have zero discharge but the cost is very high and poses unknown hazards to the environment.

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