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Efficiency evaluation of treatment methods adopted for safe disposal of rinse water generated from electrochemical processes

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ABSTRACT

Electrochemical/chemical processes play a crucial role in the fabrication of accelerator and laser components to meet specific functional requirements. These processes generate a lot of wastewater during rinsing having metallic and non-metallic ions with wide spectrum of toxicity. Wastewater generated during electrochemical processes such as electropolishing of stainless steel, electroplating of copper, nickel and anodic oxidation of aluminium is collected in two storage tanks of capacity 10 m^3 each. Method of treatment consists of a pre-treatment section, a plant which is combination of clarifier-platter, slaked lime dosing system and storage tank. The pre-treated water is then passed through a reverse osmosis (RO) system of capacity 3 m^3 per hour to remove the ions that were not removed in the pre-treatment section. By combining these two methods we were able to remove the metallic and non-metallic impurities up to 99% from the electrochemical rinse waste making it suitable for safe disposal or reuse. In this paper, we describe about our studies in determining the efficiency of these treatment methods (pre-treatment and RO) adopted. We also discuss about the reuse of treated water for electroplating activities by integrating an ion-exchange plant with the existing treatment system.

Keywords: Electrochemical processes; Wastewater; Toxicity; Pre-treatment; Reverse osmosis; Efficiency of treatment methods; Reuse

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1. Introduction

The characteristics of electroplating wastewater are a function of plating processes, rinsing methods and plating practices. The composition of electroplating effluent is complicate and may contain acid–alkali wastewater, heavy metal wastewater and cyanide-containing wastewater [1–3]. Effluents released from surface finishing and plating industry generally contain metal ion concentrations much higher than the permissible levels and must be treated before being discharged. On the other hand, electrochemical processes have proved to be very efficient in the treatment of wastewater generated from various industries. Development, design and application of electrochemical technologies like electrochemical reactors for metal

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recovery, electrocoagulation, electroflotation and electrooxidation in wastewater treatment was reviewed in detail by Guohua Chen [4]. Electrocoagulation is particularly employed in treating waste waters from textile industries [5,6] and from other industries also [7]. Photovoltaic electrocoagulation (PV-EC) process combines the autonomous and environmentally friendly photovoltaic (PV) solar energy with the capability of iron electrocoagulation (EC) to effectively reduce both trivalent and hexavalent chromium ions from electroplating effluents [8].

Some of the specific waste treatment processes for electroplating industry include neutralization for highly acidic or basic wastes, hydroxide and sulphide precipitation of toxic heavy metals, oxidation for cyanide destruction, reduction and neutralization of chromium wastes. It is easier if the waste streams are segregated and subjected to suitable treatment methods. Other techniques like adsorption, ion-exchange and reverse osmosis (RO) are also employed for treatment of metallic and non-metallic ions present in the wastewater [9]. Conventionally, precipitation with alkali hydroxides and coagulation with $FeSO_4$ or $Al_2(SO_4)_3$ has been the method most often used to remove heavy metals [1]. The choice of chemicals for neutralization is a question of weighing costs and efficiency against each other. Sodium hydroxide or potassium hydroxide are more expensive chemicals, but provide a faster and more efficient neutralization resulting in smaller amount required than as in case of lime or lime stone. Precipitation with lime gives better sedimentation and dewatering properties of the formed metal hydroxide. Phosphoric acid present in the electropolishing solution imparts phosphate ions and are precipitated as calcium phosphate with lime treatment and is found below detectable limits. Lime also binds with the fluoride to form calcium fluoride which have low solubility in water (0.016 g/l) and will precipitate with sludge. Sodium fluoride (NaF) will form when neutralizing with NaOH, but the solubility in water (41.3 g/l) is higher than for CaF_2, which makes the fluoride reduction more efficient when using lime. However, this method does not ensure total compliance for various metals present in the waste stream since all metal hydroxides do not completely precipitate at a single pH. Nitric acid present in mixed pickling acids are converted to soluble nitrates during neutralization and are not removed from the wastewater.

Electrochemical/chemical processes play a crucial role in the fabrication of accelerator components to meet specific functional requirements. Chemical Treatment Facility at Raja Ramanna Centre for Advanced Technology, Indore is involved in the treatment and modification of various metallic surfaces of components used in the fabrication of accelerators. Chemical cleaning, electropolishing, electro-deposition and anodising [10] are some of the methods regularly used to attain specific surface properties. Rinsing of these components in between various steps of above-mentioned processes is essential to avoid contamination of electrolytes. Rinsing [11] generate a lot of wastewater having metallic and non-metallic ions like Ni^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^- and F^-. Some of these ions are toxic in nature and will have harmful effects on physiochemical and biological processes of living organisms if discharged directly into water bodies. Increased levels of phosphates and nitrates often indirectly harm the environment by causing bacterial growth and huge algae blooms [12]. Higher turbidity content in the wastewater causes adverse effect on water bodies by increasing the temperature as suspended particles absorb more heat and decreasing dissolved oxygen due to reduced photosynthesis. Metal ions can cause hyper tension, gastrointestinal disturbances, head ache, nausea, vomiting, liver damage [13] and long-term exposure of heavy metal ions may lead to cancer.

Generally electroplating effluents are neutralized with either sodium hydroxide or calcium hydroxide and disposed off after separating the solid waste by filtration. In the case described above, it is being planned to reuse the treated electroplating waste after subjecting to different treatment methods. In this paper, we describe about our studies in determining the efficiency of treatment methods (Pre-treatment with lime and RO) adopted. We will also discuss about the reuse of treated water for electroplating activities by integrating an ion-exchange plant with the existing treatment system.

2. Methodology

Fig. 1 shows the various type of processes employed for the processing of accelerator components along with chemicals used in each process. Metallic and non-metallic ions expected in the wastewater generated from these processes are also mentioned. Fig. 2 shows the overall scheme for the existing and proposed facilities for the treatment of wastewater.

Rinse water generated during electrochemical processes is collected in two storage tanks of capacity 10 m^3 each. Method of treatment consists of a pre-treatment section, a plant which is combination of clarifier-platter, slaked lime dosing system and storage tank. The untreated effluent is transferred to the especially designed clarifier having capacity to treat 1 m^3

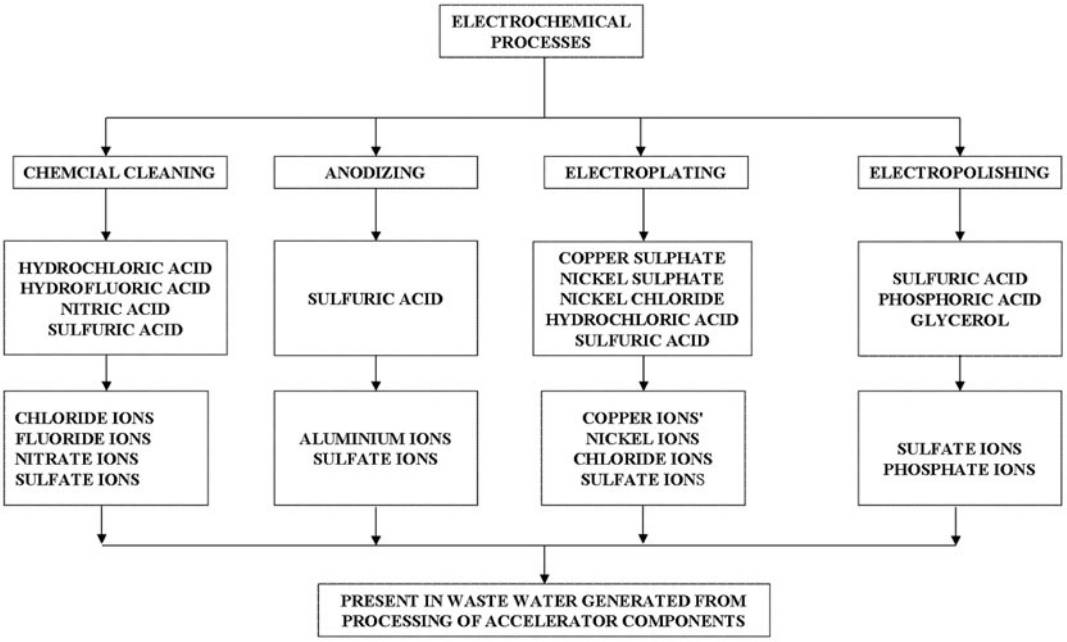

Fig. 1. Processes adopted indicating chemicals used and ions generated.

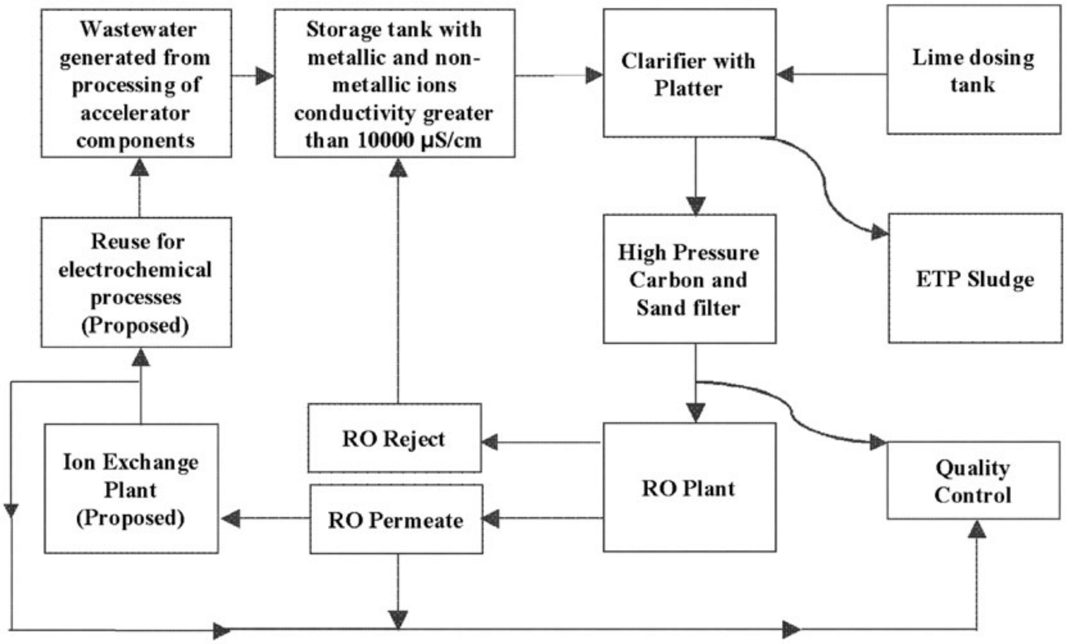

Fig. 2. Flow chart for treatment of wastewater.

of waste per hour. Slaked lime is dosed carefully and it is allowed to react with metal and non metal ions (specifically fluorides and phosphates). Chemically transformed effluent is then passed through the platter that separates solid waste from liquid stream and is collected in 5 m^3 storage tank for further treatment. Pre-treated wastewater is then passed through treatment section consisting of sand filter and high-pressure carbon filter to remove suspended particles and organic carbon. The filtered water is then passed through a RO system of capacity 3 m^3 per hour to remove nitrate, sulphate and any other ions that were not removed in the earlier process. An average of 100 m^3 of wastewater is treated annually with the existing system.

Analysis of the rinse water samples were carried out before and after treatment. The analytical data generated was for a period of three years and is indicative of the maximum changes taken place in ionic concentration of rinse water due to different processes.

2.1. Pre-treatment (Chemical transformation)

Wastewater generated is acidic in nature (pH 0.8–1.2) and pre-treatment is designed in such a way that the neutralization and precipitation for most of the ions occurs in a single step. For this purpose, 3–5% calcium hydroxide solution is used instead of sodium hydroxide solution. Metallic ions are converted into their insoluble hydroxides while anions like fluoride, sulphate and phosphate are transformed into their respective insoluble salts of calcium. The precipitate generated is land filled after separation by using sludge de-watering system.

Reactions involved are:

$$M^{n+} + n\ OH^- \longrightarrow M(OH)_n$$

$$SO_4^{2-} + Ca^{2+} \longrightarrow CaSO_4$$

$$2PO_4^{3-} + 3Ca^{2+} \longrightarrow Ca_3(PO_4)_2$$

$$2F^- + Ca^{2+} \longrightarrow CaF_2$$

The advantage of this process is that it is economical and will reduce the load on the RO plant (Treatment process). Some amount of fluorides and sulphates will be carried over with pre-treated water based on their solubility product. Nitrates and chlorides are not precipitated in this process as they are converted into soluble calcium chloride and nitrate, respectively, that will be removed in the RO system. Fig. 3 shows the pre-treatment set-up consisting of clarifier, platter and slaked lime dosing system.

2.2. Reverse osmosis

Fig. 4 shows the RO system with high-pressure filters, RO membranes and on-line dosing systems. Pre-treated water is then let into the RO plant through two high-pressure filters filled with pebbles (sand filter) and carbon (IV 900 mg/g) for removing suspended particles and organic matters, respectively. The ions present in the pre-treated water will exert a pressure of 3–7 kg/cm^2 on the RO membrane. The pressure was calculated on the basis of Morse equation (π = iMRT) and analytical data obtained. To this concentration of ions, 30% extra ionic load was added to arrive at maximum working pressure of 7 kg/cm^2. Extra ionic load was included to accommodate sudden changes in process activities and soluble calcium salts present in RO feed due to lime treatment. RO plant with four polyamide low fouling composite membranes (LFC) of size 20.32 × 101.6 cm in series at a working pressure of 7 kg/cm^2 are being used. 5% v/v hydrochloric acid (20 ml/minute) and 3% w/v sodium meta-bisulphite (20 ml/minute) were also added by on-line dosing pumps along with pre-treated wastewater to maintain the pH and for controlling free chlorine present in hydrochloric acid, respectively.

Fig. 3. Pre-treatment system.

Fig. 4. RO plant.

Table 1
Analytical results of untreated, pre-treated and RO-treated rinse wastewater

Parameter	Untreated	Pre-treated	RO permeate
pH	0.8–1.2	7.5–8.5	6.3–7.2
κ (μS cm^{-1})	8,000–12,000	1,000–2,000	43–140
Turbidity (NTU)	87–98	47–56	BDL
TDS (mg L^{-1})	5,600–8,400	700–1,400	30–98
SS (mg L^{-1})	109–120	4–7	Nil
TS (mg L^{-1})	5,709–8,520	704–1,407	30–98
TH^a (mg L^{-1})	400–750	600–900	BDL
$TH_{Ca}{}^a$ (mg L^{-1})	380–690	593–885	BDL
$TH_{Mg}{}^a$ (mg L^{-1})	20–60	7–15	BDL
Chloride (mg L^{-1})	68–320	65–317	2.8–3.2
Sulphate (mg L^{-1})	6,000–7,600	567–620	12–25
Phosphate (mg L^{-1})	100–500	1–3	BDL
Nitrate (mg L^{-1})	25–2,440	22–2,130	0.8–3.6
Fluoride (mg L^{-1})	27–36	0.2–1	BDL
Nickel (mg L^{-1})	23–80	0.3–1.0	BDL
Copper (mg L^{-1})	16–120	0.6–1.0	BDL
Iron (mg L^{-1})	8–22	0.1–3.0	BDL
Aluminium (mg L^{-1})	0.5–6.1	0.77–1.0	BDL
Zinc (mg L^{-1})	0.1–0.9	BDL	BDL
Lead (mg.L^{-1})	2–4	BDL	BDL
DO (mg L^{-1})	2.8–4	3.8–4.2	4.88–6.3
COD (mg L^{-1})	140–390	70–140	10–25
BOD (mg L^{-1})	20–43	2–7	1–3
Surfactants (mg L^{-1})	60–80	2–13	BDL

[a]as $CaCO_3$.

2.3. *Analytical methods*

Analysis of untreated and pre-treated waste along with RO permeate [14] was carried out for the following parameters; pH, conductivity, turbidity, total solids (TS), total dissolved solids (TDS), suspended solids (SS), total hardness (TH), calcium hardness (TH_{Ca}), magnesium hardness (TH_{Mg}), chloride, sulphate, phosphate, fluoride, nickel, aluminium, iron, copper, nitrate, zinc, lead, dissolved oxygen, COD, BOD and Surfactants (total, anionic and cationic). Methods used for analysis of various samples include titrimetry, spectrophotometry and potentiometry using Spectroquant, Pharo 100 (Merck, Germany), Aquarius series 7500 double beam UV–visible spectrophotometer (CECIL, UK), COD automatic titrator CT 15 (Spectralab, India), BOD incubator IPP 400 (Memmert, Germany), Multiparameter meter (Orion, US) and AQUAfast II, (Thermoelectron corporation, US).

3. Results

Table 1 shows the analytical results for untreated, pre-treated and RO-treated rinse water generated during a particular period. The results for different parameters are expressed in ranges since the nature of rinse water and its ionic concentration depends on the substrate being processed and type of electrochemical process carried out. By combining different methods of treatment, we were able to achieve a removal efficiency of 93–100% for different contaminants. The removal efficiency for individual parameters is given in Fig. 5.

4. Discussion

Turbidity, one of the important physical parameter has been taken care by the treatment process and is brought down from 98 NTU to BDL by the combination of treatment process with 100% efficiency. pH changes from acidic to neutral after treatment of wastewater. The reduction in conductivity from 12,000 down to140 μS cm^{-1} indicates that the quality of water is better than raw water (340–390 μS cm^{-1}) due to removal of metallic and non-metallic ions. The main parameter used for identifying the pollution level, i.e. DO, COD and BOD were also brought to acceptable limits after treatment. Increase in the DO and decrease

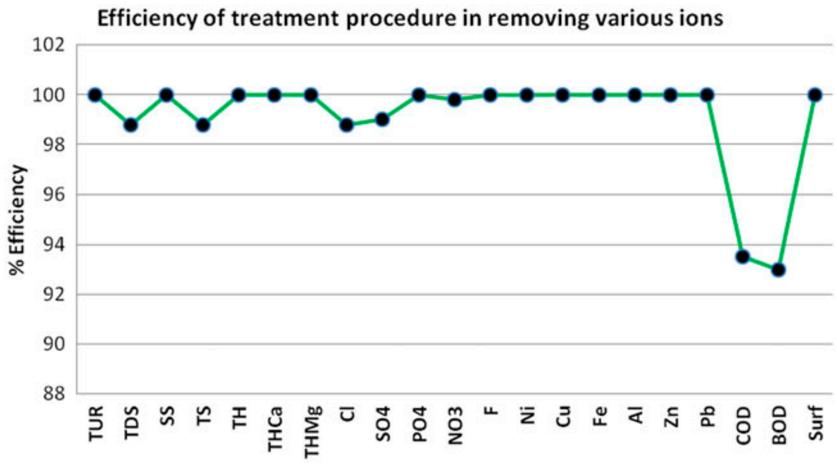

Fig. 5. Efficiency of treatment method in removing contaminants from electrochemical wastewater.

in COD and BOD is the sign that the pollutants from waste stream that consume oxygen is efficiently being removed by the treatment methods adopted. The increase in hardness values is attributed to incorporation of calcium ions during pre-treatment. These ions were removed and brought down to BDL after RO treatment. Anions like fluoride and phosphate are removed to a maximum extent during pre-treatment with slaked lime by precipitation as insoluble fluorides and phosphates of calcium. Removal of sulphate ions was 90% during pre-treatment which was finally brought down to 25 ppm (99.6% removal) after passing through RO plant. Nitrate and chloride were not affected in the pre-treatment process and removed by the RO method. Metal ions were removed completely (100%) by the combination of these treatment methods. This water can either be disposed off safely to environment or can be reused by addition of some more treatment methods.

It is being planned to install an ion-exchange plant and its integration with the outlet of existing RO plant. For achieving this, experiments were carried out [15] for identifying the type of resins to be used. 225 H for cation removal, NIP for anion removal and combination of 225 H and FFIP for mixed bed (Polisher) were chosen for further treatment of permeate from RO outlet.

5. Conclusions

Wastewater generated from electrochemical processes is complex in nature and depends on the type of processes and practices being carried out. Segregation of electroplating wastewater at the source and its collection as cyanide, acid/alkali/metal ions and chrome containing effluent is essential for proper treatment and disposal. Lime treatment is beneficial over sodium hydroxide for neutralization during pre-treatment as it precipitates anions like fluoride sulphate and phosphate as insoluble salts. RO process after pre-treatment is effective in removing soluble nitrates and other ions that were not completely removed in the earlier step. Hazardous solid waste generated from lime treatment is being land filled after proper treatment through Madhya Pradesh Waste Management Project. Integration of ion-exchange plant with RO system and Pre-treatment plant will result in reuse of water for electroplating applications. Presently around 100 m^3 of wastewater per year is being treated, which is expected to increase in future. Reuse of this wastewater by integrating with different treatment methods will result in conservation of precious water.

Nomenclature

π — osmotic pressure (kg cm$^{-2)}$
IV — iodine Value (mg/g)
T — temperature (°K)
M — molarity (moles dm^{-3})
R — gas constant (L atm K^{-1} mole^{-1})
i — dimensionless vant’Hoff factor
κ — conductivity (µS cm^{-1})
BDL — below detectable limit for adopted analytical procedure

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