Electrolytic recovery of dilute copper from a mixed industrial effluent of high strength COD

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ABSTRACT

In this study, the electrochemical treatment has been investigated in the real acidic effluent of copper-phthalocyanine dye manufacturing plant. Galvanostatic batch electrolyses have been carried out in an undivided cell using stainless steel as cathode, dimensionally stable anode (DSA) and graphite as anodes at different current densities and temperatures. The influence of these variables on current efficiency, cell voltage, energy consumption and deposit quality was reported. Under optimized conditions, the maximum copper recovery of 98% and COD removal efficiency of 87.3% with the energy consumption of about 11.23 kWh/kg of Cu and 6.08 kWh/kg of COD, respectively at 30 °C were achieved in the acidic raw effluent using 2D parallel-plate cathode. While in 3D stainless steel turning cathode reactor, 99.5% of copper can efficiently be recovered from dilute solution with an acceptable current efficiency of about 56.8% with minimum energy consumption of 2.37 kWh/kg of Cu. The experimental results suggested that the efficiency of copper removal is hindered by the presence of organic species in the mixed industrial effluent.

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1. Introduction

Dyes and pigments are indispensable part of the modern lifestyle and have found wide application in fabrics, home interiors, leather accessories, plastic, automobile and paper industry [1]. On the other hand, dye industries are one of the major industries for water pollution among most of the polluting industries, as they consume substantial volumes of water and chemicals.

Since early this century, the syntheses of phthalocyanine compounds have established themselves as blue and green dyestuffs par excellence. They are the important industrial commodity (output 1 lakh MT per annum) used primarily in inks (especially ball point pens) colouring for plastics and metal surfaces and dyestuffs for jeans and other clothing. Among these, the copper phthalocyanine is the most brilliant and is highly coloured blue to green. However, the process wastewater coming out from the copper phthalocyanine manufacturing plant is enriched with high COD content and significant amount of copper. This type of contamination can lead to the formation of mixed effluent, containing both heavy metal ions and organic materials which is a measure of the toxicant. The discharge of such mixed effluent into the environment is a serious problem facing numerous industries. The conventional treatment of metal ions in wastewater generally requires various processing steps such as chemical neutralization, precipitation of metals as hydroxide sludge and filtration followed by transportation and dumping. This treatment causes a loss of a few hundred tons of metals per annum and also contributes to environmental problems [2].

In view of the measures exposed above, electrolytic treatment is a promising process that has been investigated as an alternative to treat wastewaters since the early 1960s [3] without producing or with minimum quantities of sludge [4] permitting the recovery of metal along with the oxidation of organic contaminants in solution with minimum consumption of chemicals. This method has been successfully tested with various industrial wastewaters such as metal plating industries [5] in the detoxification of wastewater containing cyanides [6–8], phenols [9–12], wastewater from dye production [13,14], tannery [15,16] and others [17–19].

In recent years, there is an increasing interest in the development of effective electrochemical methods for the removal of metal ions from wastewaters [5,20]. The metal ions can be effectively recovered from dilute solution using ion exchange technique, but the high cost of resin limits its application [21,22] while, the electrolytic process has the advantages of metal recovery without further sequential treatment.

Generally in electrolytic metal recovery, the rate of metal ion transfer in dilute solution is low. To overcome this problem, three-dimensional cathodes in different forms have been investigated by many researchers because they provide high specific surface area and high mass transfer rates [23–25].

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Table 1
Characteristics of the Cu-phthalocyanine dye process stream.

Parameters	Value
COD (mg/l)	23,000
TOC (mg/l)	7584
Copper (mg/l)	~1450
pH	<1
Free acid (sulphuric)	10–15%
Total dissolved solids (mg/l)	97,180
Chlorides (mg/l)	735
Sulphates (mg/l)	168,138

Marco et al. studied a very dilute effluent (Cu = 340 mg l^{-1}, COD = 10,000 mg l^{-1}, SO$_4{}^{2-}$ = 30,000 mg l^{-1}) of the same industry using three-dimensional copper foam electrodes and they achieved 90% copper recovery at 140 min with the CE of 20.1% and 15.23 kWh/kg Cu [26].

In the present study, the authors investigated the technical feasibility of the metallic copper deposition on stainless steel cathode and oxidizing the organic contaminants from the real mixed effluent of copper-phthalocyanine dye industry by varying the experimental conditions such as temperature, current density and anode materials. In addition to that, experiments were conducted to evaluate the influence of 3D stainless steel turning cathode on copper recovery with high current efficiency (η) and less energy consumption.

2. Materials and methods

The wastewater containing the copper ions and high strength COD used for the present study was collected from the filtration unit of the copper-phthalocyanine dye manufacturing plant with an average effluent discharging capacity of 100 m^3/day which is produced by a discontinuous process using phthalic anhydride, urea and cupric chloride. The characteristics of the effluent were determined according to the standard methods [27] and given in Table 1. The batch electrolytic experiments have been carried out in the raw effluent without changing the pH under galvanostatic condition. The electrolysis cell used in the present study consists of a glass beaker of 250 ml capacity closed with a PVC lid having provision to fit a cathode and two anodes. Salt bridge with reference electrode (SCE) was inserted through the hole provided in the lid (Fig. 1). The cathode was a stainless steel material type 304 purchased from Lawrence Metal Suppliers, Chennai (India) with effective area of 27.3 cm^2 and a commercially available DSA (TiO$_2$–RuO$_2$–IrO$_2$, a mixed triple oxide coated on titanium mesh) of area 23.6 cm^2 was used as anode. The electric power was supplied by a DC Aplab 7771 power unit (Aplab limited, Chennai, India) and stirring was done with a magnetic stirrer. The effluent volume of 200 ml was taken for all the experiments. Electrolyses were carried out as such in the raw effluent at different current densities (5, 4, 3, 2 and 1 A dm^{-2}), temperatures (30, 40, 50 and 60 °C) and different anode materials such as graphite, RuO$_2$/Ti and SnO$_2$/Ti. The above oxide anodes RuO$_2$/Ti and SnO$_2$/Ti were prepared in the laboratory by thermal decomposition of the precursors with RuCl$_3$·nH$_2$O, H$_2$IrCl$_6$, TiCl$_3$ and SnCl$_4$·5H$_2$O SbCl$_3$, H$_2$IrCl$_6$, TiCl$_3$, respectively dissolved in propane-2-ol and hydrochloric acid under O$_2$ flux. The appropriate precursor mixtures of each electrode composition are applied by brushing both sides of the pre-treated Ti-support. After application of each coating, the electrode was heated in an air furnace at 100 °C for 5 min to polymerise the coating, then calcinated at 500 °C for 5 min. The electrode was coated with 10–12 layers to achieve the desired loading.

In order to study the influence of the high organic contaminants on the recovery of copper from the raw effluent, experiments have been carried out in the synthetic effluent without any organic
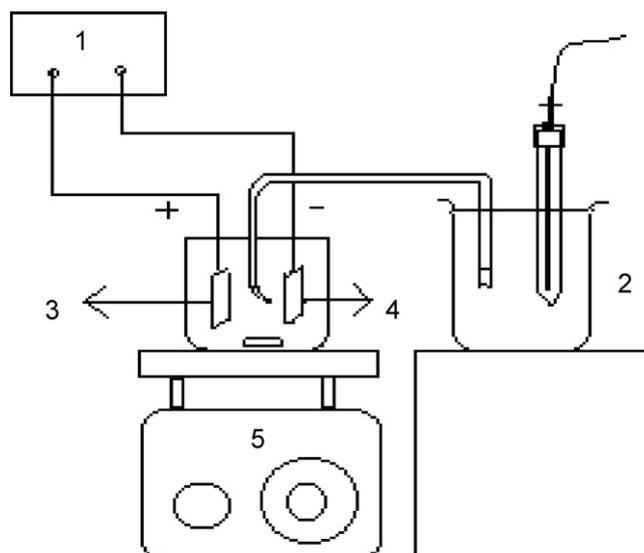
Fig. 1. A schematic view of batch experimental setup: 1. power supply 2. reference electrode 3. anode 4. cathode 5. magnetic stirrer.

contaminants containing ~1450 mg l^{-1} of Cu in 15% H$_2$SO$_4$. The reproducibility was checked by performing all the experiments to a minimum of at least three times. The samples were collected at different time intervals and analysed for Cu, COD and TOC. The Cu was determined using the atomic absorption spectrometer GBC-932 plus model, the COD was determined by open reflux dichromate titration method according to the standard methods [27] and the TOC of the initial and electrolyzed solutions was determined using TOC analyzer micro N/C model (Analytika Jena, Germany).

The current efficiency related to the recovery of copper (η_{Cu}) and removal of COD (η_{COD}) was calculated using Eqs. (1) and (2):

$$\eta_{Cu} = 100 \times \frac{2F \times (Cu_{ini} - Cu_{fin}) \times V}{63.5 \times It} \tag{1}$$

$$\eta_{COD} = \frac{100 \times (COD_{ini} - COD_{fin})V}{\text{mass of oxygen equivalent to electricity}}$$

$$= \frac{100 \times 2F \, \Delta COD \, V}{16Q} \tag{2}$$

where (Cu$_{ini}$ and Cu$_{fin}$) and (COD$_{ini}$ and COD$_{fin}$) are the copper (mg l^{-1}) and COD (mg l^{-1}) concentrations at initial and final times, respectively, and I is the current passed (A), T is the electrolysis time (h), F is the Faraday constant (26.8 A h), V is the volume of electrolyte (dm^3) and Q (A h) is the charge passed for the electrolysis.

3. Results and discussion

3.1. Effect of temperature

Investigations have been carried out in the raw effluent (~1450 mg l^{-1} of Cu) under galvanostatic condition in a batch electrolytic undivided cell. In order to obtain maximum copper recovery, experiments were conducted at 1 A dm^{-2} of low hydrogen evolution condition by varying the temperatures (Fig. 2). The depletion of the copper ions is evaluated by measuring the remaining Cu^{2+} concentration in the electrolytic cell as a function of electrolysis time and the results are presented in Table 2. From the results, it is evident that the copper exists as free ions in the effluent and hence the maximum recovery of copper of about 98% could be obtained at 30 °C. It is implicit that the experiments carried out in the temperature range of 40–60 °C would not result in any significant variation (<1%) in the recovery of copper (97.7–98.6%).
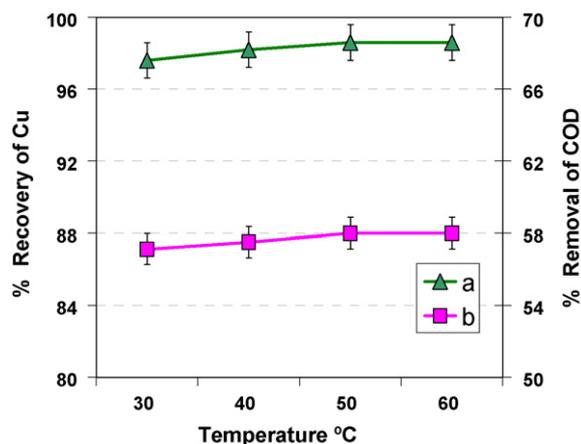
Fig. 2. Effects of temperature on the efficiency of (a) recovery of Cu and (b) COD removal in the electrochemical treatment of Cu-phthalocyanine dye process stream after a 5-h electrolysis. Experimental conditions: CD: $1\,A\,dm^{-2}$, anode: DSA.

Similarly with the increase of temperature, a minor variation (<1%) was noticed for the COD removal efficiency. At 30 °C, nearly 57.2% of COD was removed which may be attributed to the direct and indirect oxidations. It is a known fact when chloride ions are present in acid media (pH <2), the main active species is Cl_2 which is an indirect oxidant. Hence, the COD removal in the treatment could have been facilitated by the active chlorine generated at the anode. With increase of temperature, there is a possibility for the escape of chlorine. Hence in this case one would expect lower COD removal value but it was observed from the results that the COD removal value lies within a narrow range (57.2–58%) (Fig. 2). This can be accounted for the role played by the catalytic anode in enhancing the oxidation and maintaining the degradation rate constant. Thus, the electrolysis at $1\,A\,dm^{-2}$ and 30 °C, is considered to be the optimum condition for the maximum recovery of copper with a simultaneous removal of COD from the effluent.

3.2. Effect of cell current density

For the electrochemical treatment of industrial effluents, it is very important to achieve high current efficiency in order to provide a cost-effective process. The effect of current density was studied using a commercial DSA as anode material and the results are presented in Fig. 3. The results reveal that the COD removal increases significantly from 58% to 87% with the increase of current density from 1 to $5\,A\,dm^{-2}$ both at 30 and 50 °C. In the case of copper recovery only a marginal increase is noticed at 30 °C (Fig. 3A), whereas a gradual decrease is observed at 50 °C (Fig. 3B) with the increase of current densities. These results reveal that at higher current densities, the anodic oxidation of organics was enhanced owing to the electro-catalytic activity of DSA whereas the efficiency of copper recovery was lessened with increase of current density at high temperature owing to the high hydrogen evolution at the cathode resulting in the peal off of the powdery copper deposits formed on the electrode surface. From the above investigations, it is evident that the maximum copper recovery was achieved at $1\,A\,dm^{-2}$ and 30 °C. The adherent deposit was seen at $1\,A\,dm^{-2}$ and 30 °C with 100% copper as revealed by SEM and EDX (Fig. 4A).

At $5\,A\,dm^{-2}$, the copper recovery of 96.5% and COD removal efficiency of about 87.3% with the energy consumption of about 59.01 kWh/kg removal of Cu was achieved at 5-h of electrolysis at 30 °C (Fig. 3A). It implicit that in dilute solution, while increasing the current density, the transport rate of copper ions from the solution to the cathode surface was much slower than the reduction rate of Cu^{2+} ions (Fig. 5A). The CE was found to be very low of about 2.5%
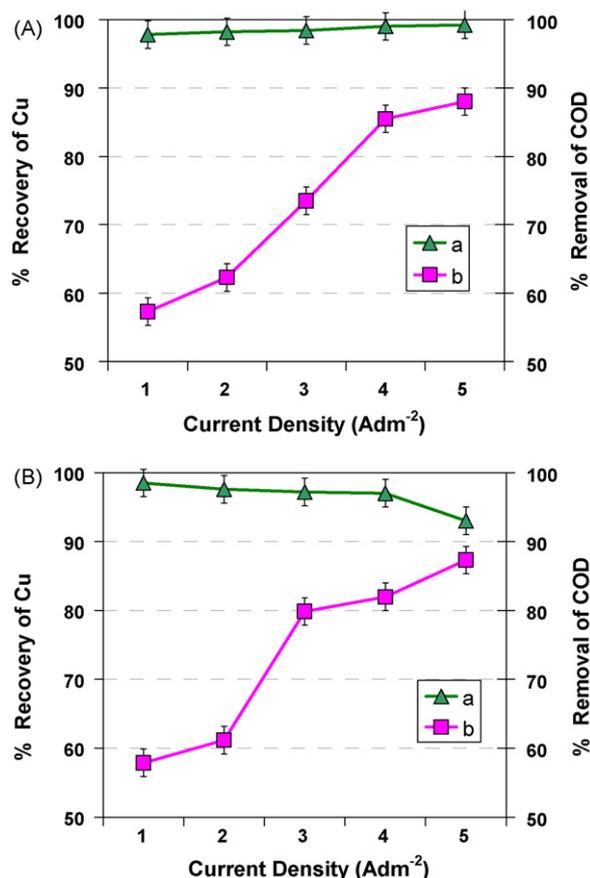
Fig. 3. Effects of current density on the efficiency of (a) recovery of Cu and (b) COD removal in the electrochemical treatment of Cu-phthalocyanine dye process stream at different temperatures after a 5-h electrolysis. Experimental conditions: (A) $T = 30$ °C and (B) $T = 50$ °C, anode: DSA.

(Fig. 5B). The SEM and EDX studies confirm the granular deposition of copper (Fig. 4B) and the oxide formation near the edges of the electrode surface (Fig. 4C) at high current density.

Depending on the solution composition of the effluent, different reactions can occur at the electrodes. In the present study, following possible reactions would have taken place within the electrolytic cell.

Cathode

$$Cu^{2+} - phthalocyanine + 2e^- \rightarrow Cu \tag{3}$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (acid)} \tag{4}$$

Anode

$$organic\ pollutants \rightarrow oxidised\ products\ +\ CO_2 +\ ne^- \tag{5}$$

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \text{ (acid)} \tag{6}$$
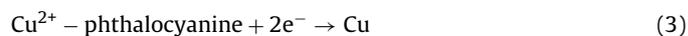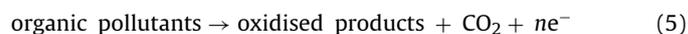
The prevalence of more or less constant cell voltage and electrode potentials throughout the electrolysis (Table 2) has evidenced the fact that neither the formation of non-conductive film nor the occurrence of corrosion at the electrode surface.

3.3. Effect of anode materials

The anodic oxygen evolution is in fact the main cause for the high energy consumption in wastewater treatment, which in turn reduces the overall current efficiency for both direct and indirect oxidation. Therefore, the use of an anode material of catalytic nature or electrode with higher oxygen over voltage which exhibits a better performance is desirable, as this can
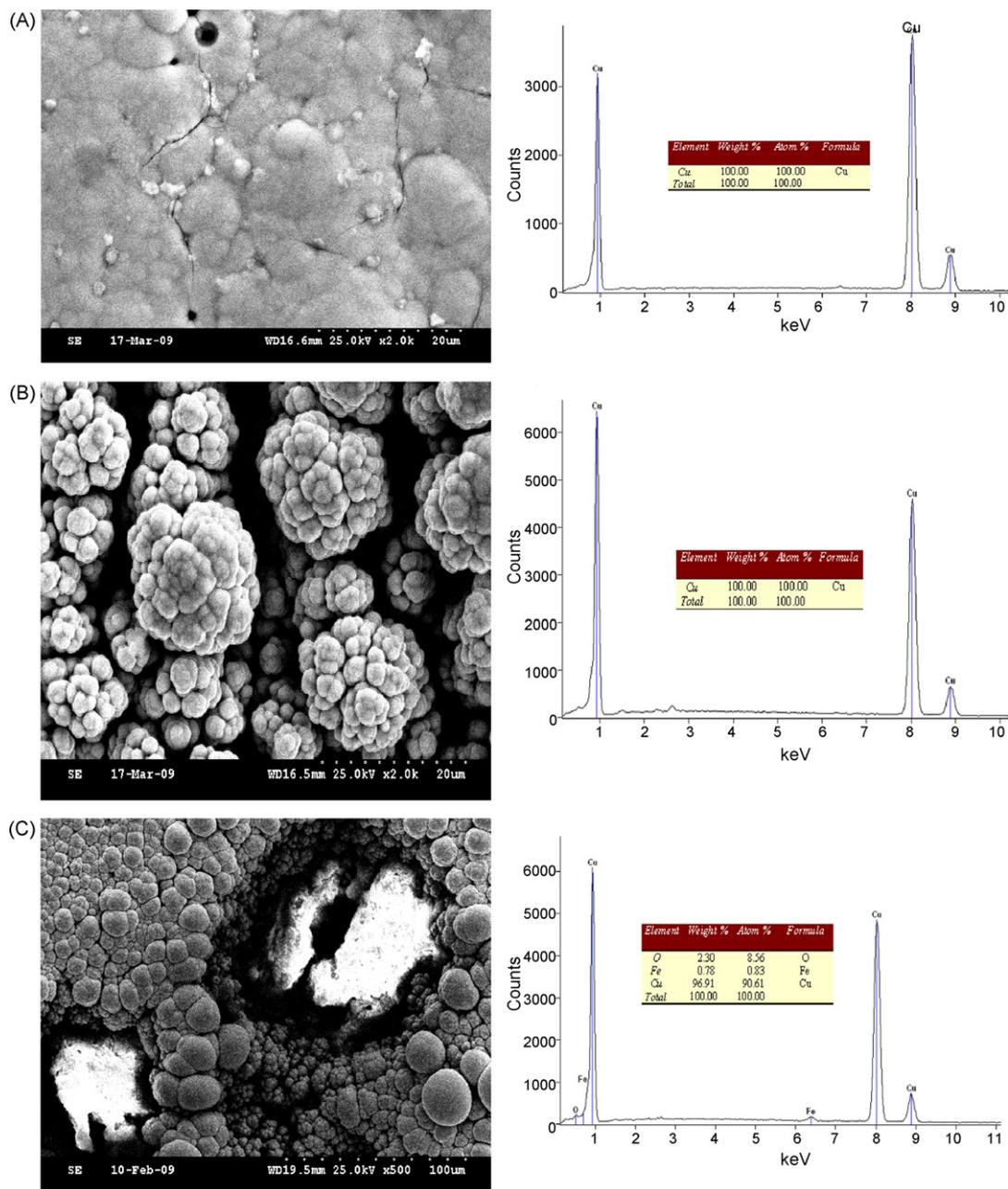
Fig. 4. SEM surface images and EDX spectrum of copper deposition on stainless steel plate from the copper- phthalocyanine process stream at different current densities: (A) 1 A dm^{-2} (100% Cu), (B) 5 A dm^{-2} (100% Cu), and (C) 5 A dm^{-2}. Oxide formation (96.9% Cu).

minimize the unwanted power loss. In the present investigation though the copper recovery from the highly acidic effluent is the prime objective, the stability and the influence of anode materials on the concomitant removal of COD, were also been studied, to have a better understanding on the synergistic phenomena. Hence, three different anode materials such as graphite, RuO$_2$/Ti, and SnO$_2$/Ti anodes have been employed in the present study. Fig. 6 shows the effect of the above anode materials on the electrolytic treatment of the effluent at different experimental conditions. Among the three electrodes, the energy consumption was slightly higher when graphite was used and RuO$_2$/Ti exhibited the highest COD removal efficiency. The advantages claimed for RuO$_2$/Ti and SnO$_2$/Ti (DSA) anodes over a graphite electrode are the (i) lower cell voltage, (ii) lower power consumption, and (iii) electrode erosion did not take place unlike graphite electrode [28].

3.4. Influence of organic contaminants on copper recovery

In a mixed industrial effluent the presence of metal ions retard the destruction of organic contaminants and the presence of the organic species reduce the efficiency of recovery of the metal [29]. Hence, the recovery of copper from the effluent is compared with a synthetic effluent free from organic compounds (15% H$_2$SO$_4$ containing ~1450 mg l^{-1} copper) using RuO$_2$/Ti anode and stainless steel cathode at two different temperatures and current densities for which the results are presented in Table 2. At low current density, the CE for the recovery of copper is around 30.3% and 12.2% for the synthetic and real effluents, respectively. The very low CE in real effluent is mainly attributed to the presence of large amounts of organic species (high COD) that hinder significantly the rate of copper recovery and enhances the energy consumption during the electrolysis (Fig. 6B and C). The energy consumption for the recov-

Table 2

Influence of cathodic current density and temperature on the electrolytic recovery of copper from (a) 15% H_2SO_4 containing ~1450 mg/l copper and (b) Cu-phthalocyanine dye process wastewater using 2D-SS cathode and DSA anode after a 5-h electrolysis.

T (°C)	$CD_{cathodic}$ (A dm^{-2})	CV (V)		Charge (Ah)		%Removal of [a]Cu		[a]$\eta_{cathodic}$ (%)		Energy consumption kWh/kg removal			%Removal of TOC[b]
		a	b	a	b	a	b	Cu[a]	Cu[b]	Cu[a]	Cu[b]	COD[b]	
30	1	1.1	1.6	0.8	2	99	97.5	30.3	12.0	3.06	11.23	1.19	15.8
	5	1.6	2.4	1.5	10	99	98.6	16.2	2.41	8.35	83.94	6.08	23.9
50	1	1.3	1.8	0.7	2	99	98.5	34.6	12.1	3.17	12.60	1.34	5.7
	5	1.6	2.5	2.0	10	99	93.0	12.1	2.27	11.15	92.69	6.16	14.8

[a] η—current efficiency corresponding to the recovery of copper in the respective conditions.
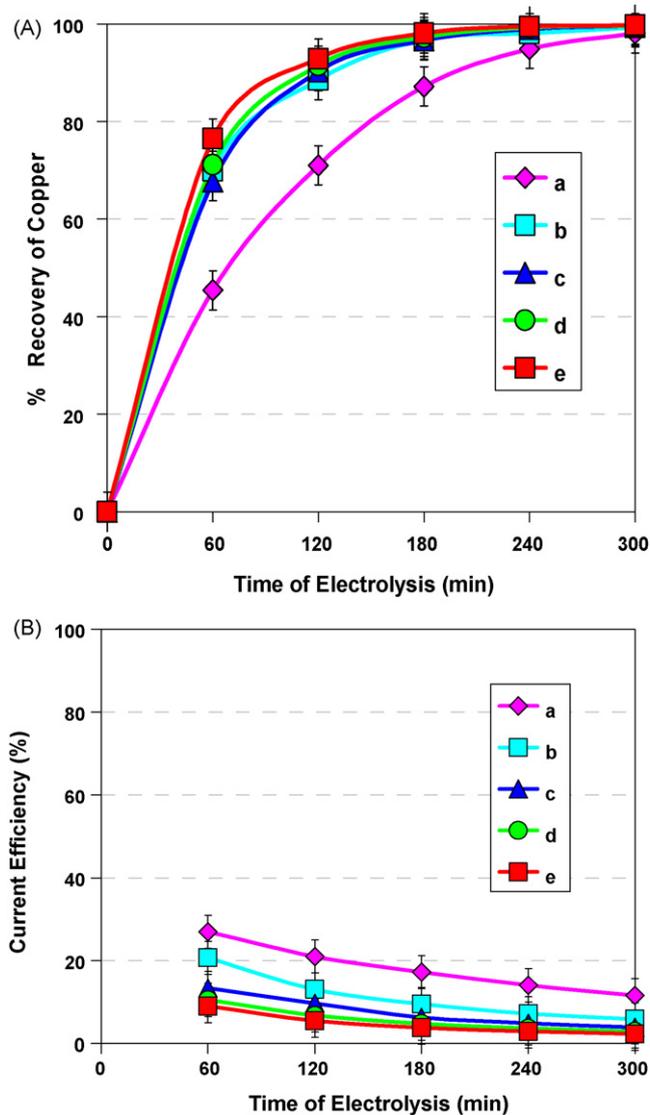
Fig. 5. Effects of cathodic current density on copper recovery from the Cu-phthalocyanine dye process stream during the electrolytic treatment. (A) Copper recovery efficiency and (B) current efficiency. Experimental conditions: CD (A dm^{-2}) (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5. $T = 30$° C, anode: DSA.

ery of copper from the real effluent is 3.5 times higher than that of the synthetic effluent (15% H_2SO_4) containing only ~1450 mg l^{-1} copper without other impurities (Table 2).

3.5. Energy cost for copper recovery on 2D and 3D electrode

In this study, initially the feasibility of the copper recovery was experimented using 2D stainless steel cathode reactor and subsequently in order to improve the metal recovery and CE, the
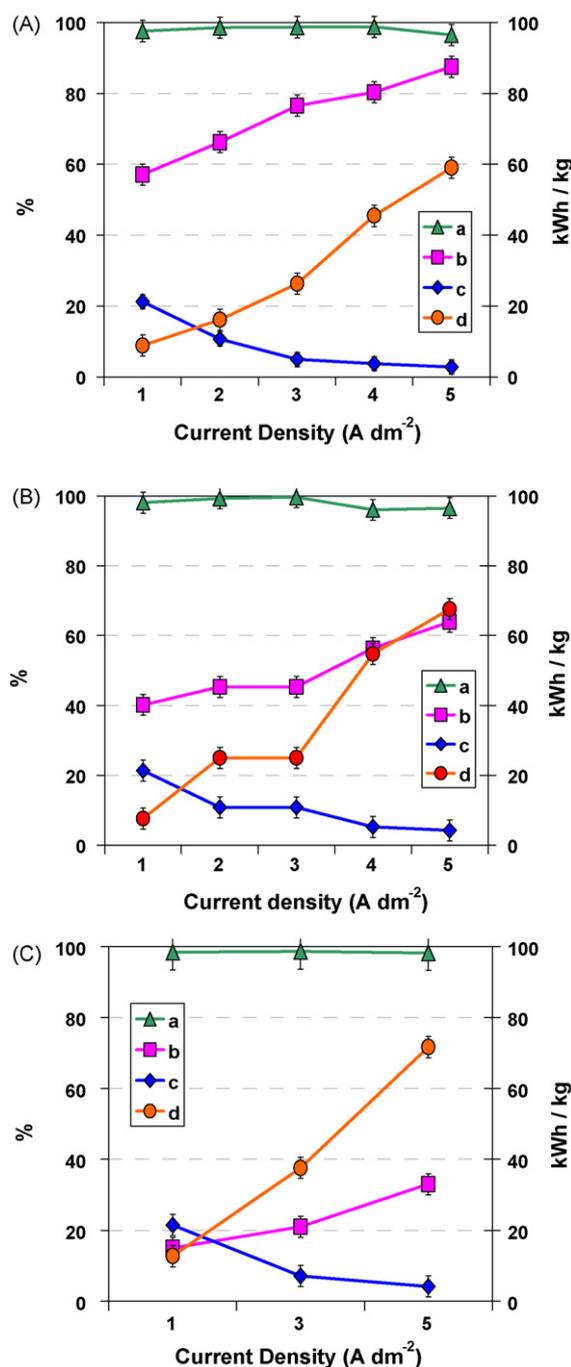
Fig. 6. Effect of current density on the electrochemical treatment of Cu-phthalocyanine dye process stream using different anode materials after a 5-h of electrolysis. (A) RuO_2/Ti, (B) SnO_2/Ti, and (C) Graphite. (a) Recovery of Cu (%), (b) COD removal (%), (c) cathodic current efficiency (%), and (d) energy consumption for removal of copper (kWh/kg). Experimental conditions: $T = 30$ °C.

Table 3

Electrolytic recovery of copper from the highly acidic Cu-phthalocyanine dye process stream using 3D stainless steel turnings at 0.5 A dm^{-2} at different time intervals (cathode area = 172.25 cm^2).

S. No.	Time (min)	CV (V)	% Removal of copper	η_{cathodic} (%)	Energy consumption kWh/kg removal of Cu
1	10	1.3	48.2	82.3	1.33
2	20	1.5	75.8	64.7	1.95
3	30	1.6	99.5	56.8	2.37

electrolysis has been carried out using 3D stainless steel turning cathode reactor, which has a large electrode surface area and high mass transfer rate. The energy consumption for each process at a given time (t) was obtained from the following equation:

$$\text{energy consumption (kWh/kg)} = \frac{\text{energy}}{\text{recovery of copper}} \qquad (7)$$

$$\text{energy} = V\,(\text{V}) \times I\,(\text{A}) \times t\,(\text{h}) \times 10^{-3}$$

$$\text{recovery of copper (kg)} = (\text{Cu}_{\text{ini}} - \text{Cu}_{\text{fin}}) \times \text{volume of effluent (l)} \times 10^{-6}$$

where V—average cell voltage, I—current passed, t—electrolysis time.

A 3D stainless steel turning cathode reactor could rapidly recover 99.5% of copper from real effluent with an acceptable current efficiency of about 56.8% and minimum energy consumption of 2.37 kWh/kg removal of copper, in comparison to a 2D parallel-plate reactor (Tables 2 and 3).

By applying Eq. (7), the energy cost for the electrolytic treatment of the effluent was calculated in a flow condition. From these experimental results, it was observed that the energy required for the treatment of 3 dm^3 effluent (98.2% copper recovery of about 4.272 g with 0.08178 kWh) using 2D electrode, i.e. the specific energy consumption required for this treatment process was around 19 kWh/kg recovery of copper, while using the 3D stainless steel electrode in the above treatment condition, it was observed that (99.5% copper recovery of about 4.33 g and energy of 0.01759 kWh) the specific energy consumption drastically reduced to 4.064 kWh/kg. The average energy consumption for treating 1000 dm^3 of the copper phthalocyanine process stream in a 2D reactor is ~27.3 kWh whereas that in a 3D reactor is only 5.86 kWh and the quantity of copper recovered from this volume is around 1.443 kg. Moreover, the surface area provided by the 3D electrode is around 10 times higher than the 2D electrode of the same weight of stainless steel used in this study. Thus, the 3D electrochemical treatment can be operated with minimum capital investments and moreover, a significant savings in the purchase of chemicals (used in the chemical treatment process) could be achieved, as there is no need of chemicals to be added in the effluent for the maximum recovery of copper and substantial amount of COD removal.

4. Conclusion

The copper recovery is the first step in the sequence of operations of the wastewater management of copper-phthalocyanine dye process industry. In this paper, electrochemical investigations have been carried out to study the simultaneous recovery of copper and removal of COD from the acidic process stream of copper-phthalocyanine dye production unit without altering the pH or adding any chemicals with a considerable reduction in the amount of sludge to waste. Using 2D stainless steel cathode under favorable condition, 98.2% of copper was recovered with an energy consumption of 11.23 kWh/kg and CE of 12%, after a 5-h of electrolysis from the raw effluent. The presence of large amount of organic contaminants in the effluent (high COD), hinders significantly the

rate of copper recovery and enhances the energy consumption during the electrolysis. No significant variation could be observed for copper recovery using different anode materials. Among the three electrodes studied, the COD removal efficiency was highest for RuO$_2$/Ti electrode. The 3D stainless steel turning cathode reactor could rapidly recover copper of 99.5% from effluent with an acceptable current efficiency of about 56.8% and minimum energy consumption of 2.37 kWh/kg removal of copper. Thus, the electrolytic treatment was found to be a promising and cost-effective treatment for the copper-phthalocyanine dye effluent compared to the traditional treatment techniques, as an additional savings due to the marketing of the recovered copper, elimination of hazardous sludge handling and disposal costs is also accomplished in this electrochemical treatment. After the electrolytic treatment, the effluent (<10 mg/l Cu and COD ~10,000 mg/l, pH <1) becomes easy for further treatment. As a second phase, to mineralize the copper recovered effluent and also to extend the present experimentation for industrial trial run, bench scale studies are under progress in our lab by adopting suitable treatment techniques such as advanced oxidation processes followed by electro coagulation and ultra filtration. Finally the treated water can be reused for various process activities of the plant.

Acknowledgements

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