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Copper recovery and simultaneous COD removal from copper phthalocyanine dye effluent using bipolar disc reactor

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ABSTRACT

Electrochemical treatment of real acidic effluent of copper phthalocyanine dye manufacturing plant with a view to explore the feasibility of the simultaneous removal of copper and phthalocyanine using a bipolar disc electrochemical reactor has been investigated. Experiments were conducted in a bipolar capillary gap disc stack electrochemical reactor under batch recirculation mode. Electrodes were RuO_2 and IrO_2 coated on titanium as anode and titanium as cathode. Effects of current density, electrolysis time and effluent flow rate on copper recovery and simultaneous COD removal and energy consumption were critically examined. The current density of 2.5 A dm^{-2} and flow rate of 20 L h^{-1} achieved 91.1% COD removal and 90.1% copper recovery with the energy consumption of 50.86 kWh kg^{-1} for COD removal and simultaneous recovery of copper in a bipolar disc stack reactor.

Keywords: Bipolar disc stack reactor; Batch recirculation; Electrochemical oxidation; Copper recovery; Phthalocyanine removal

1. Introduction

The syntheses of phthalocyanine compounds have established themselves as blue and green dyestuffs par excellence. They are important industrial commodity, used primarily in inks (especially ball point pens), colouring for plastics and metal surfaces, and dyestuffs for jeans and other clothing. Copper phthalocyanine is the most brilliant and is highly coloured dyestuff, a blend of blue to green. The process wastewater let out from the copper phthalocyanine manufacturing plant has a high COD content and significant amount of copper. This type of contamination leads to the formation of mixed effluent, containing both heavy metal ions and organic materials which are toxicants depending on their concentration. It is mandatory to treat the effluent before letting it out. Conventional treatment techniques are inadequate. In this context, researchers have been trying various alternative processes such as electrochemical techniques (Panizza and Cerisola, 2009; Martinez-Huitle and Brillas, 2009; Raghu and Ahmed Basha, 2007; Koparal et al., 2007), ozonization (Lackey et al., 2006), photocatalytic methods (Gumuş and Akbal, 2011; Bizani et al., 2006), sonication (Dehghani et al., 2010), etc. Researchers are also using, for example in indirect oxidation-electrochemically generated oxidant, chlorine, hypochlorite, peroxide, ozone and Fenton's reagent for pollutant degradation (Li and Pang, 1994).

Electrochemical methods have been successfully applied in treatment of several industrial wastewaters (Faouzi et al., 2006; Panizza et al., 2007; Mahesh et al., 2006). The choice of electrode material is of fundamental importance from

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electrochemical point of view. Boron doped diamond (BDD) and dimensionally stable anode (DSA, titanium substrate is covered by metallic oxides such as TiO_2, IrO_2, RuO_2, SnO_2) materials were widely studied for application in waste treatment systems (Costa and Olivi, 2009; Kapałka et al., 2008; Maezono et al., 2011; Miwa et al., 2006; Rodriguez et al., 2009; Scialdone et al., 2009; Sirés et al., 2008; Zhou et al., 2011). Some researchers are focused on bipolar disc stack reactor for effluent treatment processes. Bonvin and Comninellis (1994) studied bipolar stack reactor scale up and developed a relation for the current bypass in terms of dimensionless number. Muthukumar et al. (2004) studied the treatment of textile dye wastewater using bipolar disc stack reactor. The electrode was made up of RuO_2 coated titanium as anode and titanium as cathode. The authors reported that higher flow rate and lower reservoir hold-up gave a higher COD removal. Bhadrinarayana et al. (2007) studied the electrochemical oxidation of cyanide and cadmium removal using graphite in the bipolar disc stack reactor. The authors observed more than 99% cyanide destruction and 98% removal of cadmium in the plating rinse water. Panizza et al. (2000, 1999) studied a very dilute effluent (Cu^{2+} 340 mg L^{-1}, COD 10,000 mg L^{-1}, $SO_4{}^{2-}$ 30,000 mg L^{-1}, copper phthalocyanine 4900 mg L^{-1}, Cl^- 5000 mg L^{-1}) of ACNA, Cengio, Italy, using three-dimensional copper foam cathode and O_2-evolving DSA coated titanium mesh anode in a pilot plant and achieved 90% copper recovery at 140 min with the Current Efficiency of 20.1% and Energy Consumption of 15.23 kWh (kg Cu)$^{-1}$. Chellammal et al. (2010) and Subbaiah et al. (2003) studied the process wastewater coming out from the copper phthalocyanine manufacturing plant in a galvanostatic batch reactor using stainless steel as cathode, DSA and graphite as anodes and optimized conditions for the maximum copper recovery of 98% and COD removal efficiency of 87.3%.

Bipolar disc stack reactors have been attracted great interest, because of their simple geometry. The radially divergent flow in gaps will highly enhance the rate of electrochemical reaction for low-conducting fluids. A planar radially symmetric flow is enforced at the inner edge of the disc and directed outward through gaps. As the flow proceeds in the radial direction, the channel is widened, in proportion to the increasing radius. Therefore, we have a laminar decelerating divergent flow. Bipolar disc reactors are widely preferred for electrochemical reactions due to their compactness and the lower cost of the electrical equipment. The main disadvantage of this electrochemical reactor is the presence of parasitic electrical currents or bypass currents, in the electrolyte inlet and outlet of the electrode stack. The objective of the present investigation is simultaneously removing the copper-phthalocyanine dye manufacturing plant using the bipolar cell using titanium disc electrodes and each one of the discs coated with RuO_2 and IrO_2. On one side of the disc electrode copper got deposited due to electrochemical reduction and simultaneously on other side phthalocyanine concentration also got reduced due to electrochemical oxidation.

2. Materials and methods

The effluent containing the copper ions and high strength COD, used for the present study, was procured from (M/s Mazda Colours Limited, Mumbai) the filtration unit of the copper-phthalocyanine dye production plant (discharging an average effluent capacity of 100 m^3 day^{-1} 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 (Clesceri et al., 1998) and they are given in Table 1.

Table 1 – Characteristics of the copper-phthalocyanine dye process stream.

S. No.	Parameters	Value
1	COD (mg L^{-1})	23,500
2	TOC (mg L^{-1})	7584
3	Copper (mg L^{-1})	1450
4	pH	<1
5	Free acid (sulphuric)	10–15%
6	Total dissolved solids (mg L^{-1})	97,180
7	Chlorides (mg L^{-1})	735
8	Sulphates (mg L^{-1})	168,138

2.1. *Experimental setup*

The schematic diagram of the experimental setup is shown in Fig. 1a, with a perspective view of the disc stack system (Fig. 1b). The setup consists of a reservoir, a magnetically driven self-priming centrifugal pump, a rotameter and the electrolytic cell connected to an electrical circuit consisting of a 3 A/120 V regulated DC power supply, an ammeter, and a voltmeter. The electrolytic cell is made of perspex that contained 11 titanium disc electrodes and each one of the discs coated with RuO_2 and IrO_2. The cell stack consists of two circular polyvinyl chloride (PVC) end frames 1.25 cm thick. A hollow cylindrical perspex rigid tube with an inner diameter of 5 cm and height of 11 cm is placed between these two frames. The two titanium discs were fixed onto the two PVC end frames. One titanium disc and another titanium disc having RuO_2 and IrO_2 coating was placed at each end frame. Theses two discs act as feeder electrodes, and the remaining nine discs are arranged between these two discs. The inner radius (r_i) and outer radius (r_o) of the disc are 5 mm and 24.5 mm, respectively. The spacers (s), which are comprised of 3-mm-thick polypropylene bits, isolate the electrodes from each other (see Fig. 1b). A feeder electrode at the top acts as the anode while the bottom electrode acts as the cathode. In this way, the reactor acts as a stack of 10 unit cells fed into the solution in a parallel manner, maintaining the current series and flow parallel configuration system. The stack of circular disc electrodes has a 1-cm central bore, through which the electrolyte flows inward and the overflow was collected in the reservoir from the top of the reactor and continuously recirculated. Provisions have been made for the electrolyte inlet and outlet. The free volume of the electrolyzer is 40 mL, and the reservoir capacity is 1.0 L. The area of each disc is 0.18072 dm^2. Thus, the total area of anode/cathode for 10 unit cells is 180.72 cm^2. The effluent from the filtration unit of the copper-phthalocyanine dye manufacturing plant was taken without changing the pH.

2.2. *Experimental procedure*

Electrolysis was conducted under galvanostatic condition in a batch continuous recirculation mode. One litre of raw effluent was taken for each experiment and circulated at the flow rate of 20 L h^{-1} through the reactor, and the current density applied was 2.5 A dm^{-2} for the electrolysis. The extent of COD removal as well as the extent of copper recovery was studied under various conditions such as different current densities