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Electrochemical degradation of textile dyeing industry effluent in batch and flow reactor systems

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ABSTRACT

Electrochemical oxidation of organic pollutants present in the dye-bath and wash water effluents from the textile industry was carried out in batch, batch recirculation and recycle reactor configurations under different conditions of current density, treatment duration, effluent flow rate and electrode specific surface. COD reduction of 52.63% to 82.61% could be obtained when the Procion blue dye-bath effluent was treated in the batch reactor for 8 h. In batch recirculation reactor, the reduction was 94.3% for dye-bath effluent and 91.4 for wash water effluent after 6 h of operation at a current density of 5.0 A dm^{-2} and flow rate of 100 L h^{-1}. The specific energy consumption was found to be 4.32 kWh $(kg\ COD)^{-1}$ for dye-bath effluent and 83.8 kWh $(kg\ COD)^{-1}$ for wash water effluent. The results for wash water effluent under continuous operation of recycle reactor conditions showed 52.86% of COD removal at recycle flow rate of 100 L h^{-1} with discharge flow rate of 3 L h^{-1}. The specific energy consumption was found to be 11.9 kWh $(kg\ COD)^{-1}$.

1. Introduction

Textile processing industries consume large volumes of water and chemicals generating effluents which when discharged cause undesirable water pollution. Even the presence of very low concentrations of dyes in effluent interferes with the penetration of light in water bodies and may affect the aquatic biota [1]. Some dyes and their degradation products have been shown to be toxic, mutagenic and carcinogenic in nature [2]. Physicochemical processes such as adsorption, biosorption, membrane filtration, coagulation by salts, biological oxidation, chemical degradation etc., are some of the generally employed methods for treating textile industry wastewater. The physicochemical methods have many disadvantages in terms of efficiency, cost, regeneration or secondary pollution. Conventional activated sludge and other types of bioreactors fail to remove sufficient color and other micro-pollutants present in textile effluents [1]. Novel, low cost efficient processes are needed in view of the more stringent environmental regulations and in this context, processes such as, electrochemical techniques [3–8], ozonization [9], photo-catalytic methods [10–11], sonication [12], enzymatic treatments [13], and engineered wetland systems [14] are being tried by researchers for the treatment of textile wastewater.

The choice of electrode material is important in any electrochemical study. Dimensionally stable anode (DSA) material has found wide application in electrochemical wastewater treatment, the most common being the $Ti/Ru_{0.3}Ti_{0.7}O_2$ (Cl_2-evolution) anode, which has been extensively used in the chlor-alkali industry for long. DSA has been classified as “active” or “non-active”, depending on its chemical nature [14–16]. When active electrodes are present, they mediate the oxidation of organic species by the formation of higher oxidation state oxides of the metals. When non-active electrodes are present, there is no higher oxidation state and the organic species are directly oxidized by an adsorbed hydroxyl radical, generally resulting in complete combustion of the organic molecule (e.g., SnO_2, PbO_2, boron doped diamond, and Ti/Pt).

The biodegradability index (BI) is defined as the ratio of BOD to COD and is a useful indicator of the total oxidation that occurs during electrolysis [16–19]. Morais et al. [17] reported that effluents with BI smaller than 0.3 are not suitable for biological degradation. According to Chamarro et al. [18] the effluent must have a BI of at least 0.4 for complete biodegradation. It is reported that a waste with BI of >0.4 can be treated by a biological system while a BI of <0.25 indicates a toxic waste [16–19].

When an active electrode is used for mineralization, BOD initially marginally increases and COD decreases thus enhancing the BI. When an inactive electrode is employed, the organic species is directly oxidized by an adsorbed hydroxyl radical, resulting in complete combustion of the organic molecule thereby decreasing the BOD, COD and BI or marginally enhancing the BI [20–22]. Sakalis et al. [23] studied the electrochemical degradation of azo dyes in batch and continuous flow

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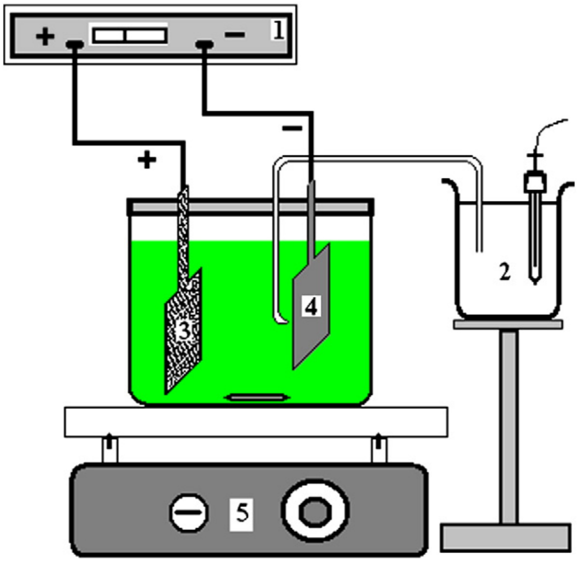

Fig. 1. A schematic view of batch experimental set-up (1. Regulated power supply, 2. Reference electrode, 3. Noble oxide coated catalytic anode, 4. Cathode 5. Magnetic stirrer.).

experiments using Ti/Pt anode for both real and synthetic wastewater samples and reported an increase in BI value from 0.23 to 0.28 due to partial combustion of the organic molecule. When commercial pesticides were treated in a laboratory scale electrolysis using Ti/Pt as anode and stainless steel 304 as cathode the BI ratio was found to increase considerably from 0.125 to 0.36 [24] indicating that the electrochemical oxidation can be a possible pretreatment method for pesticide detoxification.

Electrochemical oxidation of refractory organic contaminants present in effluents by noble oxide coated anode tends to increase BOD (by forming group –OH, –CHO, –CO, and –COOH) decrease COD and marginally increase BI. The dye house of a textile processing industry releases two types of wastewater, viz., dye-bath wastewater and wash wastewater in volume ratios of 15% and 85% respectively. The dye-bath wastewater causes more pollution and its treatment is more difficult due to its intense color, high COD, low biodegradability and high-salt content.

In the present study, the dye-bath and wash water effluents of a textile industry were subjected to electrochemical oxidation in batch reactor, batch recirculation flow reactor and continuous recycle reactor with the objective of reducing the color and the COD. Experiments were conducted under different conditions of current density, flow rate, specific electrode surface and electrolysis time and the performance was analyzed in terms of specific power consumption. The dye-bath and wash water effluents were treated separately instead of treating them after mixing them as generally practiced. Ultimately a sort of pinch technology can be devised, to integrate electrochemical technique (the knowledge of specific energy/charge required), with the conventional biological treatment method for complete mineralization of the effluent.

Table 1
Characteristics of selected dye bath and wash water.

Characteristics	Dye-bath effluent	Wash water
Color	Purple blue	Dark olive green
Initial COD (mgL^{-1})	5800	560
Initial BOD ($mg\,L^{-1}$)	181	30
BI (=BOD/COD)	0.03	0.05
Chloride content (mgL^{-1})	38995	1500
Total dissolved solids (mgL^{-1})	52,000	3200
Suspended solids (mgL^{-1})	2000	800
pH	9	8

2. Materials and methods

All the reagents, used in this study, were of analytical grade. Procion Blue hydrolyzed dye-bath wastewater and wash water samples were collected from a dyeing industry located in Tiruppur, Tamilnadu, India. The effluent samples were analyzed according to American Public Health Association (APHA) procedures [25] and their characteristics are given in Table 1. Experiments were carried out using a RuO_x–TiO_x coated [26] titanium substrate insoluble anode (TSIA) and a stainless steel cathode.

2.1. Batch reactor

Fig. 1 gives the schematic diagram of the batch reactor. It consists of a cylindrical glass container closed with a lid in which electrodes of size 7.7 cm × 6.5 cm are fitted with constant gap between them. The lid is designed so as to facilitate sample collection and to enable the connection of reference electrode through the salt bridge. The electrical energy for the system was drawn from a regulated power supply and a magnetic stirrer was employed for stirring the effluent. Experiments were conducted at room temperature under galvanostatic conditions with a mixture of reactive hydrolyzed dyes effluent of initial COD 5800 $mg\,L^{-1}$ and BOD 181 $mg\,L^{-1}$ under various operating conditions of reactor holdup volumes (300 mL, 400 mL, and 500 mL), and current density (1.0, 2.0, 3.0, 4.0, and 5.0 $A\,dm^{-2}$). The electrode area exposed to the effluent varied with the volume of effluent thereby varying the current passed to give the required current density. All experiments were carried out for 8 h and the cell voltage, anode potential and cathode potential were noted down periodically. The samples were collected every hour, kept at acidic conditions and analyzed for COD. After electrolysis, chlorides, hypochlorites and chlorates concentrations were determined and percentage reduction of COD, energy consumption and rate constant were computed experimentally.

2.2. Batch recirculation reactor

The electrolytic flow reactor set-up, operated in batch recirculation mode is shown in Fig. 2a and b. It consists of an expanded mesh of titanium (coated with TiO_x–RuO_x) anode and stainless steel flat plate cathodes in between a PVC frame. The anode mesh is fixed in between two parallel cathode plates (7 cm × 7 cm) with an inter-electrode gap of 1.25 cm. The available effective electrode area is 39.2 cm^2 for anodic reactions. The electrodes are connected to a 5 A, 30 V DC regulated power supply, an ammeter and a voltmeter in order to supply a constant current. The reactor with a holdup volume of 0.588 dm^3 has an inlet and outlet and is connected using silicon rubber tubes to a reservoir of 2.5 L volume, a magnetically driven self-priming centrifugal pump and a rotameter. The set-up can be operated either in batch recirculation or in continuous recycle mode wherein streams 10 and 12 are in closed state for the former and are in open state for the latter.

1.5 L of dye-bath effluent having initial COD of 5800 $mg\,L^{-1}$ and BOD of 181 $mg\,L^{-1}$ was taken and experiments were carried out at two different current densities of 2.5 $A\,dm^{-2}$ and 5.0 $A\,dm^{-2}$. At each current density, experiments were conducted for five different flow rates of 20, 40, 60, 80 and 100 $L\,h^{-1}$. The electrode plates were cleaned manually by washing with distilled water before every run. All the experiments were carried out for 6 h in batch recirculation mode under galvanostatic conditions during which the cell voltage was noted and the samples were collected periodically for COD analysis. The dye-bath effluent feed and the samples obtained when treated under the current density of 5.0 $A\,dm^{-2}$ and flow rate of 80 $L\,h^{-1}$ were subjected to spectral analysis.