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Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment

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Abstract

The present investigation revealed that all the reactive dyes were degraded in chlorine mediated electrochemical oxidation. Titanium based dimensionally stable anode (DSA) was used for in situ generation of chlorine in the dye solution. All classes of reactive dyes (100 mg/L) showed a complete color removal at a supporting electrolyte concentration of 1.5 g/L NaCl and 36.1 mA/cm² current density. The chemical oxygen demand (COD) and total organic carbon (TOC) removals were from 39.5 to 82.8% and from 11.3 to 44.7%, respectively, for different reactive dyes. It can be concluded in general that the triazine containing higher molecular weight diazo compounds takes more time for complete de-colorization than the mono azo or anthraquinone containing dye compounds. The degradation rate of mixed dye compounds was affected by reaction temperature, current density, NaCl concentration and initial dye concentration. However, the initial pH of the dye solution ranging from 4.3 to 9.4 did not show significant effect on de-colorization. A complete color removal with 73.5% COD and 32.8% TOC removals were obtained for mixed reactive dyes (200 mg/L) at the end of 120 min of electrolysis under the optimum operating conditions of 4 g/L NaCl concentration and 72.2 mA/cm² current density.

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Keywords: Reactive dyes; Electrochemical oxidation; DSA; Active chlorine; COD; TOC; UV-vis spectra; Wastewater treatment

1. Introduction

Textile processing industries nowadays are widespread sectors in developing countries. Among the various processes in the textile industry, dyeing process uses large volume of water for dyeing, fixing and washing process. Thus, the wastewater generated from the textile processing industries contains, suspended solids, high amount of dissolved solids, un-reacted dyestuffs (color) and other auxiliary chemicals that are used in the various stages of dyeing and other processing. The presence of even small amount of dye in water (example 10–20 mg/L) is highly visible and affects the water transparency and the gas solubility of water bodies [1]. Among several classes of textile dyestuffs, the reactive dyes contribute about 50% [2] of the total market share and the most common group used as chromophore is the azo (70%), followed by anthraquinone [3].

Several wastewater treatment technologies have been applied for color removal, including physical, chemical and biological process. All of them have advantages and drawbacks and a combination of different technologies are generally required. The biological treatment of textile wastewater showed low degradation efficiency because of the presence of biologically inert high molecular weight dyestuffs [4,5]. The conventional method of textile wastewater treatment consists of chemical coagulation (using ferrous, lime and polyelectrolytes), biological treatment followed by activated carbon adsorption. The conventional coagulation process generates huge volume of hazardous sludge and poses a problem of sludge disposal. In order to meet the legal requirements for the discharge of textile wastewater, researchers are attempting a combination of two or more treatment methods for the complete and successful removal. Combination of electrochemical treatment and chemical coagulation [6], combined chemical coagulation, electrochemical oxidation, and activated sludge process [7], and combination of electrochemical method, chemical coagulation, and ion exchange [8] were reported for textile effluent treatment to comply with the legal requirements or for reuse standards. However the previous investigators demonstrated combined process successfully, the generation of iron sludge due to the usage of sacrificial iron electrodes is another problem.

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Hence, many investigators are studying alternative oxidation methods like ozonation, photocatalytic oxidation, electrochemical oxidation, etc. The photocatalytic oxidation experiments were conducted for acid blue 80 [9], acid orange 7 [10], brilliant orange K-R [11], and reactive orange 16 [12]. However, this process may not have practical feasibility for real textile industry wastewater treatment due to the inhibition of photocatalytic activity at low pH. Because, the isoelectric point of TiO₂ is around 6.3, so the TiO₂ particles carry positive charges when the solution pH is lower than 6.3. Thus, chloride ions can be adsorbed to the positively charged TiO₂ particle surface at low pH due to ionic force. Similarly, surficial holes of TiO₂ will be blacked by chloride ions will lead to decrease the formation of hydroxyl radicals, resulting in the low photocatalytic efficiency since the dyeing industry wastewater contains large amount of chloride in the effluent. The electrochemically assisted photochemical degradation was also conducted to improve the degradation efficiency of the dye [13]. Ozonation process was studied for the removal of color and chemical oxygen demand (COD) [14]; however, this process showed a less COD removal [15].

Electrochemical treatment is an emerging technology used for the removal of organic and inorganic impurities from water and wastewater. Hence, many researchers are attempting to use electrochemical methods for the treatment of wastewater. In the electrochemical process, the pollutants are destroyed by either the direct or indirect oxidation process. In a direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In an indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, and hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in situ and are utilized immediately [16]. Among the oxidants, generation of hypochlorite is cheaper and most of the effluents have a certain amount of chloride. Though direct electrolysis of organic compounds at the anode surface is also possible, a major portion of oxidation is mediated by active chloro species when conducting electrochemical oxidation in the presence of chloride using an undivided cell.

Anode:

$$2Cl^{-} \rightarrow Cl_2 + 2e^{-} \tag{1}$$

Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (2)

Bulk solution:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$
 (3)

$$HOCl \rightarrow H^{+} + OCl^{-} \tag{4}$$

The application of indirect electrochemical oxidation mediated by chlorine/hypochlorite was studied for textile industry effluents by several investigators. Vlyssides and Israilides [17] studied the electrochemical degradation of textile dye and finishing wastewater using Ti/Pt anode. At the end of 40 min of elec-

trolysis, there was 92% COD, 92.2% BOD and 94% color reduction with energy consumption of 44 kWh/kg of COD removal. Szpyrkowicz et al. [18] conducted experiments using seven different electrode materials for the degradation of disperse dyes. The best results were obtained in a chloride rich medium under acidic pH using Ti/Pt-Ir anode. Muthukumar et al. [19] studied the textile wastewater treatment using Ti/RuO2 anode and reported that a maximum COD reduction was observed at an optimum operating conditions of 80 dm³/h flow rate and 5 A/dm² current density. Recently, boron doped diamond (BDD) anode was studied for dye degradation using sodium sulfate as supporting electrolyte. Degradation of acid orange 7 by electrochemical method using BDD anode showed a complete color removal with more than 90% COD reduction [20]. Similarly, Chen et al. [21] reported a very high COD removal for various dye compounds with high current efficiency using the BDD electrode.

Since the real textile dyeing industry is using different kinds of dyestuffs with varying concentrations, nine dye compounds containing azo, antraquinone and triazine groups were selected for chlorine mediated electrochemical degradation. Though, sodium sulfate or sodium chloride is the common salts used for the dyeing process, most of the textile processing industries are using sodium chloride due to less cost. Hence, it was decided to study with sodium chloride as supporting electrolyte using a titanium based dimensionally stable anode (DSA).

2. Materials and methods

Bulk oxidation of reactive dyes was carried out using an undivided electrochemical cell in a galvanostatic condition. The anode was a titanium mesh coated with oxides of titanium, ruthenium and iridium available in the commercial market. The cathode was stainless plate. The effective surface area of anode and cathode were 27.7 and 50 cm², respectively. The electrodes were positioned vertically and parallel to each other with an inter-electrode gap of 10 mm in a 1 L reactive dye solution. A dc power supply was used as the source of constant electric current for the experiments (UP-3010S model, Unicorn Co. Limited, South Korea). To enhance the mass transport and to maintain a uniform concentration of the electrolyte, the reactor solution was constantly stirred at 300 rpm using a magnetic stirrer. The temperature of the reactor was maintained constantly using an external water re-circulation system. A schematic illustration of the experimental setup is shown in Fig. 1.

The temperature and pH values were measured using Hanna Instruments pH meter equipped with a temperature sensor. The initial pH of the dye solution was set appropriately using dilute solutions of either sodium hydroxide or sulfuric acid. UV–visible spectra during the degradation of dyes were recorded between 200 and 800 nm using a scanning UV–visible spectrophotometer (Jasco model V-530, Japan). The visible color removals for the mixed reactive dyes were measured at optimum absorption wavelength of 516 nm in order to study the effects of various operating parameters. The color removals during the experiments with individual dye compound were measured at their optimum visible absorption wavelength. Samples

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