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Electrochemical oxidation of textile wastewater and its reuse

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Abstract

It is attempted in the present investigation to treat organic pollutant present in the textile effluent using an electrochemical treatment technique. Experiments are carried out in a batch electrochemical cell covering wide range in operating conditions. Due to the strong oxidizing potential of the chemicals produced, the effluent COD is reduced substantially in this treatment technique. The influence of effluent initial concentration, pH, supporting electrolyte concentration and the anode material on pollutant degradation has been critically examined.

It is further attempted in the present investigation to reuse the treated wastewater for dyeing purpose. Several cycles of dyeing operations have been performed with the treated textile wastewater and the dye uptake and water quality have been critically examined at each cycle of dyeing process. The results indicate that the electrochemical method is a feasible technique for treatment of textile wastewater and electrochemically treated wastewater can be effectively reused for dyeing application.

Keywords: Electro-oxidation; Wastewater treatment; Reuse

1. Introduction

The day-to-day human activities and industrial revolution have influenced the flow and storage of water and the quality of available fresh water. Many industries like textile, refineries, chemical, plastic and food-processing plants produce wastewaters characterized by a perceptible content of organics (e.g. phenolic compounds) with strong color. For example, a typical textile dyeing process consists of desizing, scouring, bleaching, dyeing, finishing and drying operations. Except the last two stages, each operation is associated with rinsing step, requires large amount of water. In general, textile industries generate effluent at an average of 100–170 l kg^{-1} of cloth processed, which is characterized by strong color, high COD with wide variation in pH [1,2].

Conventionally effluents containing organics are treated with adsorption, biological oxidation, coagulation, etc. Though the conventional methods have individual advantages, they are lacking of effectiveness if applied individually. For example, biological treatment is the most efficient and economic way of reducing the environmental impact of the industrial effluents containing organic pollutants, but this technique is time consuming and cannot be employed for textile effluent, as textile effluent is recalcitrant to biodegradation. On the other hand, the physical adsorption is expensive and difficult for adsorbent regeneration. Further, biological and chemical methods generate considerable quantity of sludge, which itself requires treatment. Due to the large variability of the composition of textile wastewater, most of the traditional methods are becoming inadequate [3–5]. As environmental regulations become stringent, new and novel processes for efficient treatment of various kinds of wastewater at relatively low operating cost are needed. In this context, researchers are trying various alternative processes, such as electrochemical technique, wet oxidation, ozonization, photocatalytic method for the degradation of organic compounds. Among these advanced oxidation processes, the electrochemical treatment has been receiving greater attention in recent years due to its unique features, such as versatility, energy efficiency, automation and cost effectiveness [6,7].

In electrochemical technique, the main reagent is the electron, called 'Clean Reagent' degrades all the organics present in the effluent without generating any secondary pollutant or

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by-product/sludge. The electrochemical technique offers high removal efficiencies and has lower temperature requirements compared to non-electrochemical treatment. In addition to the operating parameters, the rate of pollutant degradation depends of the anode material. When electrochemical reactors operate at high cell potential, the anodic process occurs in the potential region of water discharge, hydroxyl radicals are generated [8]. On the other hand, if chloride is present in the electrolyte, an indirect oxidation via active chlorine can be operative [9,10]. Naumczyk et al. [11] have demonstrated several anode materials, such as graphite and noble metal anodes successfully for the mediated oxidation of organic pollutants. Comninellis [12] experimented anodic oxidation of phenol in the presence of NaCl using tin oxide coated titanium anode and reported second order kinetics for the degradation of phenol at the electrode surface. Fernandes et al. [13] studied the degradation of C.I. Acid Orange 7 using boron-doped diamond electrode and reported that more than 90% of COD removal. Anastasios et al. [14] demonstrated 94% dye removal using a pilot plant electrochemical reactor for textile wastewater treatment.

The use of new anodic materials like boron-doped diamond (BDD) has also been reported in recent years as BDD electrodes present additional properties including high resistance to corrosion, high thermal stability, hardness, good electrical conductivity, etc. Panizza et al. [15] have demonstrated 2-naphthol oxidization in acid media using synthetic BDD thin film electrodes and reported complete incineration of 2-naphthol. Bellagamba et al. [16] reported on electro-combustion of polyacrylates [PA] under galvanostatic conditions using BDD anode at various current densities and in a wide range of PA concentrations. Canizares et al. [17] studied the electrochemical oxidation of several phenolic aqueous wastes using bench-scale electrochemical flow cell with boron-doped diamond anode. Complete mineralization of the waste was obtained in the treatment of phenols not substituted with chlorine or nitrogen. The authors reported that efficiencies of the process depend strongly on the concentration of organic pollutants and on their nature, and not on the current density, at least in the operation range studied.

The reported works are intended to treat the textile wastewater to a level that meets the discharge standards of pollution control board. However, due to dwindling water supplies, increasing demand of the textile industries and stringent pollution control board regulations, a better alternative is to further elevate the quality of treated wastewater to a standard where it can be reused. Though extensive work has been reported on various treatment techniques, the literature on reuse of treated wastewater is scarce. The objective of the present work is thus to study the electrochemical treatment of textile effluent using oxide coated anodes and reuses the treated wastewater for dyeing process.

2. Theory

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode; on anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where they are generated continuously [indirect electrolysis]. In direct electrolysis, the rate of oxidation is depending on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions [18]. The reactions of anodic oxidation of chloride ions to form chlorine is given as

$$2Cl^- \xrightarrow{k_1} Cl_2 + 2e^- \tag{1}$$

The liberated chlorine form hypochlorous acid (Eq. (2))

$$Cl_2 + H_2O \xrightarrow{k_2} H^+ + Cl^- + HOCl \tag{2}$$

and further dissociated to give hypochlorite ion (Eq. (3)).

$$HOCl \underset{k_3'}{\overset{k_3}{\longleftrightarrow}} H^+ + OCl^- \tag{3}$$

The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation. The direct electro-oxidation rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density. A generalized scheme of the electrochemical conversion/combustion of organics of pollutant [19] on noble oxide coated catalytic anode (MO_x) is given below. In the first step, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction.

$$MO_x + H_2O \rightarrow MO_x(^\bullet OH) + H^+ + e^- \tag{4}$$

In the second step, generally the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide MO_{x+1}.

$$MO_x(^\bullet OH) \rightarrow MO_{x+1} + H^+ + e^- \tag{5}$$

At the anode surface, the “active oxygen” can be present in two states. Either as physisorbed (adsorbed hydroxyl radicals ($^\bullet OH$) or/and as chemisorbed (oxygen in the lattice, MO_{x+1}). In the absence of any oxidizable organics, the “active oxygen” produces dioxygen according to the following reactions:

$$MO_x(^\bullet OH) \rightarrow MO_x + \tfrac{1}{2}O_2 + H^+ + e^- \tag{6}$$

$$MO_{x+1} \rightarrow MO_x + \tfrac{1}{2}O_2 \tag{7}$$

When NaCl is used as supporting electrolyte Cl ion may react with $MO_x(^\bullet OH)$ to form adsorbed OCl radicals according to the following [20]:

$$MO_x(^\bullet OH) + Cl^- \rightarrow MOx(^\bullet OCl) + H^+ + 2e^- \tag{8}$$

Further, in presence of Cl ion, the adsorbed hypochorite radicals may interact with the oxygen already present in the oxide