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Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes

S. Karthikeyan, A. Titus, A. Gnanamani, A.B. Mandal, G. Sekaran *

Environmental Technology Division, Council of Scientific & Industrial Research (CSIR)-Central Leather Research Institute (CLRI), Adyar, Chennai, 600 020, India

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ABSTRACT

In the present investigation an attempt was made to degrade organic pollutants in the textile effluent by homogeneous and heterogeneous Fenton systems. Experiments were carried out under the batch as well as under the continuous operating conditions. The effect of time, pH, H_2O_2 concentration, $FeSO_4.7H_2O$ concentration and the mass of mesoporous activated carbon on the degradation of organics in the wastewater were critically examined. The kinetic constants and the thermodynamic parameters for the oxidation of organics in wastewater were determined. The quantitative removal of COD, BOD and TOC from the wastewater was evaluated. The degradation of organics in textile wastewater was confirmed through FT-IR, UV–Visible spectroscopy, and cyclic voltammetry.

1. Introduction

Textile Industry employs a wide spectrum of chemicals viz. enzymes, detergents, dyes, acids, sodium salts etc. for the conversion of natural fibers into textile fibers. The conventional treatment systems that are used in the effluent treatment plants or in the common effluent treatment plants, include primary clarifier, secondary biological aerobic system, secondary clarifier, sand filter and activated carbon filter [1]. The wastewater discharged from the textile industry seldom meets the discharging standards prescribed by the pollution control boards in India. This is due to the presence of high COD to BOD ratio, unspent dyes and total dissolved solids. The poor biodegradability of wastewater is due to the presence of high concentration of azo dyes. The major pollutants identified in the textile wastewater are high pH, color, nutrients (nitrogen and phosphorus), inorganic salts and refractory organics [2,3].

The azo and other chromophoretic groups in the dye matrix render geno toxicity to the biodiversities in the environment. Advanced Oxidation Processes (AOPs) have been suggested for the partial or complete removal of pollutants in the wastewater or their transformation into less toxic and more biodegradable products. Furthermore, the partial decomposition of non-biodegradable organic pollutants can lead to biodegradable intermediates. There are indications of partial decomposition, elimination of chromophoretic groups, increase in the solubility index of the compounds and reduction in the aromaticity which lead to an improvement in the biodegradability of the textile wastewater by AOPs.

Fenton oxidation, one of the AOP's was studied extensively by many researchers for the treatment of wastewater containing refractory/xenobiotic organic compounds [4,5]. The sequential steps that take place in the process of Fenton oxidation of organics in wastewater are shown below.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \qquad k = 70\ M^{-1}\ s^{-1} \tag{1}$$

$$OH^{\bullet} + RH \rightarrow CO_2 + H_2O \qquad k = 10^9\text{–}10^{10}\ M^{-1}\ s^{-1} \tag{2}$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{3}$$

$$H_2O_2 + Fe(OH)_3 \rightarrow H_2O + O^{\bullet} + Fe(OH)_3 \tag{4}$$

Eq. (1) suggests that there is a wide scope for the precipitation of ferric ion with hydroxide ions as ferric hydroxide. The ferrous ion is excessively used in order to sustain the Fenton oxidation reaction. This demands a post treatment for the Fenton oxidized wastewater for the decontamination of heavy metal pollution. Moreover, the ferric hydroxide sludge produced is the source for the decomposition of hydrogen peroxide. Thus, the generation of sludge and huge consumption of chemicals were the identified disadvantages of homogeneous Fenton oxidation of organics in wastewater. This can be overcome by the following two methods (i) providing a sink to abstract an electron from hydroxyl ion to generate hydroxyl radical [6] and (ii) providing a second matrix phase to prevent the ferric ion from combining with the hydroxyl ion. Mesoporous Activated Carbon (MAC) has been shown to possess the above two characteristics. The active sites of MAC are made available for the adsorption of organic compounds according to the energy

* Corresponding author at: Environmental Technology Division, Central Leather Research Institute, Adyar, Chennai, 600 020, India. Tel.: +91 44 24452491; fax: +91 44 24912150.
E-mail address: ganesansekaran@gmail.com (G. Sekaran).

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possessed by them [7]. The organic compounds are oxidized by hydroxyl radicals into their end products. Considering the favorable characteristics of MAC many researchers have applied it as heterogeneous catalyst for the oxidation of organics in wastewater [8–10]. However, it has been observed that the application of MAC for the Fenton oxidation of organics in the textile wastewater is limited. Thus, the focal theme of the present investigation was to demonstrate the performance of the Homogeneous followed by Heterogeneous Fenton oxidation processes (using MAC as heterogeneous catalyst) for the removal of dissolved organics in the wastewater at low residence time and with the low consumption of Fenton's reagent under batch and continuous mode operations [11].

2. Materials and methods

2.1. Preparation of electron rich activated carbon matrix

Rice husk, a precursor material obtained from the agro industry was used for the preparation of MAC in sequential steps such as carbonization at 400 °C and activation using phosphoric acid at 700 °C, 800 °C and 900 °C. The activated carbon samples were washed with distilled water until the wash water showed negative test for phosphate. The washed mesoporous activated carbon was dried at 110 °C to get the finished product and they were labeled as MAC_{700}, MAC_{800}, and MAC_{900} respectively.

2.2. Characterization of MAC samples

MAC_{700}, MAC_{800}, and MAC_{900} samples have been characterized for surface area, pore volume and pore size distribution using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer). The free electron density of MAC was determined by electron spin resonance spectroscopy (Bruker IFS spectrophotometer ESR). The elemental composition (Carbon, Hydrogen and Nitrogen content) of the MAC samples was determined using CHNS 1108 model Carlo-Erba analyzer. A Philips X' pert diffractometer was used to determine the crystallites present in the MAC_{800} sample by X-ray diffraction technique (XRD) and a Perkin-Elmer infrared spectrophotometer was used for the investigation of the surface functional groups in the MAC samples. The surface morphology of MAC was determined using Leo–Jeol scanning electron microscope and the Energy gap value of MAC was determined by using Diffuse Reflectance Spectroscopy.

2.3. Collection and pre-treatment of wastewater

The wastewater was collected from the overflow of a primary clarifier in an effluent treatment plant of a textile industry in Tamil Nadu, India. The wastewater was screened to remove the floating solids and was sand filtered to remove the suspended solids.

2.4. Fenton oxidation of organics in textile wastewater under batch mode

The effect of pH (2.5, 3.5, 4.5, 5.5, 7.0), the effect of concentration of hydrogen peroxide (3, 6, 9, 12 and 15 mM/L) and the effect of concentration of $FeSO_4.7H_2O$ (0.4, 0.8, 1, 1.4 to 1.8 mM/L) and effect of temperature (303, 313, 323, 333 K) were carried out to determine the optimum conditions for the oxidation of organics in the textile wastewater. The process consists of adjusting the pH of the sand filtered textile wastewater to the desired pH level using sulfuric acid (36N, sp. gr. 1.81, 98% purity). The homogeneous Fenton oxidation was carried out by dosing the textile wastewater with H_2O_2 and $FeSO_4.7H_2O$. Aliquots of samples were withdrawn every 1 h and analyzed for pH, ORP, BOD, COD and TOC according to the procedure reported in the standard methods for analysis of water and wastewater. The heterogeneous Fenton oxidation was carried out by dosing the wastewater with H_2O_2 (30% w/v) and FeSO4.7H2O followed by the addition of MAC_{800} (10 g/L). Air at a flow rate of 1.2 L/h and at a pressure 0.6 kg/cm^2 was applied at ambient temperature and pressure maintained for homogeneous and heterogeneous Fenton oxidation processes. The COD measured in the wastewater samples after Fenton oxidation of organics was corrected in accordance with the equation shown below to prevent the interference of H_2O_2 in COD analysis

$$COD_A = COD_M - R_P * 0.25 \quad (5)$$

where COD_A is the actual COD in the sample; COD_M is the measured COD and R_P is the residual hydrogen peroxide in the wastewater sample after Fenton oxidation.

2.5. Integrated homogeneous and heterogeneous catalytic treatment of organics in textile wastewater under continuous mode

A PVC reactor of height 50 cm and diameter of 6 cm was fabricated. The volume of reactor was 1 L with the working volume of 400 mL. The bottom of the reactor was filled with quartz stones covering a height of 8 cm and gravel above it for about 2 cm. The reactor was then filled with 150 g of the MAC and provision was made to distribute air in the MAC bed to facilitate oxygen transfer for oxidation as shown in Fig. 1. The outlet of the homogeneous reactor was the inlet to the heterogeneous reactor in the integrated catalytic treatment process. For simplification purposes the integrated catalytic treatment process is defined as heterogeneous process throughout this manuscript. The pH of the textile wastewater was adjusted to 3.5 using H_2SO_4 (36N, specific gravity of 1.81). 2 mM/L of H_2O_2 (30% w/v) and $FeSO_4.7H_2O$ (0.1 g/L) were added to the wastewater and then applied to the reactor through sample distribution system provided at the top of the reactor in the down flow direction. The flow rate was maintained in such a way that the hydraulic retention time provided was 1 h. The aliquots of sample were collected and analyzed for pH, ORP, BOD COD and TOC.

2.6. Instrumental analysis

The raw and the Fenton oxidized samples were scanned using UV–Visible spectrophotometer (Varian, Cary 100 Conc.). The FT-IR spectra of the MAC sample, raw wastewater sample and the treated wastewater sample were recorded using Perkin-Elmer infrared spectrophotometer for the identification of the functional groups. The dried samples were mixed with spectroscopic grade potassium bromide and made in the form of pellets at a pressure of about 1 MPa of dimensions; diameter, 10 mm and thickness, 1 mm. The samples were scanned in the spectral range of 4000–400 cm^{-1}. The Cyclic Voltagram was recorded for the untreated and treated wastewater samples at potential in the range +10 V to −10 V and current in the range +250 mA to −250 mA with a cyclic voltammeter (CHI600D type). The CV was recorded with Ag/AgCl as reference electrode and Pt wire as counter electrode. The working electrode was Pt and the scan rate was 0.1 V/s.

2.7. Physico-chemical analysis of the wastewater

The primary treated, sand filtered and the Fenton oxidized wastewater samples were analyzed for pH, BOD_5 (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), TOC (Total Organic Carbon) and TDS (Total Dissolved Solids), according to the methods summarized in the standard methods for the analysis of wastewater [12].

3. Results and discussion

3.1. Characterization of MAC

The characteristics of MAC samples are presented in Table 1. The maximum reflectance at a wavelength corresponding to 800 nm