Journal of Hazardous Materials 173 (2010) 544–551

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Application of response surface methodology for optimization of peroxi-coagulation of textile dye solution using carbon nanotube–PTFE cathode

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ARTICLE INFO

Article history:
Received 7 July 2009
Received in revised form 17 August 2009
Accepted 22 August 2009
Available online 31 August 2009

Keywords:
Advanced oxidation processes
Experimental design
Carbon nanotube
Peroxi-coagulation
Decolorization

ABSTRACT

The decolorization of C.I. Basic Yellow 2 (BY2) by peroxi-coagulation process based on carbon nanotube–PTFE electrode as cathode was studied in a batch reactor. Response surface methodology (RSM) was employed to assess individual and interactive effects of the four main independent parameters (electrolysis time, initial pH, applied current and initial concentration of the dye solution) on the decolorization efficiency. A central composite design (CCD) was employed for the optimization of peroxi-coagulation treatment of BY2. A second-order empirical relationship between the response and independent variables was derived. Analysis of variance (ANOVA) showed a high coefficient of determination value (R^2 = 0.949). Maximum decolorization efficiency was predicted and experimentally validated. The optimum electrolysis time, initial pH, applied current and initial dye concentration were found to be 16 min, 3, 200 mA and 15 mg l^{-1}, respectively. Under the optimum conditions established, high decolorization (>95%) was experimentally obtained for BY2. This study clearly showed that response surface methodology was one of the suitable methods to optimize the operating conditions. Graphical response surface and contour plots were used to locate the optimum point.

1. Introduction

Advanced oxidation processes (AOPs) have received great attention during the last years for removal of hazardous organic pollutants from contaminated water. Among AOPs, Fenton-based processes, whose high performance relies on the great oxidation power of hydroxyl radicals (OH•) formed from Fenton's reaction (1), have been experiencing a remarkable development due to their promising results in combination with easy handling [1,2]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^\bullet + H_2O \quad (1)$$

Hydrogen peroxide and ferrous ions are simultaneously produced in an aqueous medium by the bi-electronic reduction of the dissolved molecular oxygen (reaction (2)) and ferric ions (initially introduced at a catalytic concentration) (reaction (3)) [3–6]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

Electrogeneration of hydrogen peroxide usually occurs at carbon-felt [7–12] and carbon-polytetrafluoroethylene (PTFE) O_2-diffusion [13,14] cathodes.

The electro-Fenton method utilizes a Pt anode, while Fe^{2+} is added to the solution. The peroxi-coagulation is carried out with a sacrificial Fe anode, which continuously supplies soluble Fe^{2+} to the solution from the following reaction [15]:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (4)$$

The peroxi-coagulation method has been used for electrochemical degradation of 4-chlorophenol [16], aniline [17], chlorophenoxy and chlorobenzoic herbicides [15], 4-chlorophenoxyacetic acid [18], 2,4,5-trichlorophenoxyacetic acid [19], 4-chloro-2-methylphenoxyacetic acid [20], vegetal tannins [21] and gallic acid [22].

In our previous works, we have studied the decolorization of BY2, a model chemical for dyes, in aqueous acidic media by the peroxi-coagulation method with a carbon-PTFE and carbon nanotube–PTFE gas-diffusion electrodes as cathode. An artificial neural networks (ANN) model was developed to predict the performance of the decolorization efficiency by peroxi-coagulation process based on carbon-PTFE electrode [23,24]. We have also reported degradation and mineralization of BY2 by total organic carbon (TOC) and GC-MS analysis previously. GC-MS analysis verified the identity of intermediates and a reaction pathway based on them was proposed [24].

In this paper, we have used the response surface methodology to study the influence of experimental parameters (initial pH, initial dye concentration, electrolysis time and applied current) on the decolorization efficiency of BY2 by peroxi-coagulation

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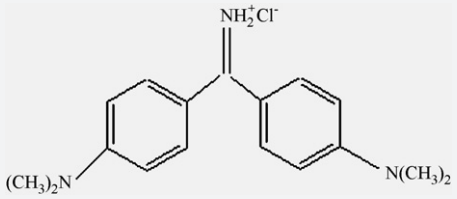
doi:10.1016/j.jhazmat.2009.08.120

Table 1
Characteristics of C.I. Basic Yellow 2.

Structure	
Commercial name	Auramin-O
C.I. number	41000
λ_{max} (nm)	432
Formula	$C_{17}H_{22}N_3Cl$
M_w (g mol^{-1})	303.83

with CNT–PTFE electrode as cathode and to determine the optimal conditions of dye decolorization. The color removal efficiency was selected as the response for optimization and the functional relationship between the response and the most significant independent variables (factors) was established by means of experimental design. Optimization of experimental parameters is usually assessed by systematic variation of one parameter while the others are maintained constant. However, this approach is unable to predict the best conditions of the process. In this respect, experimental designs are appropriate tools for this purpose. In fact, the experimental design allows considerable reduction of experiments number and a fast interpretation. In the experimental design, it is possible to study a large number of factors and to detect the possible interactions between them. All the parameters are simultaneously applied in order to calculate their relative effect [5]. Response surface methodology has been applied to model and optimize several wastewater treatment processes including adsorption [25,26], Fenton's oxidation [27] and photocatalytic decolorization processes [28].

2. Materials and methods

2.1. Chemicals

C.I. Basic Yellow 2 (BY2), a commercial dye (Boyakhsaz Co., Iran), was chosen as the model compound, whose characteristics was given in Table 1, and was used without further purification. Analytical grade sulfuric acid, anhydrous sodium sulfate, sodium hydroxide and *n*-butanol were obtained from Merck. Polytetrafluoroethylene (PTFE) solution and carbon papers were purchased from Electrochem, Iran and Pars Hydropasargad, Iran, respectively. Multi-walled CNT was produced by Cheap Tubes Inc., USA. The characteristics of multi-walled CNT have been reported previously [24].

2.2. Fabrication of the gas-diffusion electrode

Appropriate amounts of CNT (0.1 g), PTFE (0.42 g), distilled water (60 ml) and *n*-butanol (3%) were mixed in an ultrasonic bath (Grant, England) for 10 min to create a highly dispersed mixture. The resulting mixture was heated at 80 °C until it resembled an ointment in appearance. The ointment was bonded to 50% PTFE-loaded carbon papers and sintered at 350 °C for 30 min under inert conditions (N_2). The resulting plate was then cut to obtain operational CNT–PTFE plates of 25 mm diameter and about 0.6 mm thickness. The plate was placed at the bottom of a cylindrical holder of polypropylene. The cylindrical holder contains an inner graphite ring as current collector in contact with a copper wire as electrical connection. Fig. 1 shows the fabricated CNT–PTFE electrode schematically.

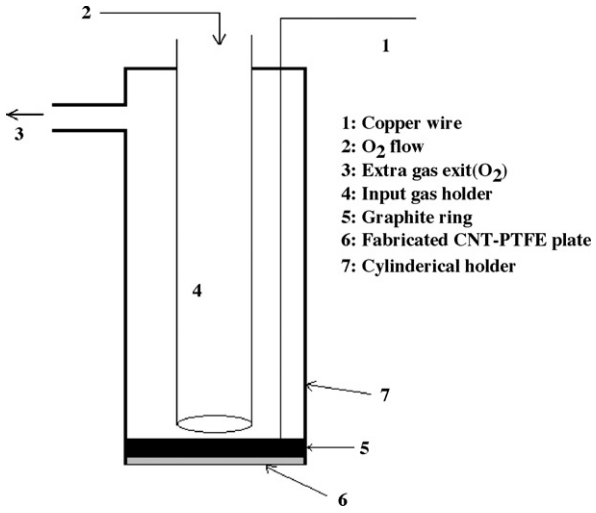


Fig. 1. Schematic diagram of the fabricated CNT–PTFE electrode.

2.3. Instruments

Electrolyses were performed with a DC power supply. The solution pH was measured with a Metrohm 654 pH-meter, Switzerland. The removal of color was followed by using UV–vis spectrophotometer (Lightwave S2000, England). Before analysis of samples extracted from solutions, they were filtered with 0.2 μm membrane filter (Schleicher & Schuell, Germany).

2.4. Electrolytic system

The experiments were conducted at room temperature in an open, undivided and cylindrical glass cell of 600 ml capacity and performed at constant current. The prepared CNT–PTFE electrode was selected as cathode and an iron sheet of 10 cm^2 area was used as anode. In all experiments, solutions were stirred magnetically. The diffusion cathode was fed with pure O_2 gas at 140 ml min^{-1} for the production of H_2O_2 from reaction (2). Samples (250 ml) containing dye concentration between 5 and 25 mg l^{-1} were comparatively degraded in the same acidic aqueous medium containing 0.05 M Na_2SO_4 as background electrolyte. The solution pH was continuously adjusted to desire pH every 10 min by adding small volumes of 0.5 M H_2SO_4 (maximum total volume added 5 ml). The decolorization efficiency (*R*%) is calculated by the following equation:

$$\text{Decolorization efficiency}\,(R\%) = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (5)$$

where C_0 and C are the dye concentrations (mg l^{-1}) at time 0 and t, respectively.

Samples were withdrawn from the reactor at desired time and the removal of color was evaluated by determining the absorbance of the solution at λ_{max} = 432 nm.

2.5. Experimental design

Response surface methodology (RSM) is a statistical method being useful for the optimization of chemical reactions and/or industrial processes and widely used for experimental design [29]. In this technique, the main objective is to optimize the response surface that is influenced by process parameters. RSM also quantifies the relationship between the controllable input parameters and the obtained response surfaces [30]. Process optimization by RSM is faster for gathering experimental research results than the rather conventional, time consuming one-factor-at-a-time approach [31].