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Research article

Enhanced sonocatalysis of textile wastewater using bentonite-supported ZnO nanoparticles: Response surface methodological approach

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ABSTRACT

The scope of this study was the use of bentonite as the carrier of ZnO nanoparticles for enhancing the sonocatalytic decolorization of Basic Red 46 (BR46) in the aqueous phase. The results demonstrated the higher sonocatalytic activity of bentonite-supported ZnO nanoparticles (BSZNs) in comparison with the suspended ZnO nanoparticles (SZNs). The particle size of BSZNs (5–40 nm) was lower than that of SZNs (20–120 nm). Due to the immobilization of ZnO nanoparticles, a specific surface area of 80.6 m^2/g was obtained for the BSZNs, which was higher than the specific surface area of the raw bentonite (42.2 m^2/g). Optimization of the process via response surface methodology (RSM) based on central composite design (CCD) showed the maximum sonocatalytic decolorization efficiency (%) of 89.92% in which the initial dye concentration, the ZnO/bentonite ratio, the sonocatalyst dosage, and the initial pH were 6 mg/L, 0.3, 2.5 g/L and 9, respectively. The byproducts generated during the sonocatalysis of BR46 over BSZNs were identified using gas chromatography–mass spectrometry (GC-MS) analysis. From an application viewpoint, the sonocatalysis of real textile wastewater resulted in a COD removal efficiency (%) of about 44% within a reaction time of 150 min.

1. Introduction

Synthetic organic dyes are widely used in various industries such as textile, cosmetics, carpet, rubber, printing, paper, leather, plastic, pharmaceuticals and refineries (Noorimotlagh et al., 2014; Tang et al., 2012). There are about 10,000 various types of synthetic dyes and over 700,000 tones are manufactured every year. About 10–20% of the produced organic dyes is lost during the process and released into the industrial effluents (Abdullah and Ling, 2010; Tang et al., 2012; Wang et al., 2007). The development of efficient methods of the decolorization is a subject of many experimental projects due to the adverse effects of synthetic organic dyes on terrestrial and aqueous environments. Most of the organic dyes can cause toxicity to aquatic life and carcinogenicity to human being (Noorimotlagh et al., 2014). Moreover, they adversely affect the nature of water body by preventing sunlight penetration (reduction in the photosynthetic phenomenon) and consuming dissolved oxygen (reduction in the self-purification capacity of aqueous environments) (Darvishi Cheshmeh Soltani et al., 2016a; Khataee et al., 2015b; Tang et al., 2012). However, conventional biological treatment technologies are not efficient enough for treating synthetic organic compounds because of the stability of synthetic dyes, low biodegradability and large number of aromatics present in their structure (Gao et al., 2015; Grčić et al., 2013). For this reason, some conventional physicochemical technologies such as adsorption, ultrafiltration, nanofiltration, reverse osmosis and coagulation-flocculation processes have been efficiently used for the removal of organic dyes. Nevertheless, these treatment processes are nondestructive and they only transfer dye molecules from aquatic phase to another phase, thereby producing secondary pollutants (Wang et al., 2007). Therefore, in recent years, too many researchers have focused on the application of advanced oxidation

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processes (AOPs), which generate one of the most powerful oxidizing agents (hydroxyl radicals ($OH^{\bullet}$)), to degrade non-biodegradable organic dyes in the aqueous phase. Among various AOPs, sonocatalytic processes using a suitable catalyst under ultrasonic irradiation can be promising technologies for the generation of $OH^{\bullet}$ in the solution and subsequently, the efficient degradation of refractory organic compounds (Darvishi Cheshmeh Soltani and Safari, 2016; Im et al., 2015; Mishra and Gogate, 2011). In this case, the ultrasonic irradiation acts as an alternative energy source for the catalyst to generate positive holes and free radicals (Darvishi Cheshmeh Soltani et al., 2016b; Eren, 2012; Hapeshi et al., 2013). In sonocatalytic processes, the presence of an efficient catalyst promote the creation of nuclei and formation of cavitation bubbles, generating more $OH^{\bullet}$ in the aqueous phase (Chakma and Moholkar, 2016; Darvishi Cheshmeh Soltani et al., 2016a; Weng and Huang, 2015). Hence, the application of an appropriate catalyst with high sonocatalystic activity could be a decisive phase in the sonocatalysis of the target pollutant. Comparatively, ZnO catalyst, in nano-size, has been considered as an efficient catalyst owing to its large surface area, low cost, long life-span, excellent stability and lower toxicity. The efficiency of sonocatalytic process is on the basis of the synergy of ultrasonic irradiation and surface characteristics of the catalyst. In this regard, increasing surface area of the catalyst leads to the enhanced generation of $OH^{\bullet}$ by heterogeneous nucleation of the bubbles, enhancing the oxidative potential of the process (Grčić et al., 2013). The results of our previous study showed that the immobilization of suspended ZnO nanoparticles (SZNs) on a suitable porous carrier named biosilica increases the sonocatalystic activity of the catalyst (Darvishi Cheshmeh Soltani et al., 2016a). However, the commercially synthesized biosilica was not suitable in terms of cost effectiveness. On account of the low cost, natural clays are attractive alternatives. These are abundant, cheap, and ecosystem-friendly, making them good carrier for various catalysts (Gao et al., 2015). Among them, bentonite is plentiful natural clay, which is widely used in many industries for various applications due to its large surface area and unique chemical properties. Because of the aforementioned characteristics, it is widely used in the production of composite substances (Caglar et al., 2009; Kaufhold et al., 2010). Prior to this, it has been successfully applied for the immobilization of some photocatalysts (Gao et al., 2015; Meshram et al., 2011). In this regard, in the present study, the potential of bentonite clay was evaluated as a low cost alternative for the immobilization of SZNs. So, the aim of the present work was to explore the suitability of bentonite-supported ZnO nanoparticles (BSZNs) in terms of exposed surface area and sonocatalytic activity for the sonocatalytic degradation of an organic azo dye (Basic Red 46 (BR46)). Afterwards, the effect of some operational parameters influencing the sonocatalysis of BR46 over BSZNs was studied using response surface methodology (RSM) based on central composite design (CCD) because of its advantages in comparison with the conventional "one-factor-at-a-time" statistical approach (Darvishi Cheshmeh Soltani et al., 2013a). The main purpose of RSM is to use a series of experimental runs to reach an optimum response (decolorization efficiency). In the following, the capability of the process for treating real textile wastewater was assessed. To date, the sonocatalysis of organic azo dyes using BSZNs has not been reported elsewhere.

2. Materials and methods

2.1. Materials

The sonocatalytic activity of as-prepared catalyst was evaluated using BR46 dye (C.I.Basic Red 46, C.I.110825), as an organic cationic azo dye, which was purchased from Alvan Sabet Co., Iran. The characteristics of BR46 are as follows: molecular formula: $C_{18}H_{21}BrN_6$, molecular weight: 401.3 g/mol and maximum absorbance wavelength: 530 nm. The catalyst was synthesized using $ZnCl_2$ and NaOH as precursors purchased from Merck Co., Germany. To prepare ZnO nanoparticles immobilized on the surface of natural bentonite, a simple route was applied according to our previous study (Darvishi Cheshmeh Soltani et al., 2016a). The only difference was that the natural bentonite was used as sonocatalyst carrier instead of biosilica.

2.2. Experimental procedure and set-up

As-prepared BSZNs was put into the Erlenmeyer flask (working volume of 50 mL), as batch flow mode experimental reactor. The reactor was placed in the middle of a James ultrasonic bath (Ultra 8060, England) for the ultrasonic irradiation at frequency of 30 kHz. The distance between the Erlenmeyer flask and bottom of the bath was set to 3.0 cm. The power of instrument was constant at 150 W. For the sonocatalysis, synthetic solutions containing desired concentrations of BR46 and as-prepared sonocatalyst were added into the reactor to begin the experiment. The initial dye concentration, the initial pH, the dosage of BSZNs and the sonocatalyst to carrier weight ratio were selected as the main operational parameters. The aforementioned experimental set-up was placed in a dark place to prevent the photo-degradation. The removal of BR46 using sonocatalysis over BSZNs was evaluated as well as the application of sonolysis alone to show the role of catalyst in the decolorization.

2.3. Experimental design and modeling

Design-Expert software presents test matrices for screening various operational variables by means of different methodologies and different designs. Among them, RSM based on CCD was applied to map out a design space with a small number of experimental runs. This approach determines the individual effect of operational variables as well as their interactions, making it possible to draw a multi-dimensional and non-linear figure. In addition, analysis of variance (ANOVA) is provided to specify significance of the statistical method. After verification of the applied model, a numerical optimization will be performed to determine the optimum operational parameters for the maximum decolorization. Accordingly, in the present work, RSM on the basis of CCD was applied to evaluate the effect of the initial BR46 concentration (mg/L), the ZnO/bentonite ratio, the sonocatalyst dosage (g/L), and the initial pH on the sonocatalysis of BR46 over BSZNs. A second-order polynomial modeling was applied to designate the relationship between the response (decolorization efficiency (%)) and the selective operational parameters. The corresponding quadratic equation is depicted via Eq. (1):

$$Y(\text{decolorization efficiency}(\%)) = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (1)$$

where b_0, b_i, b_{ij}, and b_{ii} are constant, linear, interaction and quadratic coefficients, respectively. Additionally, x_i and x_j are the coded experimental parameters (Darvishi Cheshmeh Soltani et al., 2013a,c). The ranges and levels of the selective variables are tabulated according to the data processes by the Design-Expert software (Table 1).