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Research article

Sono-assisted adsorption of a textile dye on milk vetch-derived charcoal supported by silica nanopowder

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ABSTRACT

This study was performed to assess the efficiency of silica nanopowder (SNP)/milk vetch-derived charcoal (MVDC) nanocomposite coupled with the ultrasonic irradiation named sono-adsorption process for treating water-contained Basic Red 46 (BR46) dye. Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and Fourier transform infrared spectroscopy (FT-IR) were performed for the characterization of as-prepared adsorbent. The sono-assisted adsorption process was optimized using response surface optimization on the basis of central composite design by the application of quadratic model. Accordingly, the color removal can be retained more than 93% by an initial BR46 concentration of 8 mg/L, sonication time of 31 min, adsorbent dosage of 1.2 g/L and initial pH of 9. The pseudo-second order kinetic model described the sono-assisted adsorption of BR46 reasonably well ($R^2 > 0.99$). The intra-particular diffusion kinetic model pointed out that the sono-assisted adsorption of BR46 onto SNP/MVDC nanocomposite was diffusion controlled as well as that ultrasonication enhanced the diffusion rate.

1. Introduction

The high level of production and application of organic dyes generate colored wastewaters causing serious environmental problems because of their toxicity (Darvishi Cheshmeh Soltani et al., 2016b; Dastkhoon et al., 2015). There are too many industrial activities discharging colored wastewaters, including dye manufacturing, tanneries, leather, paper and pulp mills, rubber, plastic, refineries, electroplating factories, carpet and food processing (Hassani et al., 2015b; Noorimotlagh et al., 2014; Rajamanickam and Shanthi, 2014). The removal of organic dyes is more important than other organic matters because of the fact that small amount of organic dyes (below 1 mg/L) is visible. This adversely influences the water environment (Rajamanickam and Shanthi, 2014). Moreover, organic dyes are identified as the carcinogenic substances (Darvishi Cheshmeh Soltani et al., 2015; Hassani et al., 2015b; Jorfi et al., 2016). Thus, it is essential to find an effective technique to treat colored wastewaters before being discharged into the environment. Among various treatment techniques, adsorption process using solid adsorbents has been found to be a promising method for sequestering organic dyes in terms of its simplicity, sludge-free cleaning operation and insensitivity to toxicity (Hassani et al., 2015b; Kıranşan et al., 2014). However, the application of commercially synthesized activated carbon for the adsorption process has become restricted because of its high production cost (Sarma et al., 2016). So, the application of charcoal produced from waste carbonaceous materials has been considered for the adsorption of organic dyes in the aqueous environment (Lian et al., 2016; Liao et al., 2012). Regarding the availability, in the present study, milk vetch was applied as precursor of charcoal. The low adsorptive capacity of waste carbonaceous materials could be

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overcome by developing new hybrid adsorbents to improve the removal of organic dyes from wastewaters. Metallic or semi-metallic nanoparticles have unique characteristics such as large number of vacant active sites and high number of active atoms, which are applicable for the removal of various toxic organic materials. Prior to this, the application of gold-coated activated carbon has been investigated for removing organic dyes by some researchers (Roosta et al., 2014a, 2014b). However, its applicability is limited due to expensive coating material and commercial activated carbon. Therefore, in the present study, milk vetch-derived charcoal (MVDC) was coated by silica nanopowder (SNP) to reach the aforementioned advantages for an efficient adsorption of Basic Red 46 (BR46) as an organic azo dye in aqueous solutions. Recently, the physical and chemical modification of adsorbent materials by way of ultrasonic irradiation has received much more attention. Ultrasonic irradiation leads to the generation and collapse of "cavitation" bubbles inside the aqueous environment, producing extreme pressures and temperatures around the liquid− solid interfaces (Darvishi Cheshmeh Soltani et al., 2016a; Darvishi Cheshmeh Soltani et al., 2016c; Liu et al., 2011; Nouri and Hamdaoui, 2007; Şayan, 2006). The cavitation phenomenon causes the formation of too many microcracks on the adsorbent surface, increasing the surface area between the reactants (Dastkhoon et al., 2015; Hassani et al., 2015a; Şayan, 2006). Regarding the adsorption process, the formation and subsequently collapse of "cavitation" bubbles is a useful phenomenon in breaking the affinity between adsorbent and adsorbate molecules and increasing the mass transfer rate (Dotto et al., 2015). Shock waves create microscopic turbulence around the liquid−solid interfaces and increase the pore diffusion (Markovski et al., 2014; Milenković et al., 2013; Roosta et al., 2014a). The application of ultrasonic irradiation in textile coloring is well implemented and documented in many literatures (Hao et al., 2012). In tune with above mentioned statements, the present study was conducted to synthesize SNP/MVDC nanocomposite and evaluate its efficiency for the decolorization of BR46 via sono-assisted adsorption process. Based on our literature review, no reports are available in the literature on either synthesis of SNP/MVDC or its application for removing organic dyes by means of sono-assisted adsorption process. The experiments were planned by using response surface methodology (RSM) through central composite design (CCD) to find optimum conditions for maximum decolorization efficiency (%). Based on this model, it is feasible to study the effects of operational variables (parameters) without the need to maintain none of them constant. This allows better understanding of their real interactive effects in the process (Darvishi Cheshmeh Soltani et al., 2015; Darvishi Cheshmeh Soltani et al., 2013a; Darvishi Cheshmeh Soltani et al., 2013b; Vargas et al., 2012).

2. Materials and methods

2.1. Chemicals and instruments

Basic Red 46 as a cationic organic azo dye (molecular weight of 401.3 g/mol with molecular formula of $C_{18}H_{21}BrN_6$) was supplied by Alvan Sabet Co. (Iran) and used without further purification. Silica nanopowder was provided by PlasmaChem GmbH, Germany. Milk vetch as precursor of charcoal was gathered from the city of Ilam, Iran. All analytical-grade chemicals were purchased from Merck Co. Germany. 100-mL Erlenmeyer flasks were employed as batch flow mode reactors to conduct the experimental runs. All BR46-contained solutions were prepared via deionized water. Ultrasonication of the batch reactors was carried out in a 3000-mL ultrasonic bath (James, Ultra 8060D-H, England) at frequency of 30 kHz and power of 150 W. A Sartorius pH meter (PB-11, Germany) was applied to measure the pH of as-prepared solutions. Sodium hydroxide and sulfuric acid with specified molarity were used for pH adjustment.

2.2. Preparation of SNP-coated MVDC

To prepare charcoal from milk vetch, milk vetch shrub was firstly crushed, washed and then dried in an oven at 100 °C. Under gentle mixing, milk vetch was soaked in phosphoric acid solution for 60 min in order to remove hydrocarbons and impurities. After drying, the sample was heated in an electric furnace at 600 °C for 1 h to obtain charcoal from milk vetch samples with high porosity. As-prepared charcoal was ground, sieved (between 60 and 120 mesh size) and used to be covered by SNP as follows: A 2% suspension of SNP was prepared (with working volume of 50 mL) and magnetically agitated for 20 min. The suspension was sonicated in the ultrasonic bath for 120 min at an adjusted temperature of 50 °C. Afterwards 2 g of MVDC was added gradually to the SNP suspension under magnetic stirring (MVDC to SNP mass ratio of 2:1). The mixture was sonicated for 300 min. The sample was filtered then its solid phase was dried in an oven at 80 °C. Finally, it was calcined at 500 °C for 120 min in an electric furnace. As-prepared samples were kept in a desiccator before use to inhibit the absorption of water molecules and increasing the weight of samples.

2.3. Modeling of the process

A five-level CCD was applied to assess the influence of operational parameters on the sono-assisted adsorption of BR46 on SNP/MVDC nanocomposite, including initial BR46 concentration (x_1) ranging from 5 to 25 mg/L, adsorbent dosage (x_2) ranging from 0.5 to 1.3 g/L, sonication time (x_3) ranging from 5 to 45 and initial pH (x_4) ranging from 3 to 11. Some preliminary experimental runs were performed to determine realistic levels of the parameters. The total number of experimental runs was computed by Eq. (1):

$$N = 2^k + 2k + x_0 \tag{1}$$

where N, k and x_0 are defined as the total number of experiments, independent parameters and replications (center points), respectively (Darvishi Cheshmeh Soltani et al., 2015; Darvishi Cheshmeh Soltani et al., 2013a). According to seven replications ($x_0 = 7$), the total number of experimental runs was estimated to be 31. The relationship between the independent parameters (sonication time, adsorbent dosage, initial BR46 concentration and initial pH) and the response (color removal (%)) was described using a second-order polynomial equation as illustrated in Eq. (2):

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

where Y is the predicted response and b_0, b_i, b_{ij} and b_{ii} are constant, linear coefficient, interaction coefficient and quadratic coefficient, respectively. In addition, x_j and x_i are coded values of the operational parameter (Darvishi Cheshmeh Soltani et al., 2013a; Darvishi Cheshmeh Soltani et al., 2013b).

2.4. Analytical methods

Field emission scanning electron microscopy (FE-SEM) with accelerating voltage of 30 kV was operated (Tescan, Mira3, Czech Republic) to take some images of surficial structure of as-prepared samples (pure SNP, uncovered MVDC and SNP-covered MVDC). A gas sorption analyzer (Belsorp mini II, Japan) was employed to determine specific surface area (as m^2/g) of the samples from N_2