Research article

Response surface optimization, kinetic and thermodynamic studies for effective removal of rhodamine B by magnetic AC/CeO$_2$ nanocomposite

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A B S T R A C T

The activated carbon (AC) was obtained from waste scrap tires and modified by bimetallic Fe and Ce nanoparticles in order to combine both the high surface area and the active sites for enhanced adsorption of the dye. The produced nanocomposite was used as a novel cost-effective magnetic in rhodamine B (RhB) removal from aqueous solutions. The FT-IR, SEM, EDX, TEM, and surface area analysis methods were implemented to characterize the morphological, chemical, thermal and surface properties of the developed adsorbent. The optimum batch experimental conditions were found under the response surface methodology. The adsorption equilibrium data were well fitted by the Langmuir isotherm model. The adsorption capacity was 324.6 mg g^{-1}. The kinetic and thermodynamics studies were also carried out to understand the adsorption mechanism. The study indicated that RhB adsorption by the AC/Fe/Ce magnetic adsorbent has an endothermic character and followed the pseudo-second-order kinetics model. By using ethanol solution, RhB was desorbed at high efficiency and the prepared material could be recycled for up to ten cycles. Thus, the magnetic nanocomposite is an effective and promising adsorbent for the cleaning treatment of RhB ions from wastewater by a large scale designed adsorption system.

1. Introduction

Synthetic dyes are commonly used in the textile, plastic and cosmetic industries. Some of the dyes are reported to be highly toxic, non-biodegradable and mutagenic in nature and they affect human, animal and environmental health either directly or indirectly (Khamparia and Jaspal, 2016). Synthetic dyes are investigated as prime contributors to water pollution (Robinson et al., 2001). Rhodamine B (RhB) is known as a water soluble dye which is used in the textile industry. RhB is reported to be carcinogenic (Mohammadi et al., 2010). Consequently, it is very important to remove RhB from waste water samples. Several treatment methods such as adsorption, photocatalytic degradation (Alvi et al., 2017; Mohite et al., 2016), flotation (Shakir et al., 2010), etc. have been

used for the removal of RhB from water samples. Among them, adsorption has been extensively employed for the purification of dyes from industry wastewaters. Various adsorbents such as activated carbon, biosorbents (Khamparia and Jaspal, 2016), kaolinite, polymeric materials, and composite materials were used for the removal of dyes. These adsorbents have a low adsorption capacity for the sorption of dyes.

In recent years, magnetic adsorbents have become very popular for the sorption of dyes because of their ease of operation, and their fast and high adsorption capacity (Zhang et al., 2012; Altıntıg et al., 2017). The separation of dyes from aqueous solutions is very effective by using an external magnetic field instead of filtration and centrifugation (Tang et al., 2014; Ma et al., 2016; Singh et al., 2010; Liu et al., 2016; Saleh et al., 2017a). Liu et al. reported using a metal organic framework for the removal of RhB from aqueous solutions (Liu et al., 2016). Ma et al. reported on the usage of magnetic montmorillonite for the sorption of RhB and hexavalent

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chromium (Ma et al., 2016). Singh et al. reported on designing a model for the removal of RhB from water samples by using magnetic nanocomposites (Singh et al., 2010; Saleh et al., 2017b). Zhang et al. reported using a prepared ferromagnetic $BiFeO_3$ adsorbent for the sorption of RhB (Zhang et al., 2012; Saleh, 2015). According to our survey, there have not been any studies in the literature regarding the use of an activated carbon/Fe/Ce magnetic nanocomposite as a sorbent for the removal of dyes. Moreover, this magnetic composite has a high adsorptive potential due to its high capacity, ease of producibility, practicability, cost-effectiveness, rapidity, selectivity, and sensitivity for the extraction of dye product pollution from waste waters. This work was focused on the investigation of its adsorption feasibility for the elimination of RhB dye from aqueous solutions. The chemical and surface properties of the developed nanocomposite were identified by using the FTIR, SEM, EDX, and BET techniques. The adsorption batch conditions were optimized using the RSM and CCD methods. The adsorption data were modeled with the Langmuir and Freundlich isotherm models in addition to the adsorption of the kinetic and thermodynamic evaluation of the results.

2. Experimental procedures

2.1. Reagents and equipment

Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), Ferric Nitrate (Fe $(NO_3)_3 \cdot 9H_2O$) and ethylene glycol with reagent grade were obtained from SigmaAldrich. 1000 mg L^{-1} RhB stock solution was prepared (Merck, Darmstadt, Germany) in distilled water. The pH measurement was conducted by using a Sartorius pp-15 model pH meter (Germany). The RhB concentrations were determined at 554 nm using a UV-VIS spectrometer (Perkin-Elmer Lambda 35 model; USA).

2.2. Preparation of the magnetite nanocomposite

7.0 g of AC obtained from waste tires was dispersed in 150 mL of deionized water and 100 mL ethanol by means of a sonicator for five hours. Then, a 12.53 mL of Ferric Nitrate (Fe $(NO_3)_3 \cdot 9H_2O$) solution was added gradually to the dispersion solution. This mixture was combined with 20 mL of ethylene glycol solution and then stirred for 6 h at a pH of 8–9 and at a temperature of 80 °C. The precipitate AC/Fe was filtered and dried at 110 °C and then calcined at 350 °C for 4 h. In the second stage, the fabricated AC/Fe was dispersed in ethanol solution in deionized water (100/150 mL) and after that mixed with a 20 mL ethylene glycol solution for five hours. In the final stage, a 5 mL solution of cerium nitrate hexahydrate was introduced into the obtained final solution at a pH of 8–9. The AC/Fe/Ce precipitation obtained after the reflux process at 90 °C for 5 h was washed and dried. The last nanocomposite was subjected to a calcination process at 350 °C for 4 h to make sure that there was sufficient settlement of Fe and Ce metals onto the surface of the AC.

The structure of the nanocomposite was characterized by adsorption and desorption of nitrogen at −196 °C on a Micromeritics (ASAP 2020) surface area and a porosimetry analyzer. X-ray diffraction patterns of the synthesized nanocomposites were performed on a Rigaku Miniflex II desktop X-ray diffractometer with Cu-Kα radiation (wavelength = 1.5418 A) and an X-ray gun operating at a voltage of 40 kV and a current of 200 mA. Data was collected from $2\theta = 0–80°$ at a scan rate of $4°$/min.

The surface of the synthesized nanocomposite was evaluated by a low vacuum JEOL scanning electron microscope, JSM-6610LV, with a tungsten electron gun. FT-IR was used for structural evaluation. The spectra were obtained using a Nicolet 6700 spectrometer, Thermo Electron USA, of a resolution of 2.0 cm^{-1} with a Deuterated triglycine sulfate detector and an OMNIC software. The FT-IR analyses were performed from the pellet samples with the KBr in a wavenumber range of 4000–400 cm^{-1}.

2.3. Batch adsorption procedure

The parameters were optimized using the experimental design. A total of 21 experiments were designed (Table S1) and then performed to optimize the related parameters including pH, dosage, initial concentration and contact time. Sample solutions containing 10 mg L^{-1} RhB were buffered pH 5 by using acetate buffer solutions. The adsorbent added to this solution was agitated at 120 rpm by using a thermostatic shaker with a Selecta multimatic-55 model (Spain). This process was continued until the adsorption equilibrium conditions were achieved. After each batch run, the adsorbent was recovered from the aqueous media by means of a neodymium magnet. The batch procedures were carried out under different conditions: a contact time of 20–75 min, a pH of 2–7, the initial metal concentration of 10–50 mg/L, the adsorbent concentration of 1–20 g/L and a temperature of 20–60 °C. The average values were taken into account after repeating each of the measurements three times. The percent adsorption of RhB was calculated as follows:

$$Biosorption \ (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \tag{1}$$

where C_i (mg/L) and C_f (mg/L) are the initial and final RhB concentrations, respectively.

2.4. Desorption studies

Each desorption run was carried out using 5 mL ethanol solution to extract the sorbed RhB from the adsorbent and the adsorption-elution processes were repeated for ten times under the predetermined optimized equilibrium conditions.

3. Results and discussion

3.1. Characterization

3.1.1. Structural properties of the prepared AC/Fe/Ce nanocomposite sorbent

The active sites on the sorbent are considered to be a receiver of the pollutant molecules during the adsorption. FT-IR was employed to confirm the chemical structure of the nanocomposite. Fig. 1 depicts the FTIR spectra of the AC and the AC/Fe/Ce sorbents. The FTIR spectrum of the AC indicates a sharp band at about 3400 cm^{-1} which are attributed to the stretching vibration of the OH groups. The absorption band at 1110 cm^{-1} is attributed to the bending vibration of the O–H group. The band at around 1650 cm^{-1} is assigned to the stretching vibration of the C=O group while the bands at 2924 cm^{-1} and 2855 cm^{-1} are assigned to the antisymmetric and symmetric stretching vibrations of the CH_2 group. As depicted in Fig. 1(b), the bands in the proximity of 470 cm^{-1} and 650 cm^{-1} could be assigned to the stretching vibrations of Ce–O and Fe–O which suggests the likely presence of cerium oxide (Ce_2O_3) and iron oxide (Fe_2O_3) on the carbon structure.

Fig. 2 depicts the EDX spectrum with elemental analysis, SEM image and elemental mapping of Fe and Ce on the prepared nanocomposite. The EDX spectrum of the developed nanocomposite is shown in Fig. 2(a), which indicates the presence of carbon, oxygen, iron, and cerium. Table S2 depicts the elemental analysis of the nanocomposite, indicating the wt % of these