Research article

Acridine orange adsorption by zinc oxide/almond shell activated carbon composite: Operational factors, mechanism and performance optimization using central composite design and surface modeling

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ABSTRACT

Zinc Oxide/Activated Carbon Powder was used for the adsorptive removal of Acridine Orange dye (AO) from aqueous solution. The prepared composite material was characterized using XRD, XPS, SEM, EDS, FTIR, XRF, Raman, BET surface area and TGA/DTA. The adsorption isotherms, kinetics and thermodynamic studies of AO onto the ZnO-AC were thoroughly analyzed. The kinetic modeling data revealed that the adsorption of AO has a good adjustment to the pseudo-second-order model. Langmuir isotherm model is better fitted for adsorption data and the maximum adsorption capacity was found to be 909.1 mg/g at 313 K. The negative values of ΔG showed the spontaneous nature of the AO adsorption onto ZnO-AC. The results indicated the adsorption was pH dependent which is mainly governed by electrostatic attraction, hydrogen bonding and π−π interaction. Reusability test showed a low decrease in the removal performance of ZnO-AC due to the mesopore filling mechanism confirmed by BET analysis after adsorption. Also, thermal regeneration could deposit AO dye on the surface of the composite leading to the efficiency decrease. Finally, the effect of various parameters such as pH, temperature, contact time and initial dye concentration was studied using response surface methodology (RSM). The model predicted a maximum AO removal (99.42 ± 0.57%) under the optimum conditions, which was very close to the experimental value (99.32 ± 0.18%).

1. Introduction

The removal of dye substances from water and wastewater due to their detrimental effects is essential. For instance, many treatment procedures including ion-exchange, reverse osmosis, adsorption, coagulation, membrane filtration, precipitation, advanced oxidation processes (Ozonation and photo-degradation), and biological methods have been applied to remove various dyes in the effluents (Ju et al., 2011; Ashiq et al., 2012; Ait Ahsaine et al., 2016a,b; Jayalakshmi et al., 2013; Zhang et al., 2012) Adsorption process, because of its simplicity, cost effective, and sorbent reusability, is an attractive alternative that has been extensively used to remove dyes from aqueous solutions (Ghaedi et al., 2012; Jayalakshmi et al., 2013). It is now well documented that for the

water and wastewater treatment, adsorption process has many advantages over other methods (Mittal et al., 2014, 2013). Moreover, the ability of adsorption to remove various toxic chemicals without producing any toxic byproducts, thus holding quality of water unchanged, has also popularized this treatment method in comparison to other above-mentioned processes (Mittal et al., 2013).

Numerous studies were reported using different adsorbents like activated carbon (AC) (Bello et al., 2008; Hejazifar and Azizian, 2012; Islam et al., 2017; Ozer et al., 2012; Vadivelan and Kumar, 2005), and chitosan-zinc compound nanoparticle (Salehi et al., 2010) for the removal of dyes from liquid solutions. The adsorbents should have high surface area, natural action capability and active sites on their surfaces (Ghaedi et al., 2013). AC is the most often used sorbent material that is applied for the removal of varied dyes from liquid solutions (Zhang et al., 2012). The use of metal oxide on the surface of different adsorbents (e.g. AC) has several advantages (Changsuphan et al., 2012; Ghaedi et al., 2013). This method will increase the amount of sorption active sites onto the

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adsorbent, likewise because the issues related to the separation of the nanoparticles from the solution are often resolved (Ghaedi et al., 2013). Zinc oxide nanoparticles is a promising candidate as a co-mixer to reduce the polarization of the activated carbon by impregnation onto its matrix and also owing to his multiple chemical advantages such as chemical stability, thermal stability, natural abundance, environment friendliness, efficient decomposition of organic compounds and mild operation conditions (Kalpana et al., 2006).

Acridine orange (a nucleic acid selective fluorescent cationic dye) (Lv et al., 2011) is one of these hazardous dyes, it has been the subject of extensive studies in recent years because of its dangerous biological effects (Ogunjobi et al., 2010; Saetzler et al., 1997). Different adsorbents have been used for AO synthetic dye removal from aqueous solutions such as carbon nanotubes (Jauris et al., 2016), modified maghemite nanoparticles (Arshad et al., 2017), graphene oxide (Sun et al., 2012) and magnetic nanoparticles (Qadri et al., 2009).

To the best of our knowledge, this is the first report presenting the adsorption mechanism and response surface approach of the AO dye, this study presents an understanding of the mechanism and the influence of several operational parameters on the adsorption mechanism. Optimization was performed using central composite design (CCD) combined with response surface methodology (RSM).

2. Experimental

2.1. Preparation of ZnO-AC

The activated carbon was prepared from Almond Shell. Ground Almond Shell with a particle size between 2 and 3 mm was chemically activated with KOH. For this purpose, the sample was mixed with KOH solution to obtain a solution which was heated at 60 °C for 12 h and then dried at 110 °C. Then, the sample was pyrolyzed under N2 flow (200 cm^3/min) at 300 °C for 2 h and then at 800 °C for 3 h at a heating rate of 10 °C/min. ZnO nanoparticles were prepared by co-precipitation method using a required amount of Zinc nitrate $Zn(NO_3)_2$ in 50 mL milliQ water, then 0.5 M NaOH solution was added dropwise with a constant stirring until a pH around 9–10. The white precipitate was washed several times with ethanol and MilliQ water prior to calcination at 400 °C for 3 h. Finally, the ZnO-AC composite were prepared with 20 wt% of zinc oxide prepared by co-precipitation method, the prepared composite was filtered and washed several times with distilled water and ethanol, then dried at 70 °C for 12 h.

2.2. Adsorption studies

The initial pH effect was carried out by mixing 20 mg of ZnO-AC and 100 mL of AO (100 mg/L), the initial pH was adjusted using buffer solution (2–12). Kinetic studies were done with a fixed amount of ZnO-AC 20 mg and initial AO concentration 100 mg/L. The volume of 100 mL AO solution was agitated (200 rpm) at different temperatures (293, 303, and 313 K) for different contact time (10–180 min) and the solution centrifuged to remove the adsorbent. Residual AO concentrations were determined spectrophotometrically. The isotherm studies were carried out by agitating 100 mL solution of AO of desired concentrations (10–100 mg/L) mixed with 20 mg of ZnO-AC at varying temperature (293–313 K) at pH 8 for 60 min.

2.3. Characterization methods

XPS analysis was carried out using Thermo Fisher Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy system equipped with Al Kα X-ray source = 1486.7 eV to study the chemical states synthesized ZnO-AC sample. XRD patterns were collected using an EMPYREAN PANALYTICAL diffractometer operating at 45 kV/35 mA, using CuKα radiation with Ni filter, and working in continuous mode with a step size of 0,01°. The surface morphology of the ZnO-AC before and after adsorption were obtained from a scanning electron microscopy (SEM) coupled with EDS analysis by FEI, Quanta 200-ESEM operated at 20 KeV. FT-IR spectrometer were obtained using a Shimadzu 4800S in the mid infrared region between 400 and 4000 cm^{-1} with a resolution of 2.0 cm^{-1} and with 20 scanning. Raman spectroscopy was used to characterize the prepared activated carbon. The equipment used to perform the various vibration spectra was a spectrometer NRS-5100 model jasco Raman spectrometer, using a CCD detector, a laser line of 532 nm and objective lens 100 × , with a laser power of 1.6 mW. Thermal data (TGA/TDA) of ZnO-AC were obtained by using Shimadzu Instruments DTG-60 between 25 and 800 °C (in air, 10 °C/min). The Brunauer−Emmett−Teller (BET) surface area was determined by the nitrogen adsorption and desorption isotherm, pore size distribution and specific surface area were measured using an AUTOSORB-1 surface area and pore size analyzer at 77 K. X-Ray fluorescence elemental analysis was performed using Philips spectrophotometer equipment.

3. Results and discussion

3.1. Characterization of absorbent

3.1.1. X-ray photoelectron spectroscopy

To acquire the species and chemical states of the elements in the surface of the ZnO-AC, X-ray photoelectron spectroscopy was performed. As illustrated in Fig. 1a, high-resolution C1s XPS spectrum of ZnO-AC was observed. The intense peak located at 285.09 eV can be attributed to the sp^2-bonded carbon atoms, and the broad peaks at 286.46 and 290.02 eV to C−OH and C═O bonds respectively, this shows a high presentation of oxygen-containing functional groups on the ZnO-AC (Haldorai et al., 2014). The O1s presented in Fig. 1b is characterized by large with high full width at half maximum, its deconvolution gives three crests at 532.46, 531.44, and 534.92 eV: the first value is attributed to ZnO nanoparticles, this peak is related with O^{2-} in ZnO (Wahab et al., 2009; Zhang et al., 2008), the second and third peaks were identified with surface OH and COOH bunches (Ibris et al., 2005). The high resolution XPS spectrum for Zn2p indicates two symmetric peaks (Fig. 1c): one focused at 1022.78 eV, allocated to Zn2p$_{3/2}$, and one at 1045.65 eV, which was assigned to Zn2p$_{1/2}$, showing the proximity of Zn^{2+} in the ZnO wurtzite structure (Haldorai et al., 2014). These findings confirmed the development of ZnO at the surface of the ZnO-AC (Mu et al., 2011; Zhang et al., 2008).

3.1.2. X-ray diffraction

Fig. 1d presents the X-ray diffraction profiles of the ZnO-AC composite, the diffractogram presents wide band in the range of 20−30° and 40−50° characteristic of amorphous activated carbon containing different functional groups. The strong diffraction profiles correspond to the hexagonal ZnO space group $P6_3mc$. The cell parameters of the ZnO-AC sample were refined using LeBail fit (Bail et al., 1988) giving a = b = 3.251 (4) and c = 5.209 (1). The crystallite size of the ZnO was calculated using Scherrer formula: $D=(0.9\lambda/\beta cos\theta)$.

In this expression *D* average crystallite size, λ is the X-Ray source wavelength, 0.9 for gaussian profiles, β is the broadening of Bragg and θ is the Bragg angle in Radians. The crystallite size was found to be 32 nm. Fig. S1 presents the morphological rounded shape of the