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Kinetic, thermodynamic and isotherm studies for acid blue 129 removal from liquids using copper oxide nanoparticle-modified activated carbon as a novel adsorbent

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ABSTRACT

A novel adsorbent, copper oxide nanoparticle loaded on activated carbon (CuO-NP-AC) was synthesized by a simple, low cost and efficient procedure. Subsequently, this novel sorbent was characterized and identified using different techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and laser light scattering (LLS). The effects of some variables including pH, adsorbent dosage, initial dye concentration, contact time and temperature were examined and optimized. The adsorption kinetic data were modeled using the pseudo-first-order, pseudo-second order, intraparticle diffusion and Elovich models, respectively. The experimental results indicated that the pseudo-second-order kinetic equation can better describe the adsorption kinetics. Furthermore, Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich models were applied for analyzing adsorption equilibrium data of acid blue 129 (AB 129) on the as-prepared adsorbent, which suggested that the Langmuir model provides a better correlation of the experimental data. Also, thermodynamic parameters such as ΔH, ΔS, E_a, S^*, and ΔG were calculated. It was seen that the proposed adsorbent has high tendency and adsorption capacity for AB 129 adsorption in a feasible, spontaneous and endothermic way.

1. Introduction

Nowadays, in such an industrial world one of the most important concerns is securing the health of human race and environment. Dyes and pigments present in wastewaters of manufacturing and textile industry contain dyes and auxiliary chemicals [1] lead to generation of hazardous injuries to the animal and human health [2]. Because of their complex (aromatic) molecular structures, dyes are stable towards heat and oxidizing agent and are biodegradable with difficulty. In addition, most dyes are toxic and harmful to some microorganisms and directly destroy or inhibit from their catalytic activates [3]. Colored dyes are not only esthetic, carcinogenic but also hinder light penetration and disturb life processes of living organisms in water. Acid blue 129 (AB 129), an acidic dye, is most widely used for the dyeing of cotton, wool, silk, nylon, paper and leather (Table 1 and Scheme 1) [4]. This dye may be harmful if there is contact to eyes, respiratory system and skin. Therefore, the removal of such colored agents from aqueous effluents is necessary. Because of the importance of removal of dyes from solutions, researches have tried to measure and remove dyes through various methods namely coagulation, nanofiltration and ozonolysis, membrane filtration, oxidation and adsorption process which are applied to remove color and other contaminations from aqueous media [5–9]. Recently, adsorption has become one of the most popular techniques because of some advantages such as high efficiency and ability to use generable non-toxic and cheap adsorbents [10–24]. Activated carbon appears to be the widely used technique for dye removal because of its high porosity, large surface area and high mechanical and chemical stability, with a least cost that acts as mild reducing agent and catalyst [25–27]. Also, nanoparticles as sorbents for separation, removal and or pre-concentration are applicable for enrichment of trace elements as its effective protocol [28].

The objective of the presented work is to investigate the preparation of a new and effective sorbent for the adsorption of AB 129 dye. The effects of adsorbent dosage, initial dye concentration, pH, contact time and temperature on AB 129 adsorption onto CuO-NP-AC were studied. Adsorption kinetics, isotherms and thermodynamic parameters were also evaluated and reported.

2. Materials and methods

2.1. Instrumentation

A double beam spectrophotometer (UV-1800, Shimadzu, Japan) was used for determination of concentration of AB 129 at 629 nm. The shape and surface morphology of the obtained sample were investigated by a

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Table 1
Properties of acid blue 129.

C.I. number	Acid blue 129
Chemical formula	$C_{23}H_{19}N_2NaO_5S$
Another name	Brilliant Alizarine Sky Blue BS
Abbreviation name	AB 129
Molecular weight	458.46
Name	Sodium-1-amino-4-(2, 4,6-trimethylanilino) anthraquinone-2-sulfonate
Maximum wavelength (λ_{Max})	629 (nm)
Application	Cotton, wool, silk, nylon, paper and leather
Color	Blue
Class	Acid dye

Q1

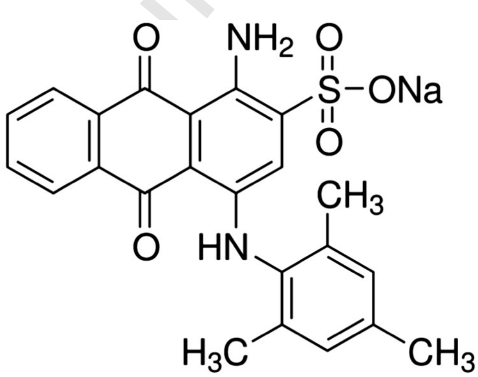
field emission scanning electron microscope (FE-SEM, Hitachi S4160, Japan) under an acceleration voltage of 20 kV. The X-ray diffraction patterns of the products were recorded by employing INEL X-ray diffractometer (model Equinox 3000). Particle size and size distribution of the CuO nanoparticles were measured by laser light scattering (Zetasizer Nanoseries, Malvern Instruments Co.). A Metrohm pH-meter (model 691, Switzerland) was used in order to adjust the pH at desirable values. Thermometer Metrohm, international ASTM sieves and Stirrer model UKA are also used in this study.

2.2. Standard solutions and reagents

All the chemicals used in this study were of analytical grade and solutions were prepared with distilled water. Applied reagents including copper iodide (I), DMSO, oleic acid, ethylene-diamine, NaOH and HCl with the analytical reagent grade were purchased from Merck (Darmstadt, Germany). A stock solution of 200 mg L^{-1} of AB 129 was prepared by dissolving 0.100 g of solid dye (Sigma-Aldrich, Germany) in water and diluting to 500 mL in a volumetric flask. All working solutions with desired concentration were prepared by diluting the stock solution with distilled water.

2.3. Adsorption studies

Concentrations of AB 129 were estimated using the linear regression equations (obtained by plotting its calibration curve). The dye adsorption capacity of the adsorbent was determined at the time intervals in the range of 1–30 min for 10 and 20 mg L^{-1} at room temperature and it was found that equilibrium was established after 20 and 25 min for 10 and 20 mg L^{-1}. The influence of some variables namely pH, adsorbent dosage, temperature, contact time and initial dye concentration on the adsorptive removal of AB 129 was examined by batch experiments. To evaluate and calculate the kinetic, thermodynamic and isotherm parameters of the adsorption process, 50 mL of 10 and 20 mg L^{-1} of AB 129 in 100 mL Erlenmeyer flasks was agitated on a stirrer at 400 rpm at room temperature and obtained experimental data at various times, temperatures and concentrations was fitted to different models.



Scheme 1. Chemical structure of acid blue 129.

The percentage adsorption R was calculated as:

$$\%\text{Dye removal},\ R\left(\frac{C_0 - C_t}{C_0}\right) = \times 100 \quad (1)$$

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the dye concentration at initial and after time t respectively and the amount of adsorbed AB 129 by adsorbent (q_e (mg g^{-1})) was calculated according to Eq. (2):

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (2)$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium dye concentrations in solution, respectively, V is the volume of the solution (L), and W is the mass (g) of the adsorbent used and the actual amount of adsorbed dye at time t, q_t (mg g^{-1}), was calculated based on the following equation:

$$q_t = (C_0 - C_t)\frac{V}{W} \quad (3)$$

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the concentrations of dye at initial and any time t, respectively, V is the volume of the solution (L), and W is the mass (g) of the adsorbent.

2.4. Preparation of CuO nanoparticles by solvothermal method

Among the various chemical approaches for the synthesis of nanoparticles, the solvothermal method was chosen to synthesize CuO nanoparticles. In fact, solvothermal synthesis is a method for preparing a variety of materials such as metals, semiconductors, ceramics, polymers and nanocrystals. One of the most important characteristics of solvothermal method is to allow for the precise control over the size, shape distribution, and crystallinity of metal oxide nanoparticles or nanostructures. These characteristics can be altered by changing certain experimental parameters, including reaction temperature, reaction time, solvent type, surfactant type, and precursor type. CuO nanoparticles in DMSO were synthesized by the following method (Scheme 2): After dissolving 3.1 g of CuI in 42.5 mL DMSO, the solution was heated to 80 °C under a constant stirring rate. Then, 1.5 and 0.1 mL of ethylenediamine and oleic acid were added to the solution, respectively. The gray solution turned black and after a few minutes copper oxide particles were precipitated at the bottom of the experiment dish. The mixture was maintained at 80 °C for 2 h and the color of the reaction solution became black completely. The resultant black products were separated from the reaction mixture and washed thoroughly with DMSO to remove CuI crystals if remained and dried at ambient condition (in a vacuum oven, 0.1 MPa) for 6 h prior to being characterized.

3. Results and discussion

3.1. Characterization of CuO nanoparticles

XRD analysis as powerful tools was used to study the crystal structures of the CuO nanoparticles. Fig. 1(a) displays the XRD spectrum of CuO nanoparticles. In XRD pattern the sample indexes to tenorite, synCuO (JCPDS number 00-045-0937) although has different intensities of crystallinity. The two reflections at $2\theta = 35.54$ [002] and $2\theta = 38.52$ [111] were observed in the diffraction patterns, and are ascribed to the formation of the CuO monoclinic crystal phase. The average size of nanocrystallites (D) was estimated by Scherrer's formula [29].

$$D = K\lambda/\beta \cos\theta \quad (4)$$

where K (=0.89) is the shape factor, λ is the X-ray wavelength of Cu K_α Q7
radiation (0.154 nm), θ is the Bragg angle and β is the experimental

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