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Ultrasonic enhancement of the simultaneous removal of quaternary toxic organic dyes by CuO nanoparticles loaded on activated carbon: Central composite design, kinetic and isotherm study

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ABSTRACT

Copper oxide nanoparticles loaded on activated carbon (CuO-NPs-AC) were prepared and fully analyzed and characterized with FE-SEM, XRD and FT-IR. Subsequently, this novel material was used for simultaneous ultrasound-assisted adsorption of brilliant green (BG), auramine O (AO), methylene blue (MB) and eosin yellow (EY) dyes. Problems regard to dyes spectra overlap in quaternary solution of this dyes were omitted by derivative spectrophotometric method. The best pH in quaternary system was studied by using one at a time method to achieved maximum dyes removal percentage. Subsequently, sonication time, adsorbent dosage and initial dyes concentrations influence on dyes removal was optimized by central composite design (CCD) combined with desirability function approach (DFA). Desirability score of 0.978 show optimum conditions set at sonication time (4.2 min), adsorbent mass (0.029 g), initial dyes concentration (4.5 mg L^{-1}). Under this optimum condition the removal percentage for MB, AO, EY and BG dyes 97.58, 94.66, 96.22 and 94.93, respectively. The adsorption rate well fitted by pseudo second-order while adsorption capacity according to the Langmuir model as best equilibrium isotherm model for BG, MB, AO and EY was 20.48, 21.26, 22.34 and 21.29 mg g^{-1}, respectively.

1. Introduction

Organic dyes widely present in wastewater of textiles, paper, plastics, leather, food, antiseptics, cosmetics, fungicides following entrance to the aquatic environment [1–3] cause toxicity, carcinogenicity and mutagenic points [2,4–6]. Therefore, their removal from wastewater is great demand and achieved by application of conventional physicochemical, chemical and biological principles that classified to coagulation and flocculation [7], adsorption [8], biosorption [9], electrochemical techniques [10] and fungal decolonization [11], while more diversity is possible in adsorption [12]. The simple design, nontoxic and low cost adsorbents, low treatment cost and mild conditions are criterion for selection of best mode and adsorbent in this approach [13]. Growing researches interest and effort lead exporting carbon-based materials that simply were modified by novel nanoscale materials. This combination is associated whit enhance in surface area porosity and rate of mass transfer [14–16]. AC as sole adsorbent due to presence of non-localized n electrons and also fictional reactive centers like OH, COOH, NH_2 and amide group seems to attract various species through Π-Π, hydrogen bonding and charge electrostatic force deepened on working pH [17,18]. On the other hands, compounded like CuO nanoparticles eagerly like to bind on AC surface through binding copper center to the functional group or non-localized M-electron through ion dipole interaction, while presence of its oxygen reactive center also favor loading process through hydrogen bonding via hard-hard interaction [18,19]. Therefore, it seems and expectable that CuO-NP-AC has greater and favorable reactive sites toward AC and/or CuO-NP as sole adsorbent. Probable back distribution of copper (ions and atoms) to environments do not generate harmful problem for living things is related to its high threshold limit suggested by world health organization (WHO) [20–22].

Procedures using ultrasonic waves are very efficient at removing chemicals and eliminating toxic contamination. Therefore,

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techniques using hybrid ultrasonic waves, together with other methods such as adsorption process are the most common uses of ultrasonic waves [23–25]. In this case the using of ultrasound waves its well-known to accelerate chemical process due to the phenomenon of acoustic cavitation, that is, the formation, growth and collapse of micrometrical bubbles, formed by the propagation of a pressure wave through a liquid [26]. As well as, ultrasound waves and its secondary effect, cavitation (nucleation, growth and transient collapse of tiny gas bubbles) improve the mass transfer and breaking the affinity between adsorbate and adsorbent through convection pathway that is emerged from physical phenomena without significant change in equilibrium characteristics of the adsorption/desorption system [27–29].

Simultaneous removal of dyes due to their absorption peak overlap is big problem that limit the simultaneous clean up procedures. The derivative spectrophotometric are good choice that cope with these problems [30,31].

Experimental design methods widely used as the efficient way for modeling, analyzing and interpreting experimental data. This method permits efficient optimization and give useful subject about individual and cooperation contribution as main and interaction on response. As well as, improve characteristics performance with at least number of experiments while minimize error of experiments [32,33].

In this work, the Copper oxide nanoparticles loaded on activated carbon (CuO-NPs-AC) synthesized and characterized via FE-SEM, XRD and FT-IR. Subsequently, simultaneous ultrasonic assistant removal performance of prepared adsorbent was investigated for BG, MB, EY and AO dyes at various operating conditions by bath method. Central composite design was used for optimization of variables (sonication time, initial dyes concentration and amount of adsorbent) and dyes spectra overlap in quaternary solution was resolved following application of first and second order derivative spectrophotometry. Kinetics and equilibrium study of adsorption reveal suitability of second order kinetic model and Langmuir model for good and efficient prediction of experimental data.

2. Experimental method

2.1. Synthesis of CuO nanoparticles loaded on AC

NH4OH solution was purchased from Chem. lab company, ($Cu(CH_3COO)_2{\cdot}2H_2O$), and activated carbon (AC) were purchased from Merck company, Dermasdat Germany. The reaction solution for CuO nanoparticles preparation is as follows: 5.0 mmol copper acetate solutions were mixed with 5.0 ml of fresh NH_4OH solution at pH = 10.4–10.7. Then, deionized water was added to the above solution to make total volume of 250 ml in a volumetric flask and 10.0 gr activated carbon (AC) was added to the mixture in Erlenmayer flask. CuO-NPs was homogenously loaded on AC after 3.0 h stirring at 55–60 °C. After 3 h, CuO-NPs-AC were filtered and several time was washed with deionized water and dried at 70 °C for 48 h.

2.2. Ultrasonic assisted dyes adsorption experiment

The simultaneous ultrasonic assisted adsorption of BG, EY, MB and AO (these dyes were purchased from Sigma Aldrich company) in quaternary solution onto CuO-NPs-AC was carried out in a batch method as follow: 50 mL of 4.5 mg L^{-1} of dyes solution at pH 6.0 (The pH/Ion meter model-686 (Metrohm, Switzerland, Swiss) was used for pH adjustment) was mixed thoroughly with 0.03 g of CuO-NPs-AC in Erlenmayer flask and immersed in an ultrasonic bath (ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System) at 40 kHz of frequency and 130 W of power was used for the ultrasound-assisted adsorption) for 4.5 min at room temperature. Finally, the sample was centrifuged and the spectrum of dyes in the effluent solutions was record by Jasco UV–vis spectrophotometer model V-530 (Jasco, Japan). All of experimental was performed 2.0 time. Then dyes removal percentage ($R\%$) and adsorption capacity (Q_e) was calculated according to below equations [14–16]:

$$R\% = \frac{C_{0i} - C_{ei}}{C_{0i}} \times 100 \quad (1)$$

$$q_i = \frac{V(C_{0i} - C_{ei})}{M} \quad (2)$$

where $C_{0,i}$ and $C_{e,i}$ are the initial and final concentrations (mg L^{-1}) of dye i in the ternary solution, respectively, V is the volume (L) of dyes solution used for the adsorption experiments, and M is the mass (g) of adsorbent [3,28].

Equilibrium adsorption isotherm studies are required to give useful information about mechanism, confirm the accuracy of our results, calculate the theoretical maximum adsorption capacity and tendency of adsorbent toward each operating adsorb [25]. As well as, adsorption kinetics is an important step to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction [34,35]. Therefore, the adsorption kinetics and isotherms of understudy dyes removal on this adsorbent at optimal condition was investigated and its applicability for treatment of wastewater and these dyes removal was investigated.

2.3. Analytical measurements

Concentrations of dyes were determined by finding out the absorbance at the characteristic wavelength using a Jasco UV–vis spectrophotometer model V-530 (Jasco, Japan). A standard solution of the dye was taken and the absorbance was determined at different wavelengths after analysis of derivative spectrophotometric method. This wavelength was used for preparing the calibration curve between absorbance and the concentration of the dye solution. The calibration plot showed a linear variation up to 10 mg L^{-1} of each dyes.

Table 1
Experimental factors and levels in the central composite design.

Factors	Unit	Surface factors				
		Levels			Star point α =±2.37	
		(Low) −1	(Central) 0	(High)+1	$-\alpha$	$+\alpha$
(X_1) Sonication time	min	3	3.5	4	2.72	4.28
(X_2) Adsorbent dosage	g	0.023	0.025	0.027	0.022	0.028
(X_3) Initial MB concentration	mg L^{-1}	4	6.5	9	2.6	10.4
(X_4) Initial AO concentration	mg L^{-1}	4	6.5	9	2.6	10.4
(X_5) Initial EY concentration	mg L^{-1}	4	6.5	9	2.6	10.4
(X_6) Initial BG concentration	mg L^{-1}	4	6.5	9	2.6	10.4