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Modeling and optimization of simultaneous removal of ternary dyes onto copper sulfide nanoparticles loaded on activated carbon using second-derivative spectrophotometry

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ABSTRACT

In this work, a response surface methodology (RSM) and artificial neural network (ANN) were used to study the ultrasound-assisted simultaneous removal of ternary toxic dyes onto copper sulfide nanoparticles loaded on activated carbon (CuS–NP–AC), while dyes contentment analysis were undertaken by derivative spectrophotometry. The influence of process variables (adsorbent mass, sonication time, MG, DB and MB concentration dyes on adsorption was investigated by central composite rotatable design (CCRD) of RSM. The experimental data obtained through CCRD was used to train the ANN model. The results reveal satisfactory results of empirical models ($p < 0.0001$) for fitting to the experimental data. According to constructed the response model the maximum removal efficiency close to 100% for all dyes at following optimum value of operating variables: 10 mg/L of MG, DB and MB, 6 min sonication time: and 0.02 g CuS–NP–AC, at pH 8.0 was achieved. The ANN based on the Levenberg–Marquardt algorithm (LMA) composed of linear transfer function (purelin) at output layer and tangent sigmoid transfer function (tansig) at hidden layer with 5, 8 and 9 neurons for MG, DB and MB, respectively, give best operation conditions for good prediction of behavior adsorption system. The maximum adsorption capacity of CuS–NP–AC according to Langmuir isotherm model was 263.2, 243.9 and 204.1 mg/g for MG, DB and MB, respectively. The pseudo-second-order model extensively with high ability is able to predict behavior of dyes adsorption onto adsorbent.

1. Introduction

Water and its resource purity and quality have great importance in organism daily lives, hence. The main pollutant enters the water system through industrial, domestic and agricultural activities [1,2].

Many industries viz. textile, dyestuffs, plastics, leather, and paper industry lead to arrival of color products to wastewaters and presence of dyes in such system undergo chemical changes, consume dissolved oxygen and also generate carcinogenic and genotoxic problem [3,4], while small dyes content are highly visible and from a serious hazardous to system [5]. Various classifications of dyes such as basic, acid, disperse, azo, diazo, metal complex and anthraquinone based [6] have synthetic origin and/or complex structure that cause their hard and difficult destruction and/or removal [7]. Malachite Green (MG), disulfine blue (DB) and methylene blue (MB) as model compounds commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on [8,9].

Thus, the removal of dyes from wastewaters before their mixing with clean water is essential. Numerous technologies such as adsorption, membrane separation, flocculation–coagulation and aerobic or anaerobic treatment are widely applied for dyes scavenging [10,11]. Adsorption extensive usage emerged from system flexibility, low cost as well as low energy consumption [12–18] to produces a high quality treated effluent to meet environmental emission standards [19].

Activated carbon (AC) is generally used for definition of highly crystalline carbonaceous adsorbents internal pore structure [20–22]. On the other hand, nano-structured metal adsorbents offer attractive features such as high surface area, low production

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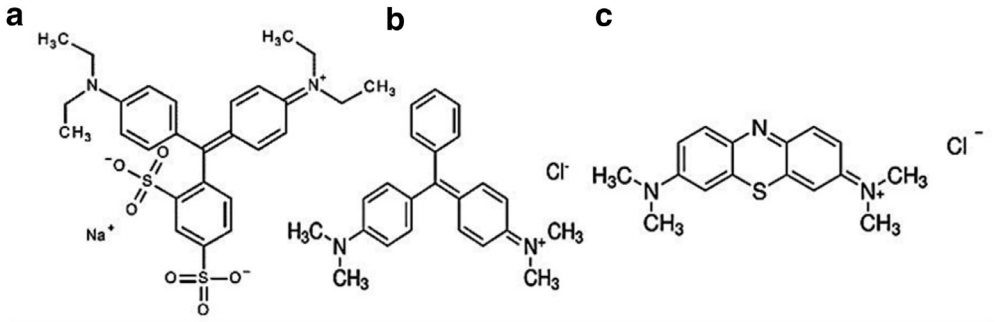

	a) Disulfine blue	b) Malachite green	c) Methylene blue
C.I number	129-17-9	42000	52015
Chemical formula	$C_{27}H_{31}N_2NaO_6S_2$	$C_{23}H_{25}N_2Cl$	$C_{16}H_{18}N_3SCl$
Molecular weight (g mol^{-1})	566.67	364.91	319.85
λ (nm)	637	617	664

Fig. 1. Information on the disulfine blue (DB), malachite green (MG) and methylene blue (MB) dyes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

costs and regeneration by combusting the adsorbed species and represent of materials with unique ability for adsorption applications [23–25].

Nanocomposites containing nanostructured transition sulfides of metals like Cd, Zn, Ni, Sn and Cu exhibit very unusual physical and chemical properties compared to their bulk phases that candidate them for construction of novel functional smart materials [26–29] through short time and low cost protocol that simultaneously enhance removal percentage.

Convention of one-factor-at-a-time optimization approach is burdensome and time consuming and fails to determine the interactive and main effects of the factors. Solving these problems is possible by application of response surface methodology (RSM) and artificial neural networks (ANN) that permit estimation of the effect of the independent variables and their interactions [30–32].

The understudy research focused on the combination of RSM and ANN to optimize and model the whole adsorption following dyes content determination by derivative spectrophotometry, while influence of parameters was fully investigated by Central Composite Rotatable Design (CCRD). First, the pH was optimized solely by one at a time and subsequently CCRD was used to study the main variables (concentration of dye, adsorbent mass and sonication time). The response surface methodology (RSM) according to the desirability function (DF) was used to achieve optimum point and subsequently achieve maximize response. The combination of CCRD with DF allows achievement of the optimum value of all variables, while an ANN model the adsorption process. Finally, the adsorption kinetic and equilibrium that correspond to dyes adsorption onto CuS–NP–AC in ternary systems was studied.

2. Experimental section

2.1. Chemicals and materials

All chemicals including hydrochloric acid (HCl), sodium hydroxide (NaOH) with the highest purity available are purchased from Merck (Dermasdat, Germany). Copper acetate [$Cu(CH_3COO)_2.H_2O$], thioacetamide (CH_3CSNH_2) and trisodium citrate ($Na_3C_6H_5O_7$) were purchased from Sigma company. Malachite green (MG), disulfine blue (DB) and methylene blue (MB) (Fig. 1a) (Merck, Germany) were purchased and used without any further purification. Their stock solutions (200 mg/L) prepared by dissolving 20 mg of their weighed quantity in 100 mL double distilled deionized water. The experimental solutions of desired concentration were prepared accordingly by diluting the stock solution with distilled water.

2.2. Instrumentation and characterization

The MG, DB and MB concentration in supernatant was analyzed by a UV–vis spectrophotometer (model V-530, Jasco, Japan) with fixed slit width of 2 nm by scan speed of 1000 nm/min. In single dye solution, their concentrations were determined by measurement of the absorbance at 617, 637 and 664 nm for MG, DB and MB, respectively. In ternary solutions, the second-order derivative spectrometry was accurately applicable of the absorbance to wavelength was used to find the optimal wavelength for each dye at which the impact of the other component was minimized.

The initial pH values of the solutions were roughly adjusted to 2.0–10.0 by adding either 0.1 mol L^{-1} HCl or NaOH using a pH-meter (Ino Lab pH 730, Germany). Powder X-ray diffraction (XRD) data were recorded and collected on the XRD model PW 1800 of Phillips Company Ltd., Holland using $Cu_{K\alpha}$ as characteristic radiation ($\lambda = 0.15418$ nm) with θ–θ configuration. The measurements were made in 2θ ranging from 20° to 80°. Analysis was mainly done by the software X'Pert High Score of the same company. Scanning electron microscopy (SEM) images were taken on a scanning electron microscope (Hitachi S4800, Japan).

2.3. Synthesis of copper sulfide nanoparticles loaded on activated carbon

The synthesis of CuS nanoparticles was based on the reaction of the mixture of copper (II) acetate [$Cu(CH_3COO)_2.H_2O$] with thioacetamide as Cu^{2+} and S^{2-} ions source in aqueous media, respectively. In this regard, 0.2 g of Cu $(CH_3COO)_2.H_2O$) was dissolved in 95 mL double distilled water. Then, appropriate amount (1.176 g) of trisodium citrate ($Na_3C_6H_5O_7$) as capping agent was added into the solution under stirring. In the next step, 5 mL of 0.4 mol/L thioacetamide solution was added to above solution drop by drop while the solution was stirred. Finally, the precipitate was separated from solutions by centrifugations and washed repeatedly with water and ethanol to removal soluble salts. The CuS nanoparticles were dried at 80°C in an oven for 8 h. Finally the prepared CuS nanoparticles mixture was agitated with activated carbon (A ratio of 1–10 AC) in thermo-bath at 60 °C for 3 h and were dried at 60 °C for 3 h and applied as absorbent for adsorption experiments.

2.4. Sorption experiments

The adsorption of dyes solutions accelerated using ultrasound power combined with CuS–NP–AC. The sonochemical adsorption experiment was carried out in a batch mode as follows: specified