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Simultaneous ultrasound-assisted ternary adsorption of dyes onto copper-doped zinc sulfide nanoparticles loaded on activated carbon: Optimization by response surface methodology

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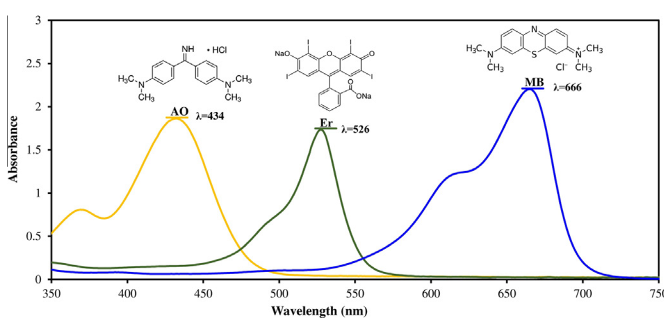
HIGHLIGHTS

- Ternary adsorption of dyes on copper-doped zinc sulfide nanoparticles loaded on activated carbon.
- We demonstrate a methodology for simultaneous dyes removal from aqueous solution.
- Application of ultrasound accelerates mass transfer and decreases the removal time.

GRAPHICAL ABSTRACT



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ABSTRACT

The simultaneous and competitive ultrasound-assisted removal of Auramine-O (AO), Erythrosine (Er) and Methylene Blue (MB) from aqueous solutions were rapidly performed onto copper-doped zinc sulfide nanoparticles loaded on activated carbon (ZnS:Cu-NP-AC). ZnS:Cu nanoparticles were studied by FESEM, XRD and TEM. First, the effect of pH was optimized in a one-at-a-time procedure. Then the dependency of dyes removal percentage in their ternary solution on the level and magnitude of variables such as sonication time, initial dyes concentrations and adsorbent dosage was fully investigated and optimized by central composite design (CCD) under response surface methodology (RSM) as well as by regarding desirability function (DF) as a good and general criterion. The good agreement found between experimental and predicted values supports and confirms the suitability of the present model to predict adsorption state. The applied ultrasound strongly enhanced mass transfer process and subsequently performance. Hence, a small amount of the adsorbent (0.04 g) was capable to remove high percentage of dyes, i.e. 100%, 99.6% and 100% for MB, AO and Er, respectively, in very short time (2.5 min). The experimental equilibrium data fitting to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models showed that the Langmuir model applies well for the evaluation and description of the actual behavior of adsorption. The small amount of proposed adsorbent (0.015 g) was applicable for successful removal of dyes (RE > 99.0%) in short time (2.5 min) with high adsorption capacity in single component system (123.5 mg g^{-1} for MB, 123 mg g^{-1} for AO and 84.5 mg g^{-1} for Er). Kinetics evaluation of experiments at various time intervals reveals that adsorption processes can be well predicated and fitted by pseudo-second-order and Elovich models.

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Introduction

Real wastewater with extensive amount of dyes and organic pollutants present in textile and other industries generates problems and hazards for different ecosystems. The dyes have diverse effects such as generation of mutagen and carcinogenic problem for living organism as well as reduction of photosynthesis following hinder from oxygen arrival to water [1]. Dyes-associated problems necessitate the development of novel, safe and efficient protocol for enhancement in quality of water through decrease in pollutants [2,3]. In this way, physical and chemical methods such as coagulation [3], reverse osmosis [4], photodegradation [5], electrochemical oxidation [6], ozonation [7], biosorption [8] and adsorption [9–13] are used for increasing water quality by reducing dyes quantity. Amongst these methods, the adsorption is a popularly good alternative procedure, following the application of low cost adsorbent. Furthermore, a suitable adsorbent should be simple in design, easy for operation, green and non-toxic. In addition, a small amount of it should be able remove huge amount of dyes in short time. As mentioned above, the wide application of adsorption is emerged from advantages including high efficiency, capacity and large scale ability of generable adsorbents [2,14–18].

Common properties of Methylene Blue, MB, (Table S1(a)) are extensively presented in our previous publications. This dye has diverse applications and it is odorless dark green powder (solid) at room temperature. Its solution in water is blue and it is used as redox indicator in analytical chemistry. MB is frequently prescribed as urinary analgesic/anti-infective/anti-spasmodic that is a combination of drugs containing phenyl salicylate, benzoic acid, hyoscyamine sulfate, and methylamine [19]. Auramine-O (AO) and its hydrochloride salt are applied for coloring paper, textiles, leather and foods [20]. International Agency for Research on Cancer included AO as most carcinogenicity agent and chemical for animals [21] that is related to its bio-transformation in rats and humans [20]. AO (Table S1(b)) is a yellow dye which is commonly used in paper and textile mills, leather and carpet industries. Erythrosine, Er, (Table S1(c)) is cherry-pink synthetic dye that is applied for coloring biscuits, chocolate, luncheon meat, sweets, chewing gums and also as pharmaceutical agent [22,23]. High amount of Erythrosine is probable to be present in aqueous media that makes urgent requirement to develop novel approach for its accurate monitoring and control in various media.

As mentioned above, nontoxic, low cost and easy-to-access adsorbents are the best choice to design efficient and feasible wastewater treatment approach. Nanostructured materials due to their distinguished properties such as high surface area, huge amount of reactive surface center, presence of metallic and non-metallic centers with different geometries and structures are good candidate and selection for efficient wastewater treatment [24]. Combination of nanostructured material with other general supports like activated carbon (AC) is universal adsorbent for the removal of pollutants [25,26]. AC contains various reactive sites such OH, COOH, C=O and amide groups which synergically improves the efficiency of adsorption procedure in conjunction with nanoparticle properties.

Ultrasound irradiation is well known to accelerate chemical process due to the phenomenon of acoustic cavitation. In this procedure, the formation, growth and collapse of micrometer-scale bubbles formed by the propagation of a pressure wave through a liquid make the mass transfer process intensified and break the affinity between adsorbate and adsorbent [27,28]. Shock waves have the potential of creating microscopic turbulence within interfacial films surrounding solid particles [25,26]. Acoustic streaming induced by the ultrasonic wave is the movement of the liquid, which can be considered to be the conversion of sound to the kinetic energy. These phenomena increase the rate of mass transfer near the surface [29–32].

In the present study RSM has been employed to model and optimize the process condition for efficiently rapid removal of dyes in ternary solutions. Influences of possibly important variables (sonication time, initial dyes concentration and amount of adsorbent) were investigated and optimized by central composite design (CCD) under response surface methodology (RSM) and regarding the desirability function (DF) as a criterion of maximizing the response following the pH optimization. The results obtained from the presented models were compared with the experimental values. The ZnS:Cu nanoparticle-loaded AC (ZnS:Cu-NP-AC) was synthesized and subsequently characterized by using different techniques such as scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis. Then the adsorption kinetics and isotherms of dye removal by this adsorbent were studied and its applicability for the treatment of wastewater polluted by the dyes AO, Er and MB was investigated. The experimental data were modeled by universal equations such as pseudo first- and second-order and intraparticle diffusion models. The present adsorbent was found to be very efficient with large volume sorption capacities for rapid removal of dyes studied.

Experimental

Instruments and reagents

All chemicals including NaOH, HCl, MB, AO and Er with the highest purity available were purchased from Merck (Darmstadt, Germany). The stock solution (200 mg L^{-1}) of dyes was prepared by dissolving 20 mg of each solid dye in 100 mL double distilled water and the working concentrations were prepared daily by their suitable dilution. An ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System) at frequency of 40 kHz with power of 130 W was used for the ultrasound-assisted adsorption procedure. The ZnS:Cu-NP-AC was characterized by SEM, TEM and XRD. The morphology and dimensions of the adsorbent were determined by TEM and FESEM (Hitachi S-4160) under an acceleration voltage of 30 kV. X-ray diffraction (XRD) pattern was recorded by an automated Philips X'Pert X-ray diffractometer (40 kV and 30 mA) for 2θ values over 20–60°. The pH measurements were carried out using pH/Ion meter model-686 (Metrohm, Switzerland, Swiss) and the AO, Er and MB concentrations were determined using Jasco UV–Vis spectrophotometer model V-530 (Jasco, Japan) at their respective wavelengths of 434, 526 and 666 nm. The STATISTICA, a statistical software package version 10.0, was used for experimental design analysis and subsequent regression analysis of the experimental data. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA).

Ultrasound-assisted adsorption method

The ultrasound-assisted removal of dyes from their ternary solutions was examined using ZnS:Cu-NP-AC. The adsorption experiments were carried out in a batch mode. 50 mL of dyes solution at known concentration (initial MB concentration of 25 mg L^{-1}, initial AO concentration of 25 mg L^{-1} and initial Er concentration of 5 mg L^{-1}) and a known amount of ZnS:Cu-NP-AC (0.04 g) were loaded into the flask and maintained the desired sonication time (2.5 min) at pH 4.0 and at room temperature. After this time, solutions were analyzed for the final concentration of AO, Er and MB via UV–Vis spectrophotometer at 434, 526 and 666 nm, respectively.