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Modified nickel ferrite nanocomposite/functionalized chitosan as a novel adsorbent for the removal of acidic dyes

Ali Zeraatkar Moghaddam *, Ebrahim Ghiamati, Atefeh Pourashuri, Ali Allahresani

Department of Chemistry, Faculty of Science, University of Birjand, Birjand, Iran

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ABSTRACT

As a new type of magnetic adsorbent, a nickel ferrite nanocomposite modified by functionalized chitosan was developed to remove methyl orange and Congo red from aqueous solutions. This new adsorbent was characterized and utilizing batch adsorption approach, the mechanism of methyl orange and Congo red removal were probed. Following that the study on pertinent parameters which could influence the efficiency of the dyes removal, i.e. pH of the solution, initial dye concentration, dose of the adsorbent, and contact time were accomplished in order to arrive their optimized values by using response surface methodology. In addition, kinetics and isotherm studies were conducted on the developed system. Langmuir model was used to probe adsorption isotherm, acquiring adsorption capacity of 551.2 and 274.7 mg g^{-1} for methyl orange and Congo red, respectively. Both of methyl orange and Congo red adsorption kinetics obeyed a pseudo-second-order kinetic model, indicating that adsorption was the rate-limiting step and only 5 min was required to remove 50% of dyes. The fitting of experimental data was fulfilled with intra-particle diffusion reaching to conclusion that the adsorption kinetic could be controlled simultaneously by film diffusion and intra-particle diffusion. Furthermore, the desorption studies of dyes showed that the adsorbent is reusable.

1. Introduction

Textile and related industries create ample dye waste releasing into environment [1]. These hazardous, toxic, non-biodegradable, and sometimes carcinogenic impart skin irritation [2], allergy and headache. Azo dyes as a largest group of colorants encompass 70% of all dyes manufactured in the world [3–5]. MO and CR as azo dyes are anionic having aromatic rings and —N═N— chromophores. A great volume of research and efforts has been conducted on dyes-removal. Some conventional techniques like coagulation, ozonation, biological treatment, ion exchange, membrane filtration and photo catalysis have extensively been used for this purpose [6–8]. Drawbacks to these techniques include fairly large flow rates, emerging effluents with harmful substances such as ozone and free radicals [9]. On the other hand, adsorption procedures are inexpensive, simple, effective bearing short treatment period [10–14]. In this regard, various types of absorbents like silica, micro particles, activated carbon and graphite have been proposed for the removal of dyes from aqueous solutions.

Chitosan, a natural bio-sorbent material, has been considered as promising cost-effective adsorbent for removal of hazardous anions in industrial wastewaters. It is the second most abundant polysaccharide in nature after cellulose, being nontoxic, bio-compatible, biodegradable and cost effective [15]. Furthermore, it is less expensive than activated carbon and it has high content of amino and hydroxyl functional groups showing high adsorption potential for various aquatic pollutants in the water pollutants treatment [16–18]. The separation of chitosan-based adsorbents from treated solution using traditional separation methods such as filtration and sedimentation could result in blocking the filters or loss of adsorbent and cause secondary pollution [19]. Moreover, magnetic separation technology by combination of chitosan and magnetic compounds is an efficient strategy to overcome this problem. The magnetic adsorption techniques which are convenient, rapid, low cost and amenable to automation [20] have been receiving considerable attention in recent years [21,22]. In addition, magnetic core–chitosan shell materials are widely synthesized and employed for the treatment of wastewaters. Magnetite is the most commonly employed magnetic cores due to high surface area, tunable morphology and its special advantage of easy separation under external magnetic fields. Magnetic adsorbents, especially magnetite, have generated increasing interests [23,24]. Meanwhile, the application of magnetite has some drawbacks which should be considered. For example, iron oxides can be affected by the acidic media and/or in the vicinity of oxygen coating them with an inert layer that can protect them negatively affecting their magnetic separability [25]. Therefore, using of spinal ferrite for magnetization of various adsorbent is a very interesting issue recently [26,27].

In the present study, new glutaraldehyde-grafted chitosan coated CuO, $CuFe_2O_4$, or $NiFe_2O_4$ (G-g-C@CuO, G-g-C@CF, or G-g-C@NF,

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* Corresponding author.
E-mail address: a_zeraatkar_m@birjand.ac.ir (A. Zeraatkar Moghaddam).

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respectively) nanocomposites acting as adsorbents with high adsorption capacity were designed. With aid of magnetic particles easy separation by positioning an external magnetic field is achieved. The coating with grafted chitosan improves the chemical stability of nanoparticles and provides new specific functionalities like selectivity for anionic dyes uptake [28]. After comparison of adsorptive capacity of the prepared nanocomposites, the synthesized G-*g*-C@NF adsorbent was selected and characterized, and its adsorption property regarding the removal of MO and CR from aqueous solution under varied experimental conditions was also investigated. For this regard, Box-Behnken design (BBD) was used to model and optimize the influence of different experimental conditions in the dyes removal procedure. The isotherm and kinetics study were performed under the defined optimum conditions, and the optimized procedure was utilized to reduce the MO and CR contamination in real wastewater sample. Furthermore, reusability of the proposed G-*g*-C@NF adsorbent was further examined.

2. Experimental

2.1. Chemicals

Chitosan (MW = 310,000–375,000 Da), MO and CR (99.8% purity) were purchased from Sigma-Aldrich, St. Louis, USA. All analytical grade solvents were provided by Merck, Darmstadt, Germany. HCl, NaOH, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$ and glutaraldehyde received from Fluka, Buchs, Switzerland. Double distilled deionized water (DDW) was used for making solutions and washings.

2.2. Instruments

FT-IR spectrum of the developed adsorbent was acquired with a Bomem MB-Series FT-IR spectrometer as a KBr pellets. Its powder X-ray diffraction (XRD) pattern was obtained using STOE STADI P with scintillation detector, secondary monochromator and Cu-Kal radiation (?? = 1.5406 Å) and its transmission electron microscope image (TEM) was prepared by Philips CM-30 TEM. An Analytikjena spectrophotometer (Specord 210, Germany) was employed to measure the concentration of MO and CR azo dyes.

2.3. Synthesis of different glutaraldehyde grafted chitosan modified adsorbents

2.3.1. Preparation of CuO

CuO nanostructures were synthesized according to Wang et al. report with some modifications [29]. Initially, 9 g of mixed sodium and potassium hydroxides was placed in a 25 mL Teflon vessel and then 2 mmol of $CuCl_2 \cdot 2H_2O$ and 0.1 g $Na_2S \cdot 9H2O$ were added. In the next step, the vessel was sealed and put in a furnace preheated to 70 °C for 16 h and then it was cooled naturally. The obtained solid was washed with DDW and ethanol several times to reach neutral pH [29] and calcinated at 700 °C for 4 h.

2.3.2. Preparation of CF

According to Jiao et al. report, 4 mmol of $FeCl_3 \cdot 6H_2O$ and 2 mmol of $CuCl_2 \cdot 2H_2O$ were dissolved in ethanol and stirred for 30 min [30]. In the next step, NaOH solution (32 mL of a 3 M solution) was added to the previous mixture to produce a coprecipitate product followed by collecting and washing with DDW and ethanol for several times to reach neutral pH. Finally, the produced solids were dried at 70 °C for 16 h and were kept at 700 °C for 4 h.

2.3.3. Preparation of NF

To synthesize NF, a modified solvothermal method was used [31], that is 25 mL of $NiCl_2 \cdot 6H_2O$, 0.20 M was mixed slowly at 30 min with 25 mL of $FeCl_3 \cdot 6H_2O$, 0.40 M solution at constant stirring. Then the pH of the resulting solution was adjusted to 10, following heating at 80 °C for 3 h. The obtained precipitate was filtered, washed with DDW and ethanol and dried in vacuum at 70 °C for 3 h [32].

2.3.4. Modification with glutaraldehyde grafted chitosan

Chitosan was dissolved in 2 wt% acetic acid, then already prepared CuO, CF, or NF nanoparticles were thoroughly dispersed into chitosan solution using ultrasonication, followed by the addition of 25 wt% glutaraldehyde solution. Upon the gel formation, the products were dried in an oven at 60 °C for 12 h, washed several times with 2 wt% acetic acid and then with DDW to remove the unreacted chitosan. The obtained glutaraldehyde-grafted chitosan coated CuO, CF, or NF (G-*g*-C@CuO, G-*g*-C@CF, or G-*g*-C@NF, respectively) were dried again at 50 °C for 12 h, grounded and stored in a desiccator for further dye removal tests.

2.4. Adsorption and desorption experiments

2.4.1. Batch adsorption studies

The adsorption of MO and CR on the proposed adsorbent was occurred in batch mode and the effects of different parameters including adsorbent dose, initial pH, initial dye concentration, and contact time (10–30 min) on removal efficiency were evaluated at 25 °C. The initial pH of the dye solutions was adjusted to proper value by adding HCl or NaOH 0.1 M solutions, following stirring for defined contact time at 800 rpm. At the end, the suspensions were separated for later analysis of dye concentration.

In order to perform isotherm studies, the experiments were carried out by varying the initial dye concentration while the other parameters were kept at their optimum values. The kinetic experiments were conducted at initial dye concentration of 1000 and 500 ppm for MO and CR, respectively, by varying the contact time under the optimum conditions. The removal efficiency and adsorption capacity values at equilibrium and time t (q_e and q_t mg g^{-1}) were calculated using the following equations:

$$\text{Removal Efficiency } (\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

$$q_e = \frac{(C_o - C_e)V}{m}, \; q_t = \frac{(C_o - C_t)V}{m} \tag{2}$$

where C_o, C_e and C_t (mg L^{-1}) are the MO or CR dye concentrations at initial, equilibrium and time t, respectively, V(L) is the solution volume and m(g) is the mass of the used adsorbent. The MO and CR dye concentrations (C) could obtained through Beer–Lambert law in which the absorbance value (λ_{max} = 505 and 497 nm for MO and CR, respectively, see Fig. 1) versus its concentration was linear.

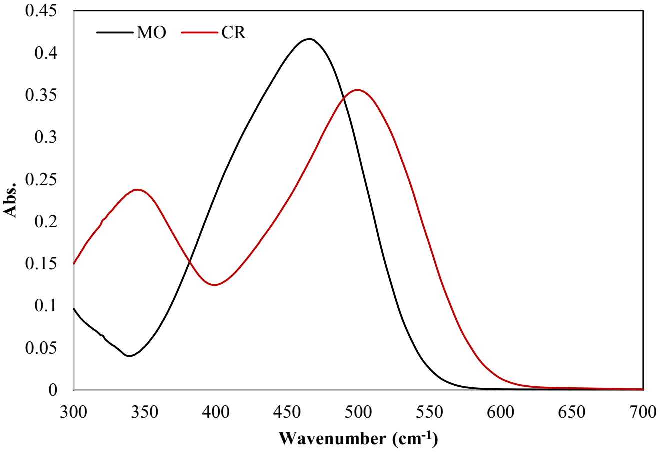

Fig. 1. The UV–Vis spectrums of MO and CR dyes.