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DETERMINATION OF ADSORPTION PERFORMANCE OF HYDROTHERMALLY SYNTHESIZED NANOCOMPOSITE

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Abstract

In this study, a novel nanocomposite was synthesized by a simple one-pot hydrothermal process and used as an adsorbent for the removal of methylene blue (MB) and methyl orange (MO) dyes from the aqueous medium. Overall findings from batch experiments demonstrated that the prepared nanocomposite material (Fe/GBHC) had good adsorption capacity for MB and MO. The maximum adsorption capacities of the Fe/GBHC were observed to be 11 mg/g for MB and 8.9 mg/g for MO at neutral pH of the solutions and at 303 K. To obtain the adsorption mechanism of the Fe/GBHC, the experiments of adsorption isotherms were researched. The adsorption isotherms of both dyes could be described by the Langmuir isotherm equation rather than the Freundlich isotherm equation, with a high correlation coefficient values. The results showed that the prepared Fe/GBHC material by the hydrothermal method could have potential application in the removal of organic dyes from waste water.

Key words: Hydrothermal synthesis, nanocomposite, adsorption performance, wastewater treatment

1. Introduction

Industrial wastewater pollution triggered by organic dyes has been recognized as a global concern. Depending on the statistics, approximately 70.000 tons of dyes are discharged into the water environment per year [1]. Methylene blue (MB) is a typical organic dye widely used in spinning and weaving, papermaking, printing and dyeing, medicine and other industries [2]. Methylene blue residual dyes in wastewater are characterized by their deep color, high permeability and strong alkalinity, which inhibit the photosynthesis of aquatic plants, cause the growth of cancer cells in animals, and disrupt ecosystem balance [3]. Methyl orange (MO) is a typical acid anionic monoazo dye. MO is one of the types of organic dyes used in the textile and printing industry. MO is commonly used in textiles, laboratory experiments and other commercial products. Excessive release of MO is highly damaging to the environment as MO and its decay products are toxic, carcinogenic and mutagenic to living beings [4].

The hydrothermal process is due to its many advantages, especially due to the simple, easy-to-use experimental device, more and more attention. The use of the hydrothermal process enables the formation of more stable condensed phases to achieve high yield and low energy consumption. Synthetic parameters such as temperature and time, pH, precursor concentration, etc., are fundamental for the successful production of high-quality nanostructures [5].

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Several traditional methods have been reported, such as coagulation, ion-selective electrodes, biosorption, photodegradation, electrochemical oxidation, ozonation, reverse osmosis and adsorption to remove hazardous contaminants. Due to its low energy cost, environmental compatibility, and ease of use, adsorption has been suggested to be a convenient approach to removing trace impurities from an aqueous solution [6].

In the present work, Fe/GBHC nanocomposite with well adsorption properties was prepared for the first time for the removal of MB and MO. The main objective of the present study was to investigate the removal of different organic dyes by Fe/GBHC. Finally, the adsorption mechanism of organic dyes on Fe/GBHC was discussed.

2. Materials and Method

2.1. Materials

Iron (III) chloride ($FeCl_3$), Methylene Blue hydrate ($C_{16}H_{18}ClN_3S \cdot xH_2O$), Methyl orange ($C_{14}H_{14}N_3NaO_3S$) and ethanol ($C_2H_5OH$) were purchased from Sigma-Aldrich Co. All the aforementioned reagents were of analytical grade and used without further purification. Deionized water was used throughout this study. As a raw material for the nanocomposite, grape bagasse (GB) was collected from a local fruit juice and wine factory in the Republic of Turkey.

2.2. Synthesis of Fe/GBHC

Nanocomposite was prepared by the simple one-pot hydrothermal method [7]. 10 g GB were to 50 ml of a solution of iron (III) chloride (0.5 M) and mix homogeneously at room temperature (100 rpm/15 min). The resulting mixture was transferred to a 100 ml Teflon-coated stainless steel autoclave and sealed immediately. The autoclave was heated at 200 °C for 1 hour and then naturally cooled to room temperature. The black solid was separated from the solution by vacuum filtration and dried in an oven at 105 ° C for 12 hours. Thereafter, the sample was calcined in a tube furnace equipped with a horizontal tube reactor made of stainless steel for 1 h at 600 °C in a nitrogen atmosphere (N_2). The system was cooled to room temperature. The resulting material was washed several times with ethanol and distilled water and dried at 60 °C for 5 hours. Here the resulting product is called Fe/GBHC.

2.3. Adsorption capacity test

Periodic adsorption experiments were performed in 100 ml. Erlenmeyer flask by adding 0.1 g of nanocomposite in 50 ml of dye solutions with different starting concentrations (20-300 mg/L) with natural pH values (6.33 for MB, 6.30 for MO). The flasks were shaken in a thermostat water bath at 303 K and 150 rpm for 24 hours. After adsorption reached equilibrium, the mixture was centrifuged and filtered with 0.45 mm nylon syringe filter and residual concentration of each dye was visualized using UV-visible (Perkin Elmer lambda 25) at 665 nm for MB and 464 nm for MO. Amounts dyes adsorbed in equilibrium (q_e) were calculated according to formula (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e (mg/g) is the amount of adsorbent adsorbed per gram, C_o and C_e (mg/L) are the initial and equilibrium dye concentrations in the solution, V (L) is the initial volume, and m (g) is the mass of the sorbent.

To evaluate the equilibrium behavior, two isothermal models were used, namely Freundlich [8] and Langmuir [9]. The linear form of these models can be expressed mathematically by the following equations:

Freundlich isotherm: $$\ln q_e = \ln K_F + \frac{1}{n_F}\ln C_e \tag{2}$$

Langmuir isotherm: $$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m}C_e \tag{3}$$

where K_F (L/g) and $1/n_F$ are the Freundlich model constants indicating the capacity or surface heterogeneity of the adsorption process. b (L/g) is the Langmuir constant, which represents the adsorption energy of the binding sites, and q_m (mg/g) is the maximum adsorption in the monolayer. The values of the isotherm parameters and the linear regression coefficients (R^2) are determined. The quality of experimental data adapted to adsorption isothermal models was evaluated using a higher R^2 value.

3. Results and Discussion

In this work, the adsorption feature of nanocomposite was investigated by selecting MB and MO as adsorbates. In Figure 1 shows the adsorption isotherms of both dyes at 30 °C on Fe/GBHC. The experimental data were selected from the models of the Langmuir and Freindlich isotherms. The calculated constants of the two equations of the isotherm are shown in Table 1. A high value of the regression coefficient (R^2) was used to determine the most suitable isotherm. When comparing the values of R^2, it was found that the Langmuir model was more favorable than the Freundlich model because of the higher values of R^2 for the dyes MB and MO, suggesting that a single-layered adsorption process took place on the surface of Fe/GBHC. The adsorption intensities (1/n) for both dyes are between 0 and 1, which indicates suitable adsorption conditions. The maximum adsorption capacity of Fe/GBHC for MB and MO was 11 mg/g and 8.9 mg/g, respectively. Therefore, the composite tested in this study can be used as a promising adsorption material for removing dyes from aqueous solutions. To demonstrate the importance of the Fe/GBHC used in this work, the maximum adsorption capacities (q_m) of Fe/GBHC were compared with various other adsorbents described in earlier work and listed in Table 2.

Table 1. Isotherm constants and correlation coefficients calculated for MB and MO dyes adsorption onto Fe/GBHC

Isotherm	*Parameters*	*Dyes*	
		MB	***MO***
Freundlich	K_F (L g^{-1})	3.80	1.79
	1/n	0.1892	0.2785
	R^2	0.9771	0.9715
Langmuir	q_m (mg g^{-1})	11.03	8.91
	b (L mg^{-1})	0.078	0.038
	R^2	0.9986	0.9986

K_F: constant in Freundlich model (mg g^{-1}) (L mg^{-1})$^{1/n}$; 1/n: Freundlich power constant; q_m: monolayer adsorption capacity (mg g^{-1}); b: constant in Langmuir isotherm model (L mg^{-1}).

Table 2. Comparison of adsorption capacities of various composite adsorbents for the removal of MB and MO dyes

Composite Adsorbents (Pollutants)	**q_m (mg g^{-1})**	**Reference**
Composite gel bead (MB)	4.85	[10]
NiO/MCM-41 composite (MB)	24.40	[11]
CMC/kC/AMMT composite bead (MB)	10.75	[12]
Fe/GBHC composite (MB)	11.03	This work
Chitosan/organic rectorite composite (MO)	5.56	[13]
Fe_2O_3/SiO_2/chitosan nanocomposite (MO)	34.29	[14]
Alginate/polyaspartate hydrogel composite (MO)	0.22-0.28	[15]
Fe/GBHC composite (MO)	8.91	This work

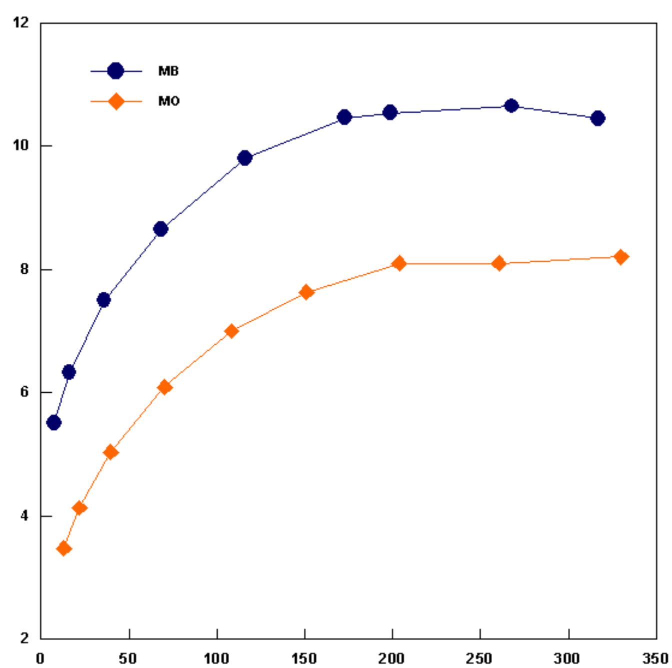

Figure 1. Adsorption isotherms of MB and MO onto Fe/GBHC

Conclusions

The new Fe/GBHC composite was successfully synthesized from GB by hydrothermal method in a single step. Fe/GBHC has shown good environmental performance. The maximum adsorption capacities for MB and MO were 11 and 8.9 mg/g, respectively. Both equilibrium adsorption data agreed well with the Langmuir model. In summary, Fe/GBHC has great potential as an alternative adsorbent.

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