Contents List available at VOLKSON PRESS

New Materials and Intelligent Manufacturing (NMIM)

DOI : http://doi.org/10.26480/icnmim.01.2018.246.249

Journal Homepage : https://topicsonchemeng.org.my/

ISBN: 978-1-948012-12-6

STUDY ON ADSORPTION OF DYE ORANGE II WITH MAGNETIC CETYLPYRIDINIUM BROMIDE

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ARTICLE DETAILS

Article History:

Received 26 June 2018
Accepted 2 july 2018
Available online 1 August 2018

ABSTRACT

The magnetic cetylpyridinium bromide was prepared and characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and other techniques. It can be used as adsorbent for removal of the dye orange Ⅱ pollutants in wastewater. The effect of some factors on the adsorption effect was studied, such as the concentration of orange Ⅱ, reaction temperature and pH value. The experimental results showed that the magnetic cetylpyridinium bromide has better adsorption capacity for orange Ⅱ. The adsorption amount increases with the increase of initial concentration and temperature. When the pH is 4, the adsorption amount reaches the maximum. Adsorption kinetics indicated that the adsorption process of orange Ⅱ by magnetic cetylpyridinium bromide was more consistent with the pseudo second-order reaction model. The isothermal adsorption linear fit shows that the adsorption of orange Ⅱ on the magnetic material conforms to Langmuir isothermal adsorption. The maximum adsorption capacity is about 270.27 mg/g.

KEYWORDS

Magnetic cetylpyridinium bromide, Orange II, Adsorption

1. INTRODUCTION

In recent years, dyes are widely used in paper, textile, food, cosmetics, printing and leather industries [1]. Among them, orange Ⅱ is one of the major contaminants in dye wastewater. With the development of industry, a large amount of waste water will be generated during the synthesis of dyes. Therefore, the removal of dyes from wastewater has attracted worldwide attention. Dye contamination has become an environmental problem that destroys ecosystems and harms human health [2-6].

Many technologies can be used for dye wastewater treatment, such as biodegradation, photocatalytic degradation, biological treatment, membrane separation and adsorption [7]. At present, the method for treating dye wastewater is mainly based on adsorption [8]. Adsorption method receives a lot of attention due to its advantages of easy operation, rapid, high efficiency and no environmental pollution [9]. Orange Ⅱ is an azo type anionic dye with good water solubility [10]. The cetylpyridinium bromide (CPB) is a cationic surfactant. It has strong adsorption capacity for anionic dyes.

The main content of this study is the magnetic cetylpyridinium bromide composite material was prepared to extract the dye Orange Ⅱ in water. The effect of the initial concentration of the dye, the adsorption time, and the pH on the adsorption effect was studied. Adsorption kinetics and isothermal adsorption equations were used to investigate the mechanism of adsorption. This study provided a theoretical reference for the treatment of anionic dye from wastewater.

2. EXPERIMENTAL SECTION

2.1 Reagents and Instruments

Orange Ⅱ and cetylpyridinium bromide were purchased from Aladdin Reagents. Ferric chloride, polyethylene glycol, ethylene glycol, anhydrous ethanol were provided by Tianjin Yongda Chemical Reagent Co., Ltd. Anhydrous sodium acetate was purchased from Tianjin Ruijinte Chemical Co., Ltd. Tetraethoxysilane (TEOS) and ammonia were purchased from Tianjin Tianyi Chemical Reagent Factory. The above chemicals are all analytically pure.

UV-visible spectrophotometer Tuopu-920 was purchased from Beijing General Analysis Instrument Co., Ltd. Ultrasonic cleaner As3120 was purchased from Autoscience, Canada. Vacuum drying oven DZF-6051 was purchased from Shanghai Yiheng Scientific Instrument Co., Ltd. The blast drying oven EP115 was purchased from Pentax Germany. The Milli-Q ultrapure water system Intergral-10 was purchased from Millipore, USA. The experimental digital electric mixer E30-H was purchased from Shanghai Ouhe Machinery Equipment Co., Ltd. Electronic balance CPA225D was purchased from Sartorius Scientific Instruments Co., Ltd. High-speed centrifuge H-1650 was purchased from Changsha Xiangyi Centrifuge Co., Ltd.

2.2 Synthesis of Fe_3O_4@SiO_2@CPB

Fe_3O_4 was synthesized by solvothermal reaction. First, $FeCl_3$•$6H_2O$ (1.35 g) was dissolved in ethylene glycol (40 mL). Then, sodium acetate (3.6 g) and polyethylene glycol (1.0 g) were added to the solution. After stirring well, the mixture was transferred to a polytetrafluoroethylene autoclave and heated at 190 °C for 8 h. The resulting black product was washed several times with ultrapure water and ethanol, and vacuum dried at 60 °C for 2 h. Fe_3O_4 nanoparticles were obtained. Fe_3O_4 (100 mg) was sonicated in 0.1 M HCl (50 mL) for 0.5 h. Then the adsorbent is washed with distilled water. After magnetic separation, it was dispersed in a mixture of ethanol (80 mL) and deionized water (20 mL). Next, 25% aqueous ammonia (10 mL) was added dropwise to the above suspension. A solution of TEOS (0.03 g) was added dropwise. The resulting mixture was stirred for 6 h. The adsorbent was solid-liquid separated by a magnet and then washed with ethanol and water several times. The product was dried in vacuum at 60 °C for 2 h. Fe_3O_4@SiO_2 nanoparticles were obtained. Fe_3O_4@SiO_2 (100 mg) was added to a mixture containing CPB (0.1 g), water (80 mL), absolute ethanol (60 mL) and 25% aqueous ammonia (1.0 mL). And a uniform black liquid was formed by ultrasonication. It was

transferred to a three-necked flask, mechanically stirred, and TEOS (0.4 g) solution was slowly added dropwise. The resulting mixture was stirred at room temperature for 6 h. The adsorbent was separated into solid and liquid by a magnet. The resulting product was washed several times with ethanol and water, then vacuum dried at 60 °C for 2 h.

2.3 Adsorption experiments

The effects of initial dye concentration, temperature, and solution pH on adsorption were studied. 100 mL of a certain concentration of orange Ⅱ dye solution was added into a conical flask, and 0.01 g Fe_3O_4@SiO_2@CPB adsorbent was added. Then it is shaken at a constant temperature with the oscillation speed of 200 r/min. Adsorbent and dye molecules fully interact with each other. After magnetic separation, the supernatant was taken and the absorbance A of the orange Ⅱ in the residual solution was measured at 485 nm by an ultraviolet spectrophotometer. The mechanism of action of Fe_3O_4@SiO_2@CPB MNPs and orange Ⅱ was investigated using adsorption kinetics and thermodynamic equations. Calculate the amount of adsorbent qt (mg/g) under certain conditions. The calculation method is shown in (1):

$$q_t = \frac{(C_0 - C_t)\ V}{m} \qquad (1)$$

where, C_0 is the initial concentration of the orange Ⅱ dye (mg/L), C_t is the instantaneous concentration at the adsorption time t (mg/L), m is the mass of the adsorbent (g) and V is the volume of the orange Ⅱ dye (L).

3. RESULTS AND DISCUSSION

3.1 Characterization of Fe_3O_4@SiO_2@CPB

Figure 1(a) is a scanning electron microscope (SEM) image of Fe_3O_4@SiO_2@CPB. It can be seen that the magnetic adsorbent shows a spherical shape. Figure 1(b) is a transmission electron microscope (TEM) image of Fe_3O_4@SiO_2@CPB. It can be seen that the Fe_3O_4@SiO_2@CPB magnetic adsorbent has a core-shell structure. Solid black spheres represent Fe_3O_4. It shows that SiO_2@CPB has been successfully coated on Fe_3O_4.

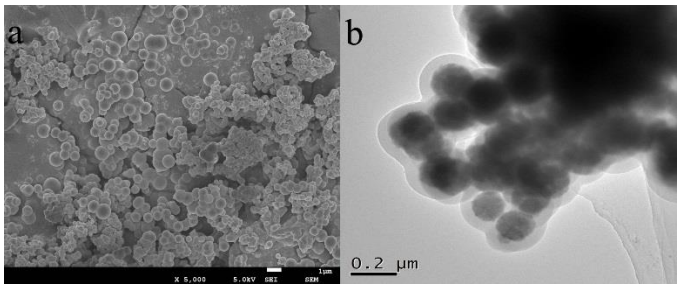

Figure 1: (a) Scanning electron microscope image of Fe_3O_4@SiO_2@CPB. (b) Transmission electron microscope image of Fe_3O_4@SiO_2@CPB.

3.2 Effect of Dye Concentration on Adsorption

Experiments were performed at different initial concentrations of orange Ⅱ. 100 mL of orange Ⅱ solution with concentrations of 50, 70, and 90 mg/L was prepared respectively. 0.01g of a magnetic adsorbent was added and shaken until the adsorption equilibrium. The absorbance was measured. As shown in Figure 2, as the initial dye concentration increases, the amount of adsorbed dye also increases accordingly. This is due to the increase of the concentration, which will provide a greater frontal driving force for the adsorption and promote the more effective collision of the active site of the orange II with the adsorbent surface, so the adsorption amount will become larger [11].

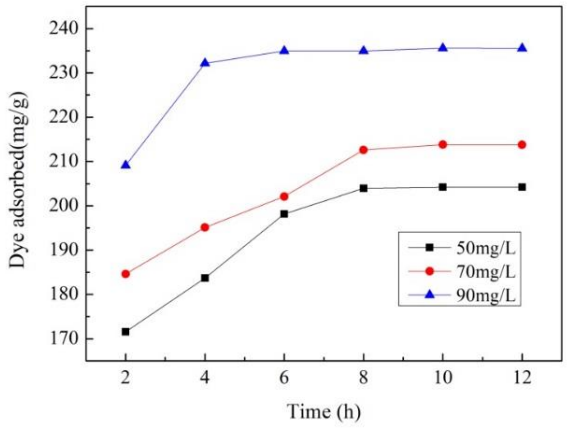

Figure 2: Effect of dye concentration on adsorption

3.3 Effect of Reaction Temperature on Adsorption Effect

Weigh 0.01g of magnetic Fe_3O_4@SiO_2@CPB into 100 mL of orange Ⅱ solution (50 mg/L), vortex for 12 h at 25, 35, and 45 °C. As shown in Figure 3, the amount of adsorption increases as the temperature of the solution increases, and each rapidly increases at the beginning and then gradually becomes constant. This may be due to the increase in the mobility of orange Ⅱ molecules, and the increase in temperature will increase the number of active sites for adsorption, which will increase the amount of adsorption [12].

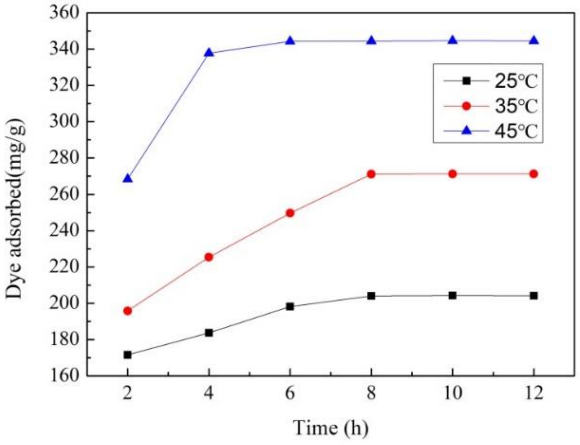

Figure 3: Effect of reaction temperature on adsorption effect

3.4 Effect of pH on Adsorption

Figure 4 shows the effect of different pH on the adsorption of orange Ⅱ solution. The amount of adsorption decreases as the pH of the solution increases. The adsorption capacity decreased from 310.26 mg/g to 169.23 mg/g. It can be seen from the figure that the adsorption effect is best at pH = 4.

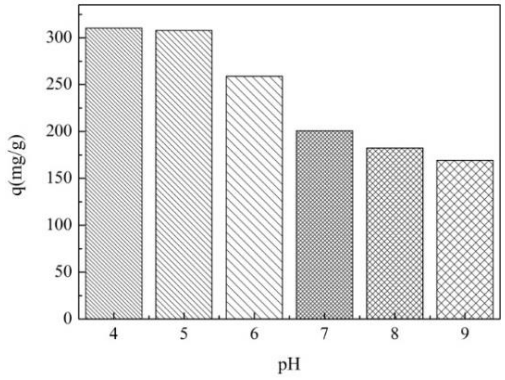

Figure 4: Effect of pH on adsorption

3.5 Adsorption Kinetics Studies

In order to study the adsorption data at different adsorption time, we use pseudo-first-order and pseudo-second-order kinetic models to model the adsorption process. It can be expressed in the following linear form:

$$\log(q_{e,exp}-q_t)=\log q_e-\frac{k_1}{2.303}t \quad (2)$$

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e} \quad (3)$$

In the formula, q_e is the adsorption amount when the adsorption reaches equilibrium (mg/g), q_t is the adsorption amount at a certain adsorption time (mg/g), and k_1 is the kinetic rate constant for the pseudo-first-order (1/min), k_2 is the kinetic rate constant for the pseudo-second-order (g/mg/min). At different concentrations, the adsorption kinetics data are listed in Table 1. As shown in Table 1, the value of R_2 is between 0.9994 and 0.9997. It shows that the adsorption and pseudo-second-order kinetic models fit well. The better adsorption efficiency is due to the strong electrostatic interaction between Fe_3O_4@SiO_2@CPB and orange Ⅱ and a large number of active sites on the adsorbent surface. Subsequently, the dye adsorbed on the surface of the adsorbent gradually increased, the adsorption rate slowed down, and finally the state of adsorption equilibrium was reached. In addition, the q_e value calculated from the pseudo-level model is more consistent with the q_e value from the pseudo-level model. Compared with the experimental $q_{e,exp}$ values, this also shows that the adsorption process of orange Ⅱ by Fe_3O_4@SiO_2@CPB is more consistent with the quasi-secondary adsorption kinetic model.

Table 1: Kinetic model parameters for the adsorption of orange Ⅱ by Fe_3O_4@SiO_2@CPB.

C_0 (mg/L)	Pseudo-first-order model			Pseudo-second-order model		
	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2
50	61.362	0.4251	0.6718	212.766	8.836×10^{-3}	0.9994
70	74.216	0.3980	0.8933	222.222	8.804×10^{-3}	0.9994
90	11.921	0.2844	0.4782	238.095	2.205×10^{-2}	0.9997

3.6 Isotherm Adsorption Linear Fitting

We used two equations for fitting. The Langmuir model equation and the Freundlich model equation fit the adsorption of Fe_3O_4@SiO_2@CPB adsorbent on orange Ⅱ in different dye initial concentration. The linear form of the Langmuir model and Freundlich model is represented by:

$$\frac{1}{q_e}=\frac{1}{q_{max}}+\frac{1}{bq_{max}C} \quad (4)$$

$$\ln q_e=\ln k_f+\frac{1}{n}\ln C_e$$

In the formula, q_e is the amount when the adsorbent adsorbs the orange Ⅱ equilibrium (mg/g), q_{max} is the maximum adsorption amount of the adsorbent to orange Ⅱ (mg/g), and C_e is the equilibrium concentration of the orange Ⅱ dye in the solution (mg/L), b is the Langmuir adsorption constant. As shown in Table 2, r_L^2 has a value of 0.991 and r_F^2 has a value of 0.8979. The experimental data shows that the Langmuir model correlation coefficient of orange Ⅱ on Fe_3O_4@SiO_2@CPB is higher than that of Freundlich model. This shows that the Langmuir model can better describe the adsorption process. It also means that the adsorption process of orange Ⅱ by Fe_3O_4@SiO_2@CPB is monolayer adsorption. The maximum adsorption capacity was calculated to be 270.27 mg/g by Langmuir isotherm adsorption.

Table 2: Isothermal adsorption model of orange yellow Ⅱ adsorbed on Fe_3O_4@SiO_2@CPB

	Langmuir			Freundlich	
q_{max} (mg/g)	b (L/mg)	r_L^2	K_f	n	r_F^2
270.27	0.0971	0.991	114.25	5.9382	0.8979

4. CONCLUSION

The Fe_3O_4@SiO_2@CPB magnetic material was successfully prepared in this study. It was used as an adsorbent for extracting the dye orange Ⅱ from wastewater. The adsorption kinetics show that the adsorption process fits well with the pseudo-second-order kinetic model. The isothermal adsorption linear fit shows that orange II is more consistent with Langmuir isotherm at Fe_3O_4@SiO_2@CPB. The magnetic Fe_3O_4@SiO_2@CPB has many characteristics, such as simple preparation method, good adsorption effect of the orange II, fast adsorption rate, and short equilibration time.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (grant numbers 21375046, 21605056); Project of Science and Technology Development of Jilin Province (grant number20140203013GX); Natural Science Foundation of Jilin Province (grant number20180101292JC); The financial support from the Key Laboratory of Fine Chemicals of Jilin Province is also acknowledged. The authors have declared no conflict of interest.

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