Adsorption mechanism of azophloxine in water by Fe$_3$O$_4$-chitosan composite material

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Abstract. Fe$_3$O$_4$-chitosan composite material was synthesized as adsorbent. The effect of solution pH value, initial concentration of azophloxine and adsorption time on the adsorption of azophloxine onto adsorbent was studied. The results show that Fe$_3$O$_4$-chitosan composite material can be magnetically separated before and after adsorbing azophloxine. It was found that the peak intensity of azophloxine was the strongest under weak acidic conditions, and the peak position hardly shifted. In the process of adsorption, it was found that Fe$_3$O$_4$-chitosan composite material adsorbing azophloxine by the surface electrostatic attraction. The optimum equilibrium adsorption capacity is at initial solution pH 6, and the equilibrium adsorption capacity is very close under weak acidic conditions. The pseudo first-order and pseudo second-order kinetic models were applied to experimental data. The adsorption process followed the pseudo-first-order kinetic model, which implied that the adsorption process was physical adsorption. The correlation coefficient for the first-order kinetic model was obtained greater than 0.99571 at room temperature, and the theoretical equilibrium adsorption capacity $q_{eq, cal}$ value also agreed very well with the experimental equilibrium adsorption capacity $q_e$ value in the case of pseudo first-order kinetics. It is suggested that Fe$_3$O$_4$-chitosan composite material has a wide application prospect in the removal of dyes as adsorbent.

1. Introduction
Azo dyes are organic compounds containing a conjugate in diazo compounds and one or more azo (-N=N-) bonds. Azo dyes are widely used in textile industry [1]. However, even if the concentration of trace azo dyes in water is as low as 1 mg L$^{-1}$, the water can also show a significant chroma. Azo dyes and their degradation intermediates have been confirmed to inhibit the growth of aquatic organisms due to their toxicity, carcinogenicity and mutagenicity. [2]. Therefore, azo dyes in wastewater must be removed before discharge. In recent years, many technologies are widely used in wastewater treatment including membrane filtration [3], microbial degradation [4], coagulation [5], adsorption [6], ion exchange [7], advanced oxidation processes [8] and so on. However, the major disadvantage of using oxidation method is that biodegradable dyes in wastewater may produce toxic by-products, which is not conducive to the complete removal of pollutants [9]. In recent years, biological treatment of dye
wastewater has a very good removal effect on dyes, which will not cause secondary pollution in the process of dye removal. However, the biological method only removes soluble dyes, which requires higher environmental conditions [10].

The adsorption method has the advantages of high efficiency, low cost, simple operation and no secondary pollution. It is one of the most attractive dye treatment technologies in wastewater treatment [11]. The selection of adsorbent should be determined according to the physical and chemical properties of the adsorbent [12]. Chitosan has broad application prospects in wastewater treatment because of its good adsorption performance [13]. The protonated amino groups formed in acidic condition can capture anionic dyes by electrostatic attraction [14], however, it is difficult to be separated.

The preparation of recyclable, environment friendly and strong adsorption materials can effectively absorb azo dyes in textile wastewater, reduce the chroma of wastewater, reduce the toxic by-products of biodegradable dyes in wastewater, improve the utilization and recovery rate of adsorbents, and reduce secondary pollution of water. It is a good method to use the magnetism of Fe₃O₄ to make the adsorbent more recoverable [15].

In this experiment, a magnetic chitosan composite adsorbent (Fe₃O₄-chitosan composite material) was successfully fabricated by combining advantages of magnetite and chitosan. Fe₃O₄-chitosan composite material has both the magnetism of Fe₃O₄ and adsorptive properties of chitosan. Effective solid-liquid separation can be achieved by magnetic separation technology after adsorbing of anionic dyes. Azophloxine was used to simulate azo dyes in textile wastewater, and Fe₃O₄-chitosan composite material was used as adsorbent to test the adsorption effect of adsorbent.

The works of this paper have three parts. First, a stable adsorbent was constructed by using the prepared magnetic Fe₃O₄ and chitosan. Second, azophloxine was used to simulate azo dyes in textile wastewater, and Fe₃O₄-chitosan composite material was used as adsorbent to test the adsorption effect of the adsorbent. Third, the performance of the adsorbent removing azophloxine was systematically investigated. The effect of solution pH value, initial concentration of azophloxine and adsorption time on the adsorption of azophloxine onto adsorbent was studied. The adsorption kinetics analysis and optimum equilibrium adsorption capacity were studied. To describe the adsorption process of azophloxine on the adsorbent, the difference between experimental data and theoretical equilibrium capacity was evaluated by using pseudo first-order and pseudo second-order kinetic models.

2. Experimental

2.1. Materials

Chitosan was purchased from Zhejiang Golden-shell Biochemical Co., Ltd., Zhejiang, China (deacetylation degree ≥ 95%, Figure 1). Ultrapure water (resistivity ≥18.0 MΩcm) was used for all the experiments. Azophloxine (Figure 2.) is biological stain. Other chemicals were of laboratory reagent grade and were used without further purification.

![Figure 1. The chemical structure of chitosan.](image1)

![Figure 2. The chemical structure of azophloxine.](image2)

2.2. Preparation of Fe₃O₄-chitosan composite material

Firstly, 0.27 g L ascorbic acid was dissolved in 50 ml ultrapure water, and 7 g FeSO₄·7H₂O was added into the solution. 13.61 g FeCl₃·6H₂O was dissolved in 50 ml ultrapure water. Then the above solutions were mixed. 1 mol L NaOH solution was mixed to the above mixed solution with peristaltic pump, at the same time, the mixed solution was mechanically stirred for half an hour at the same speed, and the pH value was kept at about 10. Chitosan solution was dripped into the above turbid solution containing
L ascorbic acid, FeSO$_4$·7H$_2$O, FeCl$_3$·6H$_2$O and NaOH by syringe, and the pH value of the solution was kept at about 10 by adding 1 mol L$^{-1}$ NaOH solution. 1% acetic acid by volume was prepared, and then 1g chitosan was added in it to get chitosan solution. The chitosan solution should be stirred until the chitosan was completely dissolved. Fe$_3$O$_4$-chitosan composite material was magnetically separated and washed repeatedly with ultrapure water and dried at 60 °C for 6 h in a vacuum drying chamber.

A UV–Vis Spectrometer (TU-1950, Puxi) was used to measure the concentration change of azophloxine, because the absorption of azophloxine has absorption bands centered at 500–550 nm.

2.3. Adsorption experiments
The batch adsorption experiments were carried out with the Fe$_3$O$_4$-chitosan composite material (0.1 g), and the batch solutions contained 50 mL of various concentrations of azophloxine solution at room temperature (25 °C). The effect of the pH value on the adsorption of azophloxine onto Fe$_3$O$_4$-chitosan composite material was investigated under following conditions. By adding H$_2$SO$_4$ (0.1 M) or NaOH (0.1 M) solution, the initial pH values of azophloxine solutions were adjusted to 2.0–10.0. Only the optimum pH value can be used for further study. The amount $q_e$ of azophloxine adsorbed per unit mass of adsorbent was calculated by Eq. (1):

$$q_e = \frac{(C_o - C_e)V}{M}$$

where $q_e$ is the azophloxine capacity of the adsorbent at equilibrium (mg g$^{-1}$), $C_o$ is the initial azophloxine concentration in the liquid phase (mg L$^{-1}$), $C_e$ is the liquid-phase azophloxine concentration at equilibrium (mg L$^{-1}$), $V$ is the volume of solution (L), and $M$ is the mass of adsorbent used (g).

3. Results and discussion
3.1. Effect of the pH value
In order to evaluate the effect of different pH values, batch experiments were carried out at five pH values: 2.0, 4.0, 6.0, 8.0 and 10.0, with the same initial concentration (36.84 mg L$^{-1}$). Figure 3. (a) and (b) show the visible spectra before and after equilibrium adsorption with the same adsorbent (0.1 g) at 5 pH values, respectively. It was found that the intensity of peaks was the strongest under weak acidic conditions, and the peak position hardly changed.

![Figure 3.](image)

Figure 3. (a) and (b) the visible spectra before and after equilibrium adsorption with the same adsorbent and initial concentration at five initial pH values, i.e. 2.0, 4.0, 6.0, 8.0, and 10.0, respectively.

The results show that the peak positions do not change after equilibrium adsorption in Figure 3. (b). After equilibrium adsorption, the peak intensity is the minimum when the initial pH is 6 in initial pH range of 2–10. The equilibrium adsorption capacity at initial pH 4 is very close to that of initial pH 6.
This phenomenon indicates it is most favorable for adsorption at about initial pH 6, and the equilibrium adsorption capacity is very close under weak acidic conditions.

3.2. Effect of the contact time

At initial pH 6, the change of azophloxine optical absorption spectra with different contact time at the same concentration (40 mg L\(^{-1}\)) is showed in Figure 4. (a). Figure 4. (b) shows the change of the concentration of azophenanthrene with the contact time. The results showed that the concentration of azophloxine \((C_0 = 40 \text{ mg L}^{-1})\) decreases significantly during the first 30 min, and reaches equilibrium within 100 min, and the positions of adsorption peak do not change.

![Figure 4](image_url)

**Figure 4.** (a) Changes in the visible absorption of the azophloxine aqueous solutions in the presence of adsorbent. (b) Effect of adsorption time on the concentration of azophloxine.

3.3. Adsorption kinetics analysis

Kinetic model can help to understand the kinetic processes of adsorbent adsorbing azophloxine and evaluate the performance of the adsorbents for azophloxine removal. The pseudo second-order and pseudo first-order kinetic models were applied to the experimental data.

The pseudo-second-order kinetic model is used to evaluate the adsorption kinetics of azophloxine onto adsorbent. It can be expressed as [16]:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad h = k_2 q_e^2
\]

where \(q_t\) is the adsorbed mass per unit mass of adsorbent during time \(t\) (mg g\(^{-1}\)), and \(k_2\) is the equilibrium rate constant for the pseudo-second-order (g mg\(^{-1}\) min\(^{-1}\)), and \(h\) is the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)). The theoretical equilibrium adsorption capacity \(q_{e,cal}\) and \(k_2\) can be obtained by fitting the curve of \(tlq_t\) against \(t\). Figure 5. (a) shows the linear relation between \(tlq_t\) and \(t\), where the fitted values of \(k_2\) and \(h\) are 1.12e\(^{-4}\) g mg\(^{-1}\) min\(^{-1}\) and 0.3017 mg g\(^{-1}\) min\(^{-1}\), respectively. However, the experimental equilibrium adsorption capacity \(q_e\) (18 mg g\(^{-1}\)) is quite different from the theoretical equilibrium adsorption capacity \(q_{e,cal} = 51.84 \text{ mg g}^{-1}\) after this short period. The correlation coefficient \(R^2\) for the pseudo-second-order kinetic model is 0.89526. The correlation coefficient obtained was found lower. These suggest that this adsorption system is not a pseudo second-order reaction.
Figure 5. (a) Pseudo-second-order kinetic model and (b) Pseudo-first-order kinetic model.

The pseudo first-order can be expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (3)

Using Eq. (3), $\ln(q_e - q_t)$ was plotted against $t$ at room temperature and first-order adsorption rate constant ($k_1$) and the theoretical equilibrium adsorption capacity $q_{e,cal}$ value was determined from the slope and intercept of the plots (Figure 5, (b)). The value of the parameters $k_1$ is 0.02153 min$^{-1}$. $q_{e,cal}$ and correlation coefficients are presented in Figure 5, (b). The correlation coefficient for the pseudo first-order kinetic model was obtained greater than 0.9957 at room temperature. The theoretical equilibrium adsorption capacity $q_{e,cal}$ value also agreed very well with the experimental equilibrium adsorption capacity $q_e$ value in the case of pseudo first-order kinetics. These suggest that the adsorption system is not a pseudo second-order reaction and that the pseudo first-order model providing the best correlation of data, which means that the removal of azophloxine proceeds in one steps: electrostatic adsorption of azophloxine onto the adsorbent, the process is described as follows:

$$\text{(CF)}^+ + \text{dye}^- \leftrightarrow (\text{CF})^+\text{dye}^-$$ \hspace{1cm} (4)

Where (CF) is Fe$_3$O$_4$-chitosan composite material. Fe$_3$O$_4$-chitosan composite material has a large number of adsorptive active sites on the surface, which can be protonated under weak acidic conditions, thus adsorbing negatively charged dye ions [16].

4. Conclusion
In this study, Fe$_3$O$_4$-chitosan composite material has been successfully prepared by coprecipitation method and it is effective adsorbent for the removal of azophloxine in aqueous solution. The adsorption characteristics at different pH and contact time have been investigated. Batch adsorption studies show that the removal capacity of the adsorbent is closely related to the initial pH value. The optimum equilibrium adsorption capacity is at initial solution pH 6, and the equilibrium adsorption capacity is very close under weak acidic conditions. The pseudo first-order and pseudo second-order kinetic models were applied to experimental data. The adsorption process followed the pseudo-first-order kinetic model, which implied that the adsorption process was physical adsorption. The correlation coefficient for the first-order kinetic model is obtained greater than 0.9957 at room temperature. The theoretical equilibrium adsorption capacity $q_{e,cal}$ value also agreed very well with the experimental equilibrium adsorption capacity $q_e$ value in the case of pseudo first-order kinetics. In conclusion, this study shows that Fe$_3$O$_4$-chitosan composite material as adsorbent has a broad application prospect in the removal of trace dyes.

Acknowledgements
This work was supported by the National Natural Science Foundation of China (NSFC, No: 11904268), and Natural Science Foundation of Hubei Province of China (No: 2018CFB403).
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