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Adsorption of natural organic matter onto a composite adsorbent prepared with chitosan and powdered activated carbon

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ABSTRACT

In this study a composite adsorbent was prepared with chitosan and powdered activated carbon (PAC). Jar tests were carried out to investigate effects of pH, adsorption time, temperature and initial concentration of natural organic matter (NOM) on the adsorbent's removal efficiency of NOM. UV absorbance at 254 nm wavelength (UV_{254}) was used as a surrogate parameter of NOM concentration. It is shown that the removal of NOM by chitosan-PAC composite adsorbent could be as high as 69% under optimal conditions. Pseudo-first-order rate expression and pseudo-second-order rate expression were fitted to the experimental results, and the latter was found to fit the experimental results quite well. The adsorption isotherm of NOM onto the adsorbent under various initial NOM concentrations was also experimentally determined. Freundlich isotherm was found to fit the adsorption data well.

Keywords: Adsorption; Natural organic matter; Composite adsorbent; Chitosan; Powdered activated carbon

1. Introduction

Natural organic matter (NOM) in rivers and lakes refers to a complex mixture of molecules with varying molecular weight and chemical nature and originates from a variety of sources such as degradation of terrestrial and aquatic organisms, biological activity in the water body, human inputs etc. NOM is primarily composed of humic substances, including humic acids (HA) and fulvic acids (FA) that result from decomposition of terrestrial and aquatic biomass [1]. Trihalomethanes (THMs) which were reported to be the dominant species of disinfection by-products (DBPs) in surface waters in Europe are formed in treated drinking water after chlorination due to reaction with NOM and bromide [2].

In recent years, many studies have been conducted on removal of NOM with a variety of methods including membrane filtration [3–5], coagulation [1,2,6], membrane filtration in conjunction with coagulation [7–11], advanced oxidation [12,13], anionic exchanger [14] and adsorption [15] etc. In this study removal of NOM with chitosan-PAC composite adsorbent was investigated.

Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. Since wastes such as shrimp, lobster, crab shells are abundantly available, chitosan can be produced at low cost as compared to activated carbon. Due to its high content of amino and hydroxy functional groups, chitosan shows high potentials for a wide range of molecules, including phenolic compounds, dyes and metal ions [16]. Moreover, chitosan is safe for humans and the natural environment due to its biodegradability. For

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the advantages above, chitosan has drawn particular attention as an adsorbent in water treatment. While chitosan has been widely studied for metal removal from aqueous solution, it is also possible to extend the application of chitosan as an adsorbent to remove charged organic compound such as NOM from water and wastewater.

However, chitosan presents several disadvantages at the same time, such as its solubility in acidic media and its nonporous structure. Activated carbon is among the most popular and widely used adsorbent in wastewater treatment applications throughout the world, whereas it is non-selective and quite expensive. So in this study a composite adsorbent was produced using chitosan and activated carbon as raw materials to combine their advantages.

2. Materials and methods

2.1. Sampling

The raw water samples were taken from the Eastern Lake located in Wuhan, Hubei Province and then stored in dark at 4°C. Test solutions at desired concentrations were obtained by diluting the samples with appropriate amounts of deionized (DI) water.

2.2. Preparation of the composite adsorbent

Chitosan was purchased from the Zhejiang Yuhuan company as a powdered material, with a deacetylation degree of 92% and molecular weight of 20×10^4. Powdered activated carbon was obtained from the Tianjing Fuchen chemical company, and was of analytical grade.

The following steps were taken in sequence to obtain chitosan–PAC adsorbent:

- Chitosan was weighed precisely and dissolved in acetic acid of 2% (v/v).
- Powdered activated carbon was placed into the chitosan solution at a dosage of 4 g/(g chitosan) with rapid stirring to make the mixture uniform.
- Glutaraldehyde solution of 25% (v/v) was added into the mixture with mixing at a dosage of 1 ml/(g chitosan) as a cross-linking agent.
- Following pH adjustment to 8–9 with NaOH solution, the mixture was put into water bath of 60°C for cross-linking reaction for 3 h.
- The composite granules were separated from the mixture by filtration, and then it was washed with DI water to neutral, next it was dried at 80°C for 8 h continuously. At last a diameter of 1.0 mm black adsorbent granules was obtained.

The optimal granule diameter and preparation process parameters (including the ratio of activated carbon to chitosan, glutaraldehyde dosage and cross-linking temperature) shown above were determined by orthogonal experiments.

2.3. Jar test procedure

A series of jar tests were performed by placing 200 mg of the composite adsorbent in a 250 ml conical flask with 100 ml NOM solution of a known initial concentration (Table 1). The pH of the solution was adjusted with HCl or NaOH solution to a desired value (Fig. 2a). The mixture in the flask was shaken on a thermostatic shaking table (model HYA, Beijing) at constant temperature (Fig. 2c) at 200 rpm for a given time and then centrifugalized at 4000 rpm for 15 min. The suspension of centrifugalization was taken and the final UV_{254} was determined. The pH value of the solution, period of time for which the mixture was shaken and temperature at which the mixture was shaken were varied in sequence to evaluate their effects on NOM adsorption onto the composite adsorbent.

2.4. Analytical methods

In this study UV_{254} was used as a surrogate parameter of NOM concentration. The measurement of UV_{254} as a surrogate parameter has several advantages, such as inexpensive instrument, convenient operation, low operating costs, good correlations to the parameters surrogated, high accuracy and excellent data reappearance in multiple measurements [17].

The correlation between UV_{254} and COD_{Mn} was studied and the results are shown in Fig. 1. A linear relationship between UV_{254} and COD_{Mn} can be seen from Fig. 1, and the linear equation is $y = 44.45x + 0.4299$ with R^2 calculated as 0.9852 by linear regression.

UV_{254} was measured by a SHIMADZU UV-visible spectrophotometer (model UV–1700, Japan) in 1-cm quartz cells. The pH was measured by an ORION pH meter (model 420A+, Japan). Dissolved organic carbon (DOC) and total organic carbon (TOC) were measured using JENA multi N/C analyzer (model 2100, Germany). UV_{254} and DOC measurement were carried out after sample filtration though a 0.45 μm filter. COD_{Mn} was determined using a method adapted from National Standard Methods for Water Quality Analysis (Chinese Environment Protection Agency, 1989).

Table 1
Raw water quality characteristics

Parameter	Value
UV_{254}, 1/cm	0.1956
DOC, mg/1	6.36
SUVA, 1/mg.m	3.07
TOC, mg/L	7.71
COD_{Mn}*, mg/L	32
pH	8.10

*COD_{Mn}: chemical oxygen demand which chemical oxidant is $KMnO_4$

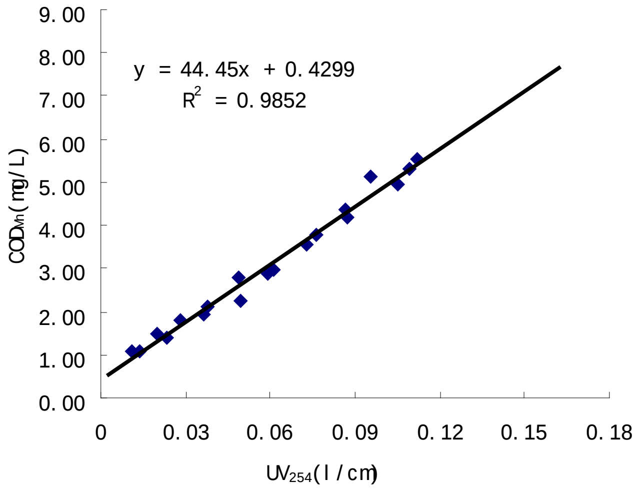

Fig. 1. Correlation between UV_{254} and COD_{Mn}.

3. Results and discussion

3.1. Raw water characteristics

Dividing UV_{254} (l/m) by DOC (mg/1) yields specific UV absorbance (SUVA, l/mg.m) which provides a quantitative measure of aromatic NOM content of which the primary sites are attacked by chlorine or other oxidants [2]. Sample parameters are given in Table 1.

3.2. Effects of pH, adsorption time, temperature and initial concentration of NOM on NOM removal efficiency when the chitosan-PAC adsorbent was used

Fig. 2 shows the effects of different physico-chemical parameters on the adsorption effect of the chitosan-PAC adsorbent.

Since pH has complicated effects on NOM, such as on its negative charge, solubility as well as its molecule size, pH may influence adsorption process greatly. Adsorption experiments were undertaken for various pH values from 3 to 12 and it was found that adsorption of NOM onto chitosan-PAC adsorbent is greatly pH-dependent. As shown in Fig. 2a, UV_{254} removal efficiency decreased almost linearly while the solution pH value increased from 4 to 10.

Similar results were found by Zhang et al. [18] — significant amounts of humic acid were adsorbed by chitosan coated granules under acidic and neutral pH conditions, but the adsorption capacity was reduced remarkably with increasing solution pH values. The conclusions above were also true with NOM adsorption onto chitosan since humic acid takes up as high as 50–90% total organic matters contained in surface water [19]. Newcombe's study on adsorption of NOM by activated carbon showed that all activated carbons display significantly higher adsorption at pH 3 than at pH 7–8 mainly due to the decrease of surface-NOM electrostatic repulsions [15]. Based on Zhang and Newcombe's studies, the effect that pH has

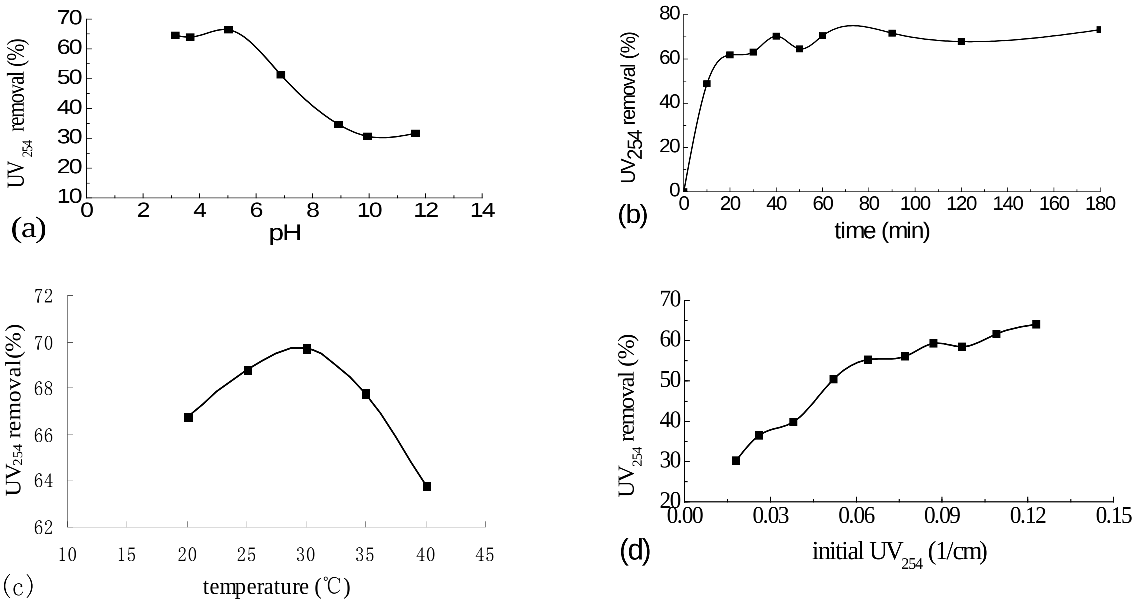

Fig. 2. Effects of different physicochemical parameters on NOM removal efficiency when chitosan-PAC composite adsorbent was used: (a) chitosan-PAC adsorbent to treat raw water with different pH; (b) chitosan-PAC adsorbent to treat raw water with pH value of 5.5 at different adsorption time; (c) chitosan-PAC adsorbent to treat raw water at pH 5.5 and adsorption time of 180 min under different temperature; (d) chitosan-PAC adsorbent to treat raw water with different initial UV_{254} at pH 5.5 and adsorption time of 180 min.

on adsorption of NOM onto chitosan-PAC can be easily understood. Based on the results above, pH 5.5 was chosen for the subsequent tests.

As shown in Fig. 2b, after 20-min adsorption, NOM removal efficiency has reached up to 84% that of the figure reached 180 min later. NOM removal efficiency tended to be constant after 60-min adsorption indicating that the adsorption equilibrium has been established. The reason for the above results can be explained according to different adsorption mechanisms. At the beginning of NOM removal onto the composite absorbent, chemical adsorption by chitosan predominated, then physical adsorption gradually predominated. Physical adsorption rate is relatively low when compared to chemical adsorption. Moreover, at the beginning of adsorption, the surface of the absorbent was relatively free of sorbate and the NOM molecules that arrived at the adsorbent surfaces may attach instantly onto it. The experimental data shown in Fig. 2b were analyzed by the Lagergren first-order rate equation and Ho second-order rate equation, so as to understand the adsorption kinetics of the composite adsorbent.

The UV_{254} removal as a function of temperature is shown in Fig. 2c. It is demonstrated that the optimal temperature for adsorption is around 30°C. UV_{254} removal firstly increased while the temperature increased from 20 to 30°C. This is due to higher diffusivity and reaction rate at higher temperature. When the temperature increased higher than 30°C, UV_{254} removal decreased, which is in line with adsorption thermodynamics that adsorption is an exothermic reaction.

NOM removal increased with the increase of its initial concentration in raw water as shown in Fig. 2d. This is possibly because that at higher NOM concentration both the rate of mass transport from the solution to the surface of adsorbent and the chemical reaction rate between NOM and adsorbent are higher, which results in a larger adsorption capacity in a given time and vice versa. The adsorption isotherm of NOM onto chitosan-PAC in aqueous solution was also determined for the experimental results above as shown in Fig. 4.

3.3. *Adsorption kinetics of NOM onto chitosan-PAC adsorbent*

The Lagergren first-order rate equation and Ho second-order rate expression have been called pseudo-first order rate expression and pseudo-second order rate expression respectively in order to distinguish kinetic equations based on the adsorption capacity of solids from the ones based on the concentration of solutions [20]. Their integrated and rearranged forms for linearized data plotting are shown by Eqs. (1) and (2) respectively [21]:

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_{S1}}{2.303}t \tag{1}$$

where k_{S1} (1/min) is the rate constant of first order adsorption; q_1 (mg/g) is the amount of solute sorbed at equilibrium; q_t (mg/g) is the amount of solute sorbed on the surface of the sorbent at any time t.

$$\frac{t}{q_t} = \frac{1}{k} + \frac{1}{q_c}t \tag{2}$$

where k (g/mg·min) is the rate constant of adsorption; q_c (mg/g) is the amount of soluted sorbate sorbed at equilibrium; q_t has the same definition as in Eq. (1).

Fig. 3a shows a plot of the linearized form of the pseudo-first order model in Eq. (1) for the adsorption of NOM onto chitosan-PAC. However, the experimental data deviate considerably from the theoretical data. Fig. 3b shows a plot of the linearized form of the pseudo-second order model in Eq. (2) for the same experimental data in Fig. 3a. The correlation coefficient for the linear plot from the pseudo-second order rate law was 0.9972 for contact time of 180 min.

Ho et al. [21] found that for all of the 12 systems they studied, chemical reaction seemed significant in the rate-controlling step and that over a long period the pseudo-second order chemical reaction kinetics provided the best correlation of the experimental data. It can be seen that this was also true for the NOM onto chitosan-PAC adsorption system studied in this paper.

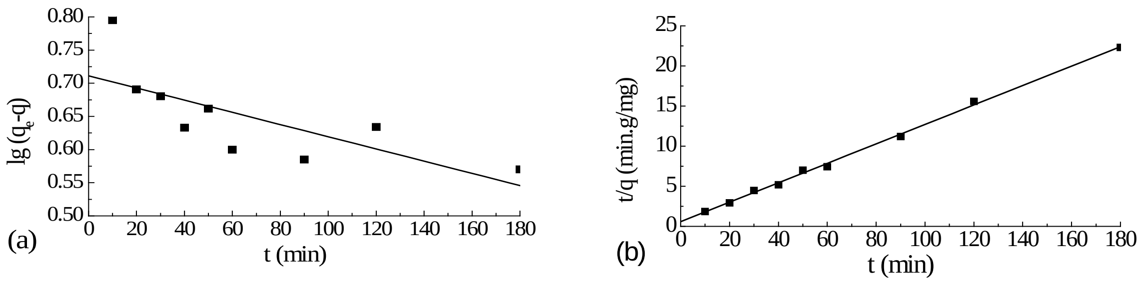

Fig. 3. Adsorption kinetics of NOM onto chitosan-PAC adsorbent (pH 5.5; solution volume: 100 ml; quantity of adsorbent: 200 mg): (a) pseudo-first order rate expression fitted to the experimental results; (b) pseudo-second order rate expression fitted to the experimental results.

3.4. Adsorption isotherms of NOM onto chitosan-PAC adsorbent

Batch adsorption isotherm experiments were conducted for various initial NOM concentrations at pH value around 5.5. The adsorption isotherm results are analyzed by the Langmuir model and Freundlich model.

The Langmuir isotherm is one of the widely used adsorption isotherms, and its linearized form is as follows:

$$\frac{1}{q}=\frac{1}{Q^0}+\left(\frac{1}{K_aQ^0}\right)\frac{1}{C} \tag{3}$$

where q (mg/g) is the equilibrium concentration of NOM in the solid phase; C (mg/L) is the equilibrium concentration of NOM in the liquid phase; Q^0 (mg/g) and K_a (L/mg) are Langmuir isotherm parameters representing the maximum adsorption at monolayer coverage and adsorption coefficient respectively.

The Freundlich isotherm is another widely used power-law type isotherm, and its log-linearized equation form is shown in Eq. (4):

$$\log q=\log K_F+\left(\frac{1}{n}\right)\log C \tag{4}$$

where q and C have the same definition as in Eq. (3); K_F (mg/g).(L/mg)^n and n are the Freundlich model parameters. The numerical value of $1/n$ represents the rate at which the adsorption capacity of the adsorbent increases with the increase of the final concentration C.

Plots of $1/q$ vs. $1/C$ and lgq vs. lg C for the experimental data are shown in Fig. 4.

From the slope and interception of the line in Fig. 4a the numerical values of the Langmuir isotherm constants were determined as $Q^0 = -0.9518$ mg/g, $K_a = -0.1305$ L/mg. From the minus values of Q^0 and K_a, it was suggested that Langmuir isotherm did not fit the experimental data.

Similarly, values of the Freundlich parameters K_F and n were determined to be 0.1104 (mg/g).(L/mg)^n and 0.6042 from Fig. 4b.

It could be seen that the Freundlich equation fitted the chitosan-PAC adsorption isotherm data more satisfactorily than the Langmuir equation did. Since the Langmuir model is usually applied to monolayer adsorption processes, and the Freundlich model to multilayer adsorption processes, it was suggested that the adsorption isotherm was probably dominated by a multilayer adsorption process than by the monolayer adsorption one.

4. Conclusions

The adsorption of NOM onto chitosan-PAC is shown to be dependent on pH, time, temperature as well as initial concentration. The results showed that the NOM removal efficiency decreased remarkably with increasing solution pH, and that the removal efficiency firstly increased quickly with time, and tended to be constant about 60 min later. Increase of solution temperature from 20 to 30°C was found to favor NOM adsorption; however, NOM removal efficiency was decreased when temperature increased higher than 30°C. NOM removal increased with the increase of its initial concentration in raw water.

Under optimum conditions adsorption achieved about 70% removal of UV_{254} absorbance. Chemical reaction seemed significant in the rate-controlling step and that over a long period the pseudo-second order chemical reaction kinetics provided better correlation of the experimental data than the pseudo-first one. The Freundlich isotherm was found to fit the adsorption data well indicating that the adsorption isotherm was probably dominated by a multilayer adsorption process.

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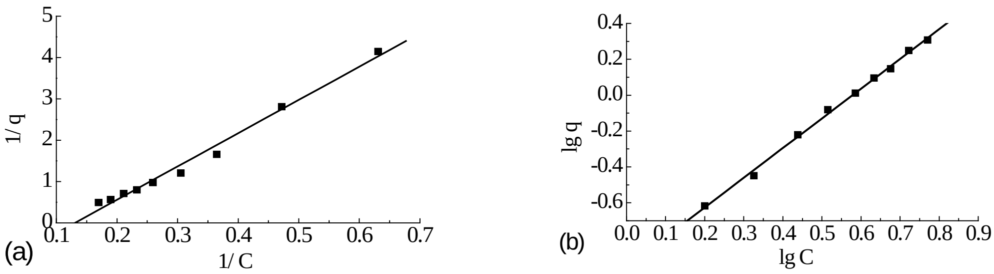

Fig. 4. Adsorption isotherms of NOM onto chitosan-PAC in aqueous solution (pH 5.5; solution volume: 100 ml; quantity of adsorbent: 200 mg; adsorption time: 180 min): (a) Langmuir model fitted to the experimental data; (b) Freundlich model fitted to the experimental data.

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