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Research Article

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Adsorption characteristics of dimethyl phthalate by modified zeolite

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ABSTRACT

Zeolite was modified in sodium hydroxide solution in order to improve the adsorption performance. The characterization of the alkali-modified zeolite by scanning electron microscope (SEM) was displayed. In the study, In order to obtain the optimum conditions for adsorption of Dimethyl Phthalate (DMP), resulting in a better removal efficiency, parameters such as the dosage of modified zeolite, adsorption time, adsorption temperature and initial concentration were examined. Results showed that the optimal adsorption conditions were dosage was 100 mg/L, adsorption time was 120 min, the adsorption temperature was 35 ℃ and the initial concentration was 10.0 mg/L. Under the condition, the maximum adsorption efficiency was 99.0%. The analysis of equilibrium isotherms data was used Langmuir and Freundlich models. The kinetics adsorption of DMP can be described by the Lagergren pseudo-second-order model better than the Lagergren pseudo-first-order model.

Key words: Adsorption, Dimethyl Phthalate, Modified Zeolite, Isotherms, Kinetics

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INTRODUCTION

Phthalic acid esters (PAEs) is an important class of persistent organic pollutants(POPs), which could interfere with the endocrine system of humans and animals, and could lead to developmental problems in reproductive systems and might also be carcinogenic[1-3]. PAEs is mainly used as plasticizers in plastics, which was not combination with other chemical substances through the chemical bond, and under a certain conditions, its easy to release to the surrounding environment, and resulting in environmental pollution[4-6]. Now, with the wide use of plastic products, PAEs already exist in the environment very common. The PAEs could been detected easily in the water environment everywhere[7-8]. Therefore, the removal of PAEs is necessary that the problems of controlling pollution be carefully solved.

The adsorption method is one of the most important methods for removal of organic matter in water condition, which has good removal effect, simple operation, easy control, cost does not produce toxic byproducts etc. [9-11]. Zeolite is a naturally occurring crystalline aluminosilicate mineral consisting of a framework of tetrahedral molecules, linked with shared oxygen atoms. Zeolite has a large surface area and high cation exchange capacity (CEC), and provides an exchange complex that can adsorb variably-sized ions[12-13]. However, the adsorption effect of low concentration of organic matter in water is not very good by using natural zeolite[14], So it is necessary to modify zeolite in order to improve its adsorption performance for organic pollutants in water[15-17].

The present work aimed to used NaOH as modifier in order to improve the adsorption ability of zeolite, then the modified zeolite was prepared and characterized by the SEM techniques. In order to obtain better adsorption performance, some parameters such as the independent variables, modified zeolite, contact time, initial concentration and temperature, were investigated, combined with the study on *adsorption isotherm and* adsorption kinetics.

EXPERIMENTAL SECTION

2.1 Material and instruments

All the reagents used in this study were analytical grade except the methanol was HPLC grade which was obtained from Germany merck Chinese company. The hydrochloric acid (HCl) and sodiumhydroxide (NaOH) were obtained from Hunan Zhuzhou Chemical Industry. The dimethyl phthalate was obtained from Shanghai Jingwei Chemical Co., Ltd. Natural zeolite was obtained from Crystal Water Treatment Material Co., Ltd. Henan Branch. The equipments used in the experimental setup were as follows:

- ● The scanning electron microscope (SEM) (JSM-6380LV, JEOL Company, Japan)
- ● Gas chromatography-mass spectrometry (GC-MS, 7890A-5975C, Agilent, USA)
- ● Water bath oscillator (THZ-82, Jintan Ronghua Instrument Manufacturing Co., Ltd., China)

2.2 Pretreated zeolite and modification

First, the zeolite was placed in a beaker which was added 100mL ultrapure water for immersing 2h, filtered, and then washed three times and dried in a vacuum at 105˚C for several days. Finally immersing the zeolite with 2 mol/L NaOH solution, In 50℃ water bath heating 4h, pouring the supernatant, washing with deionized water for 3 times, dried in a vacuum at 85˚C for use.

2.3 Batch adsorption studies

Erlenmeyer flasks (250mL) containing 100. 0 mg of modified zeolite in 100 mL of DMP solutions were employed. Modified zeolite were dosed under the rotary shaker at 150 rpm for 120 min, the mixtures were then centrifuged at 3000 r/min for 5 min. The residual DMP concentration in the solution was then determined using GC-MS. Isotherm studies were made with concentration solutions of DMP between 10.0 and 70.0mg/L. Kinetic studies were made at a concentration of 10mg/L for 30-180 min. The adsorption capacity was calculated using the following equation:

$$Qe = \frac{C_0 - C_e}{W} V$$

where Q_e is the adsorption capacity (mg/g), C_0 is the initial DMP concentration (mg/L), Ce is the final DMP concentration (mg/L), W is the weight of adsorbent used (g) and V is the volume of DMP solution (L). The experiments were carried out in triplicates to obtain average results.

2.4 Isotherm study

Isotherm study was conducted using batch equilibrium experiments. Absorbent 100 mg was added into every conical ask with 100 mL of aqueous solution containing different DMP concentrations. The pH of solution needed to adjust. The mixtures were covered and oscillation in a shaker at a constant speed of 150 r/min and temperature of room temperature. The mixtures were then centrifuged at 3000 r/min for 5 min. The residual DMP concentration in the solution was then determined using GC-MS[18].

2.5 Kinetic study

Batch kinetic experiments were performed by mixing a fixed amount of absorbent (100mg) with 100 mL DMP solution of initial concentration of 10 mg/L in a series of conical flasks. The pH of solution needed to adjust. The mixtures were covered and oscillation in a shaker at a constant speed of 150 r/min and temperature of room temperature. After a certain period of oscillation, the entire suspension was taken from a conical flask and solid-liquid separation was achieved by centrifugation at 3000 r/min for 5 min. The residual DMP concentration in the solution was then determined using GC-MS.

RESULTS AND DISCUSSION

3.1 Characterization of the product

The SEM images of modified zeolite was depicted in Figure 1. It can be seen that the surface morphology of the zeolite has been modified after NaOH treatment. There was a significant changes from the original sizes, shapes crumb structure, transformed into the pore structure. This showed that compared with natural zeolite, morphology modified zeolite structure has undergone significant changes, the formation of the porous material greater than the surface area, which facilitates the exchange of the adsorption of DMP, so compared with natural zeolites have a stronger adsorption capacity.

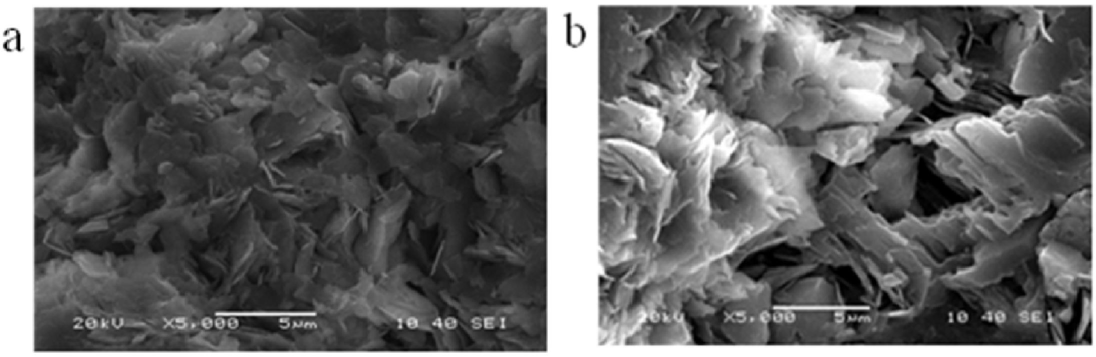


Figure 1. SEM images of modified zeolite (a)Natural zeolite, (b)Modified zeolite

3.2 Single influential factor analysis

3.2.1 Effect of modified zeolite dosage on adsorption capacity and adsorption rate

The effect of the dosage of modified zeolite adsorption was investigated. The dosage of modified zeolite ranged from 20 up to 200 mg/L was selected to investigate the adsorption effect (Figure2). As shown in when the dosage was increased, the adsorption capacity and removal rate was increased, that because with the increase of the amount of modified zeolite, the total surface area of the modified zeolite increased, which resulting in an increase of the adsorbent effective adsorption sites. When the amount of modified zeolite ranged from 20mg to 200mg, the adsorption capacity of DMP increased from 3.96mg/g to 9.91mg/g, and when the dosage was 100mg, the adsorption reached 9.72mg/g. Considered the economic costs and the adsorption effect, 100mg was chosen as an optimum dosage.

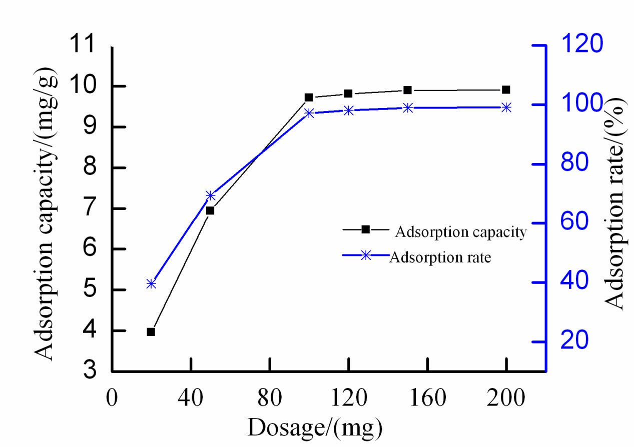


Figure 2. Effect of dosage on adsorption capacity and adsorption rate

3.2.2 Effect of contact time on adsorption capacity and adsorption rate

The effect of contact time on adsorption was investigated. The contact time ranged from 30 up to 180 min was selected to investigate the contact time (Figure 3). As shown in when the contact time was increased, the adsorption capacity and removal rate was increased, especially within 120min, adsorption and removal efficiency was increased sharply. When the time was 120min, the adsorption reached 9.81mg/g, while continuing to extend the contact time to 180min, the adsorption capacity reaches up to 9.91mg/g. Between 120-180min, the adsorption capacity increased slowly. This indicated that the adsorption process was the fast adsorption process, when the concentration of DMP was higher, the more adsorbent exposure, the more opportunities for the DMP molecular contact with the adsorbent, with the extension of adsorption time, the concentration of the DMP becoming lower and the chance of molecular adsorbent contact with the DMP reduced, resulting in the adsorption rate decreased. So, the 120 min was selected as the optimum time.

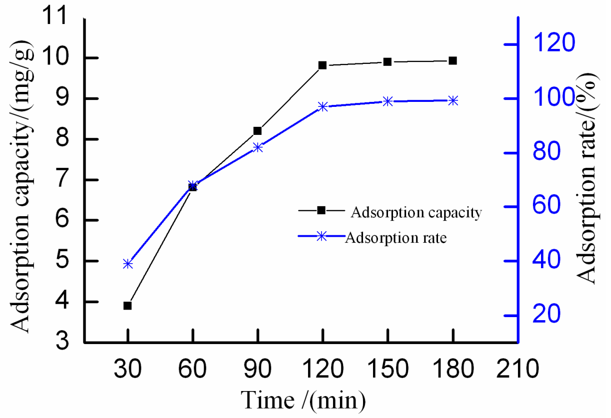


Figure 3. Effect of contact time on adsorption capacity and adsorption rate

3.2.3 Effect of DMP initial concentration on adsorption capacity and adsorption rate

The effect of the DMP concentration on modified zeolite adsorption was investigated. DMP concentration ranged from 10 up to 70 mg/L was selected to investigate the adsorption effect (Figure 4). As shown in as the initial concentration of DMP in solution increased, the removal rate of the modified zeolite of the DMP from the initial concentration of 10mg/L of 39.6% rising to 20mg/L of 93.5%, and then gradually decreased to 70mg/L of 70.0%, and adsorption by the amount of 10mg/L to 9.3mg/g to 70mg/L to 42mg/g. When the initial concentration of 50mg/L, 60mg/L, 70mg/L, the adsorption capacity of the increased slowly, which was due to the modified zeolite adsorption capacity gradually became saturated.

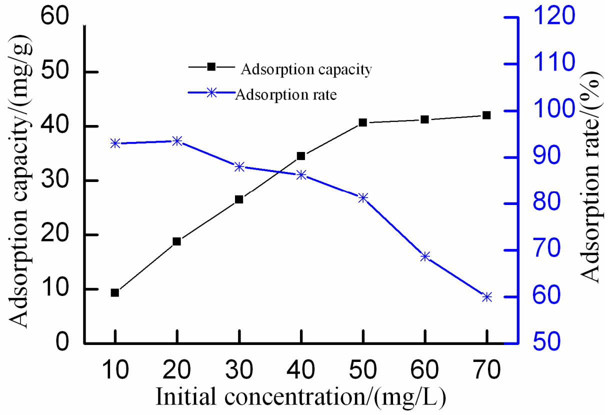


Figure 4. Effect of DMP initial concentration on adsorption capacity and adsorption rate

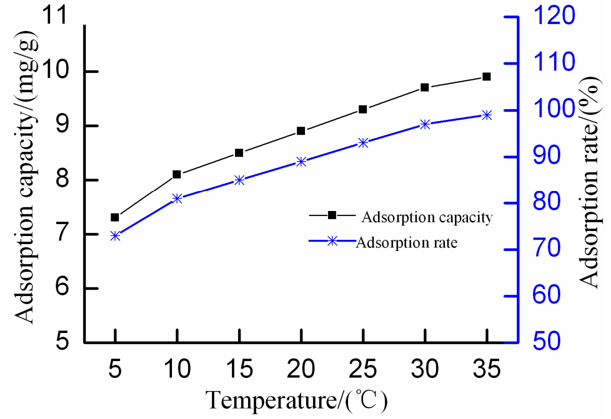


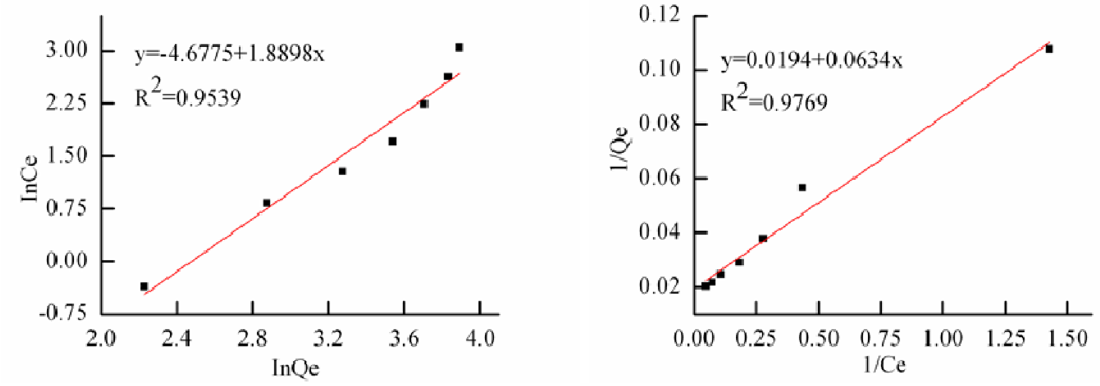
Figure 5. Effect of temperature on adsorption capacity and adsorption rate

3.2.4 Effect of temperature on adsorption capacity and adsorption rate

The effect of the temperature on modified zeolite adsorption was investigated. The temperature was ranged from 5 up to 35 ℃ was selected to investigate the adsorption effect (Figure 5). As shown in with the increased of the contact temperature, the adsorption efficiency and adsorption capacity increased. When the temperature increased from 5℃ to 30℃, the adsorption efficiency increased from 73.0% to 99.0%, the adsorption capacity from 7.3mg/g to 9.9mg/g. That because as the initial temperature of the solution increased, the movement of DMP molecular increased, which lead to accelerate the opportunity of their mutual collisions, and resulting in increased adsorption capacity and adsorption efficiency.

3.3 Adsorption isotherm

At room temperature, the initial concentration of DMP were 10mg/ L, 20mg/L, 30mg/ L, 40mg/L, 50mg/L, 60mg/L, 70mg/L, respectively, at the condition of contact time was 120min, measured the residual concentration of DMP in solution when reached the experimental adsorption equilibrium point, then calculated adsorption capacity, Langmuir and Freundlich equations were used to fit the data, the results shown in Figure 6 which was the modified zeolite adsorption isotherm of DMP, the adsorption capacity of DMP by modified zeolite increased with the increased of initial concentration, and gradually become saturated. Which due to the larger initial concentration, the greater the driving force for absorption, resulting in increased adsorption capacity. The Langmuir equation correlation coefficient was 0.9769, the Freundlich equation correlation coefficient was 0.9539, which indicated the two equations fitting resulted very well.



(a) (b)

Figure 6. Adsorption isotherm of DMP onto modified zeolite fitted to Freundlich model (a) and Langmuir model (b)

3.4 Adsorption kinetics

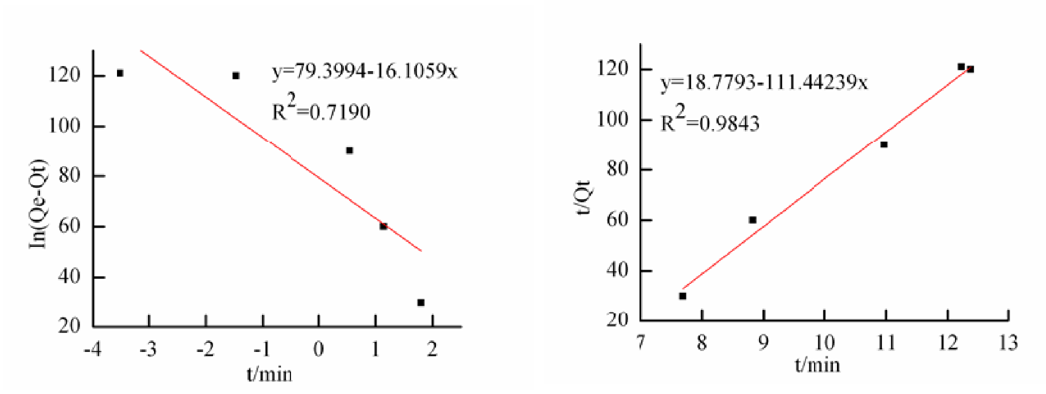
The DMP adsorption kinetics on modified zeolite was studied by using initial DMP initial concentration of 10 mg/L. As shown in Figure 7 that the DMP adsorption capacity also increased with increasing contact time. Two commonly used kinetic models, pseudo first-order and second-order kinetic models have been applied to describe the adsorption of DMP onto modified zeolite as a function of contact time. The pseud first-order kinetic model is expressed as below:

$$In(q_e - q_t) = Inq_e - k_1 t$$

where, q_t (mg/g) and q_e (mg/g) represent the amount of adsorbate adsorbed at time t and at equilibrium time, respectively, and k_1 represents the adsorption rate constant. The adsorption rate constant (k_1) was calculated from the plot of ln(q_e-q_t) against t. The pseudo second-order kinetic model can be expressed as below.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e}$$

where, k_2 (g/(mg·min)) is the pseudo second-order rate constant of sorption, q_e (mg/g) is the amount of adsorbate sorbed at equilibrium and q_t (mg/g) is the amount of adsorbate on the surface of the adsorbent at any time t. The q_e and k_2 can be obtained by linear plot of t/q_t versus t. According to the calculated kinetic parameters shown in Figure 7, it can be concluded that the pseudo second-order kinetic model can produce better fitting to the experimental data of DMP adsorption. The result revealed that the chemisorption is significant in the rate controlling step.



(a) (b)

Figure 7. Adsorption kinetics of DMP onto modified zeolite fitted to the pseudo first-order kinetic model (a) and the pseudo second-order kinetic model (b)

CONCLUSION

In this study, the adsorption test for removing DMP have been researched. The single influential factor was investigated, including the dosage of the modified zeolite, the contact time, the initial DMP concentration and the temperature of the solution. When the DMP initial concentration in aqueous solution was 10.0mg/L, the maximum adsorption efficiency was 99.0%, the adsorption capacity was 9.9mg/g when the the dosage was 10.0 mg/L, the contact time was 120 min and the temperature was 35℃. The Langmuir equation and the Freundlich equation fitting resulted very well. The kinetic process was well predicted by pseudo second-order model.

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