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Study of adsorptive removal of phenol by MOF-5

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ABSTRACT

Phenol adsorption experiments were conducted at constant temperature under oscillation conditions. The effects of the initial concentration of the aqueous phenol solution, temperature, adsorbent dosage, and initial pH of the solution on the removal rate were investigated. For an initial concentration of the aqueous phenol solution in the range 25–200 mg/L, a temperature of 40℃, a neutral solution, and a ratio of adsorbent/phenol in the range 40:1 to 2.5:1, the removal rate of phenol was 97% or more. The adsorption isotherm of phenol with MOF-5 followed the Langmuir and Freundlich models, with relative coefficients of 0.9855 and 0.9960, respectively. The adsorbent was recycled by soaking and washing with ethanol, and the recycled adsorbent gave good results after being reused six times.

Keywords: Metal–organic framework; MOF-5; Adsorption; Phenol

1. Introduction

Phenol is an important industrial raw material, and has a wide range of applications in industry, national defense, agriculture, and medicine. It is a highly toxic substance and is found widely in wastewater from chemical factories. As it has a long lifetime in the environment, causes irreversible damage to the environment and human health, and has poor biodegradability, the US Environmental Protection Agency and China have categorized phenol as a priority control organic pollutant in water. At present, phenol in wastewater is processed using physical, chemical, biological, and electrochemical methods [1]. Physical adsorption methods have received increasing attention because of their operational simplicity and low energy consumption. Research on and development of various adsorbents are hot research topics [2–5]. Porous coordination polymers, also called metal–organic frameworks (MOFs), are microporous materials with regular pore sizes and shapes, large surface areas, and high porosities. They have attracted the attention of many scientists and engineers because of their potential applications in molecular storage, heterogeneous catalysis, and gas separation via adsorption [6,7]. They are classified as polymers because of their infinite coordination-bonded structures, which are formed by the metal ions acting as nodes (or connectors) and bridging ligands acting as linkers [8]. In this study, we prepared terephthalic acid–zinc, MOF-5, as an adsorbent, to develop an effective method of treating and effectively recycling phenol in wastewater.

2. Materials and methods

2.1. Materials and instrumentation

All reagents used were of analytical grade and purchased from Sinopharm, and the test water was

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deionized water. The instruments used were a T6 New Century UV spectrophotometer (Beijing Puxi General Instrument Co., Ltd.), a BS-1E intelligent-type oscillation incubator (Jintan Zhengji Instrument Co., Ltd.), a DHG-9070A thermostated electric blast oven (Shanghai Qixin Science Instrument Co., Ltd.) an 800-type centrifugal precipitator (Shanghai Surgical Instruments Factory), a PHS-3C precision pH meter (Shanghai Precision Scientific Instrument Co., Ltd.), a hydrothermal reactor (Shanghai Qiangqiang Equipment Co., Ltd.), a XD-3 X-ray diffractometer (Beijing Puxi General Instrument Co., Ltd.) and an irprestige-21 Fourier transform infrared spectrometer (Shimadzu Co., Ltd).

2.2. Method for preparing adsorbent

MOF-5 has been reported previously in the literature [9]. Crystals of MOF-5 were prepared by adding $Zn(ClO_4)_2{\cdot}6H_2O$ (0.7509 g, 2 mmol) to an *N*,*N*-dimethylformamide (2 mL) solution of terephthalic acid (1.663 g, 1 mmol) under hydrothermal conditions. The mixture was stirred well and then sealed in a reactor and heated at 120℃ for 8 h; a white granular precipitate formed and was filtered to give the crude product. The product was washed with copious amounts of 95% ethanol, followed by vacuum drying for 8–12 h at 60℃.

2.3. Method for drawing standard curve

Under acidic and neutral conditions, the concentration of the aqueous phenol solution was in the range 0–200 mg/L. A fixed test wavelength of 270 nm was used to test the absorbance values in this concentration range. The standard curve for the phenol solution concentration vs. absorbance was a straight line. Hydrogen ion formation from the phenolic hydroxyl group occurred under alkaline conditions, and the conjugation of oxygen atoms with benzene rings caused a red shift in the absorption peak; the maximum absorption wavelength became 287 nm. A pH value of 12, phenol concentrations of 0–100 mg/L, and the fixed test wavelength of 287 nm were used to test the absorbance values to obtain a standard curve of the concentration of phenol solution vs. absorbance values.

2.4. Adsorption experiment method

An oscillation adsorption method was adopted for the experiments. Accurately weighed quantities of the adsorbent were added to 100-mL conical flasks containing 50 mL of different concentrations of phenol solution. The mixtures were stirred at 250 r/min in a constant temperature oscillation incubator, and filtered after a certain time to obtain supernatants. The absorbances of the supernatants were measured at the maximum absorption wavelength of phenol (acidic, neutral solutions: 270 nm; alkaline solution: 287 nm), using a UV spectrophotometer, to obtain the phenol concentration from the reference standard curve.

The phenol removal rate and adsorption capacity were calculated using the following equations:

$$Q_e = [(C_0 - C_e)V]/W \quad (1)$$

$$\eta = [(C_0 - C_e)/C_0] \times 100\% \quad (2)$$

where Q_e is the equilibrium adsorption quantity, mg/g; C_0 is the initial concentration of phenol, mg/L; C_e is the phenol concentration when adsorption reaches equilibrium, mg/L; V is the adsorbate solution volume, L; W is the adsorbent mass, g; and η is the adsorption rate, %.

3. Results and discussion

3.1. Effect of initial concentration on adsorption

Accurately weighed MOF-5 samples (50 mg) were added to 50 mL of phenol solutions of concentrations 25, 50, 75, 100, 125, 150, and 200 mg/L in a conical flask. The adsorption was performed in a constant temperature oscillation incubator at 40℃. The experimental results are shown in Fig. 1.

As can be seen from Fig. 1, adsorption is poor before 10 min when the initial concentration of the aqueous phenol solution is 25 mg/L, and 35 min are needed to reach adsorption equilibrium. When the initial concentration of the aqueous phenol solution is in the range 50–200 mg/L, adsorption equilibrium is reached in 30 min, and the phenol removal rate is 97% or more. So, phenol can be adsorbed on MOF-5 in this concentration range. For a high initial concentration of phenol, there is more phenol available for adsorption. The higher the solution concentration is, the greater the concentration of phenol solution in the MOF-5 surface liquid membrane, and migration of phenol from the solution to the sorbent increases.

3.2. Effect of temperature on adsorption

Accurately weighed MOF-5 samples (50 mg) were added to conical flasks containing phenol solution of concentration 50 mg/L. The adsorption rate was

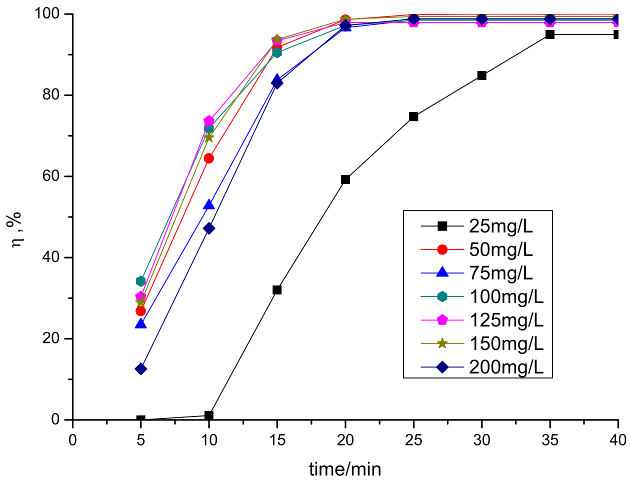

Fig. 1. Effect of initial concentration on adsorption.

investigated at 30, 40, and 50℃ under oscillation conditions. The experimental results are shown in Fig. 2.

Fig. 2 shows that for the adsorption curve at 30℃, the UV absorption rose slightly in the first 10 min. This can be attributed to molecular motion, which is not high at this temperature, the low initial concentration of phenol, and the small concentration difference between the phenol solution and the adsorbent surface liquid membrane; there were not enough migration agents, and the large phenol molecules failed to adsorb, but water molecules adsorbed on the adsorbent. The adsorption equilibrium times were compared; it took 30 min to reach adsorption equilibrium at 30℃, 20–25 min at 40℃, and there was little difference between the times taken at 50 and 40℃. The phenol removal rate curve at 40℃ was always above the other two lines, showing that adsorption was significantly better than at the other two temperatures. Clearly, the most suitable temperature for phenol adsorption experiments was 40℃.

3.3. Effect of amount of adsorbent on adsorption

Adsorbent samples (25, 50, and 100 mg) were added to conical flasks containing 50 mL of phenol solution of concentration 50 mg/L. The experimental results are shown in Fig. 3. The adsorption accelerated greatly with increasing amounts of adsorbent. When 100 mg of adsorbent were used, it took less than 20 min to reach adsorption equilibrium; 25 and 50 mg of adsorbent required 30 min to complete adsorption. Eventually, equilibrium was reached and phenol removal then gradually increased with increasing amounts of adsorbent. The values of Q_e were calculated and shown as Table 1.

3.4. Effect of solution pH on adsorption

Industrial wastewaters from different sources containing phenol may have different pH values, so we investigated the influence of pH on adsorption. In the tests, 50 mg of MOF-5 were added to 50 mL of acidic (pH in the range 3–5), neutral, and alkaline (pH 12) phenol solutions of concentration 50 mg/L. The test results show that the MOF-5 partially dissolved in the phenol solution and white turbidity appeared in the solution at pH 3 or 4. MOF-5 therefore cannot be used for phenol solutions of pH less than 5.

According to Fig. 4, MOF-5 will have the fastest adsorption rate in neutral phenol solutions, and the adsorption will reach equilibrium within 20–25 min. In

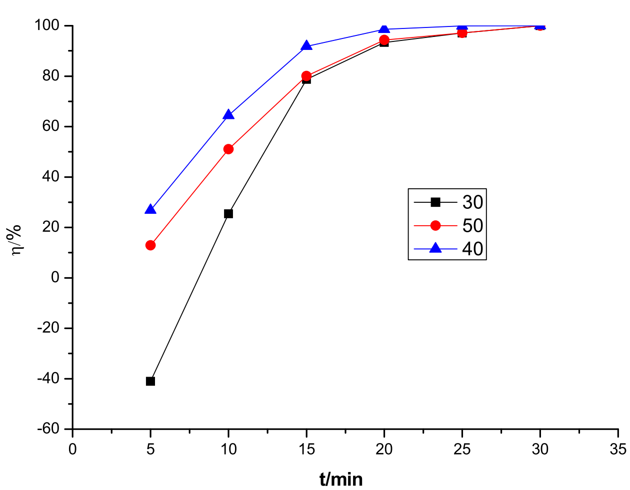

Fig. 2. Effect of temperature on adsorption.

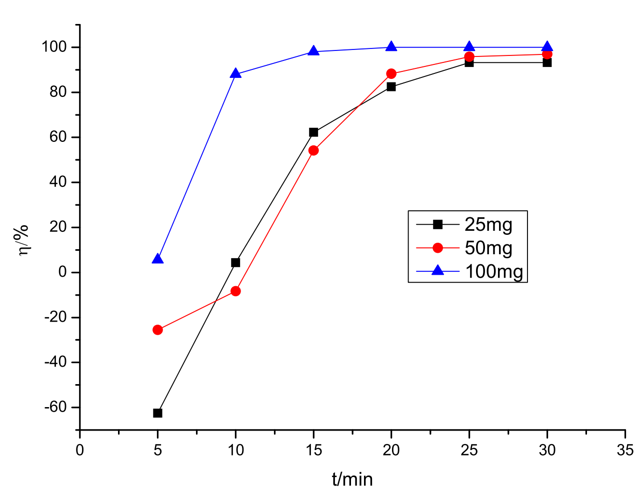

Fig. 3. Effect of amount of adsorbent on adsorption.

Table 1
The values of Q_e at different conditions

W (g)	0.025	0.050	0.100
Q_e (mg/g)	93.20	48.50	24.95

alkaline solution, the curve of removal vs. time is close to a straight line, and the removal rate is almost constant. The adsorption needed 30 min to reach equilibrium in acidic or alkaline solutions.

3.5. Adsorption Isotherms

MOF-5 samples (50 mg) were added to seven conical flasks, each containing 50 mL of phenol solution of initial concentrations 25, 50, 75, 100, 125, 150, and 200 mg/L. Oscillating adsorption was performed at the best adsorption temperature (40˚C). The Langmuir and Freundlich equations are commonly used to characterize test data for adsorption from solutions; the former represents single-molecular adsorption on the surface of the adsorbent and a similarity between the size of the target molecules and water molecules, whereas the latter describes adsorption of target molecules on heterogeneous surfaces [10]. As shown in Figs. 5 and 6, linear fittings of the adsorption isotherm curves for MOF-5 and phenol solutions are obtained, based on the Langmuir equation and Freundlich equations, respectively.

On the basis of the above linear fitting of the adsorption isotherms, both the Langmuir and Freundlich equations can be used to describe the adsorption between MOF-5 and phenol solution, but the Freundlich equation is better.

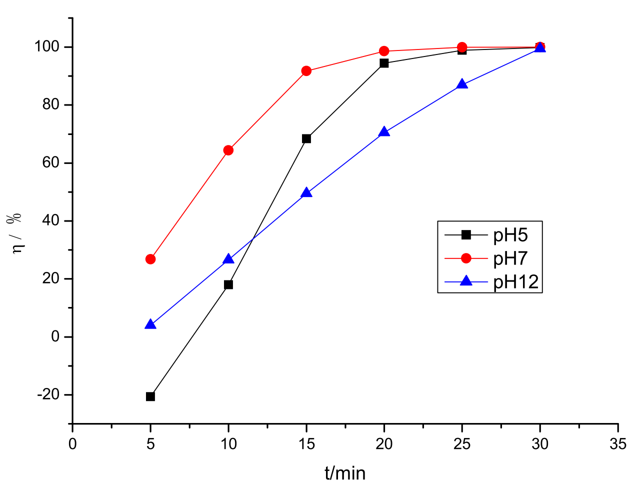

Fig. 4. Effect of solution pH on adsorption.

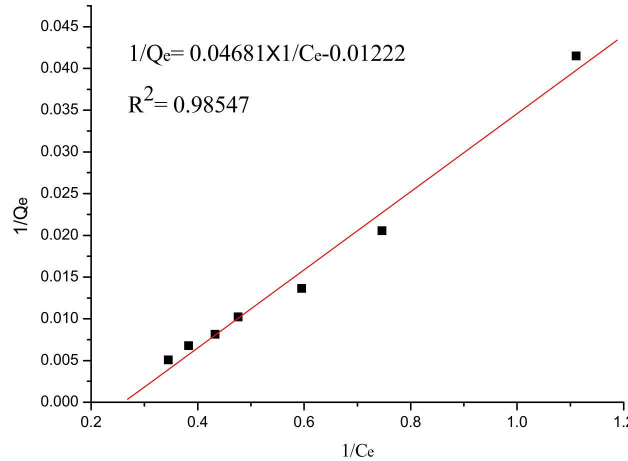

Fig. 5. Langmuir isotherm.

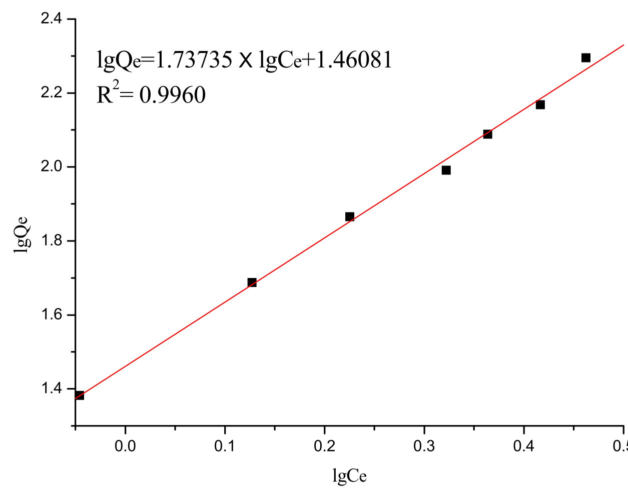

Fig. 6. Freundlich isotherm.

3.6. Regeneration of adsorbent

MOF-5 (50 mg) was added to 50 mL of phenol solution of concentration 50 mg/L. Oscillating adsorption was performed at 40˚C. After reaching adsorption equilibrium, the adsorbent was filtered off and immersed in 50 mL of 95% ethanol overnight, and then washed several times with 95% ethanol. After drying in vacuum at 60˚C, the adsorption effect was tested again; the results are shown in Table 2. There was some loss of coordination polymer in every regeneration cycle, and the recovery rate was approximately 93%. Reduced-pressure distillation can be used to recycle alcohol and phenol from the regeneration waste alcohol. The structure stability of the adsorbent wase also checked by X-ray diffraction and IR spectroscopy. The contrast charts were shown in Figs. 7 and 8, which showed that MOF-5 had enough structural stability to be reused.

Table 2
Effect of number of regeneration cycles on phenol removal rates

	Regeneration times					
	1	2	3	4	5	6
Removal ratio of phenol (%)	97.32	97.28	97.29	97.30	97.35	97.30

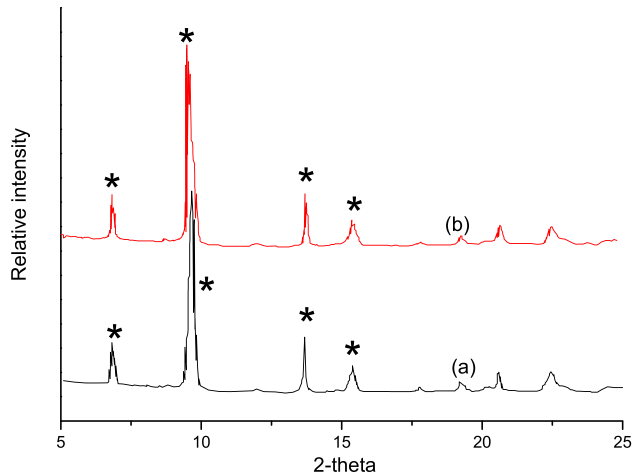

Fig. 7. XRD patterns of MOF-5 (a) before adsorption (b) after adsorption and being regenerated.

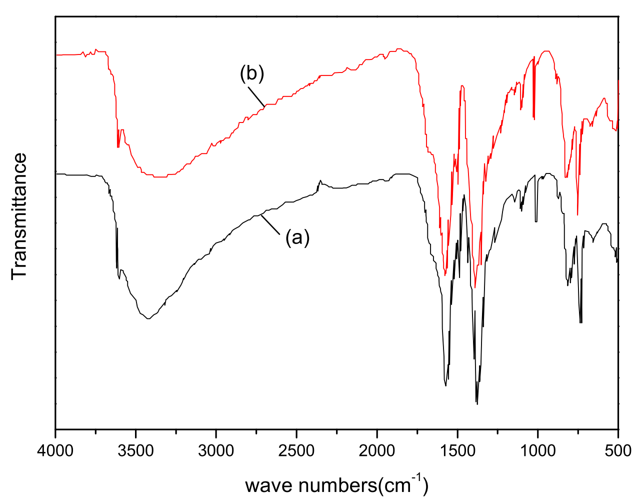

Fig. 8. FTIR spectra of MOF-5 (a) before adsorption (b) after adsorption and being regenerated.

4. Conclusion

The coordination polymer MOF-5 can be used in wastewater treatment because of its abundant channels, regular structure, ease of preparation, and low cost.

(1) The adsorption of phenol by MOF-5 generally reaches equilibrium within 30 min. The initial concentration of the aqueous phenol solution, temperature, adsorbent dosage, and initial pH of the solution influence the removal rate. When the initial concentration of the aqueous phenol solution was in the range 25–200 mg/L, the pH value of the solution was in the range 5–12, the temperature was 40℃, and the ratio of adsorbent/phenol was in the range 40:1 to 2.5:1, the phenol removal rate was 97% or more.
(2) When the temperature was 40℃, the adsorption isotherm of phenol with MOF-5 followed the Langmuir and Freundlich models; the Freundlich model gave a better fit. The relative coefficients were 0.9855 and 0.9960, respectively.
(3) The adsorbent was recycled by soaking in and washing with ethanol, and the adsorption effect was still good after the adsorbent had been reused many times.

Acknowledgments

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