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Adsorption process optimization for phenolic wastewater treatment with macroporous resin

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ABSTRACT

The treatment of phenolic wastewater was studied with macroporous resins. Under the experimental conditions (C_0 = 877 mg·L^{-1}, t = 2.5 h and pH 7), the favorable resin was selected upon the phenol adsorption capacity. Based on the experiment and mass balance, a semi-empirical model was put forward to evaluate and optimize the column adsorption process. The effect of the operation parameters as temperature, initial concentration of phenol, volumetric flow rate and pH was put forward. Under the experimental conditions (C_0 = 1,000 mg·L^{-1}; a = 2 h, b = 0.1 L, T = 298 K and pH 7), the minimal value of the total treatment time t can achieve at v = 0.688 BV/h and pH 6–7, where the treatment efficiency achieves the maximum. The results show that the semi-empirical model can do help for optimizing the adsorption process by estimating and controlling the feed rate and the pH of the solution in the process of fixed-bed column adsorption.

Keywords: Adsorption; Separation; Wastewater treatment; Phenol; Macroporous resin

1. Introduction

Phenolic compounds are widely used in the industries as dyes and drugs [1,2]. However, phenol is toxic and hazardous compound. It can cause health diseases and environmental problems [3] and it should be removed from the wastewater before discharge [4].

Many technologies have been employed to treat phenolic wastewater [5], such as physical adsorption and extraction [6], magnetic separation [7] and chemical oxidation [8]. In this case, the adsorption process with macroporous resins shows the advantages as high efficiency and low economic investment [9], and has been used to remove phenolic pollutions from wastewater [10]. The adsorption behavior of macroporous resin was studied with high adsorption rate of phenol [11]. The adsorption process of H-103 resin with different phenol concentration (600–1,000 mg·L^{-1}) was studied [12], and the results showed that the adsorption equilibrium can be achieved within 20 min.

In order to study the involved interactions during the adsorption process, a number of models have been developed using data from adsorption isotherms [13]. Because of its mathematical simplicity, Langmuir adsorption model is widely used for predicting adsorption equilibrium [14]. However, when it comes to the fixed-bed adsorption column, the model development for the dynamic adsorption process to optimize the efficiency (as the operation time, the adsorption amount of the adsorbent) was still a complex and hard work [15].

In this paper, the adsorption processes of phenolic wastewater treatment were studied with macroporous resins. A semi-empirical model was established to optimize the operation conditions, and the effect of the operation conditions as initial concentration of phenol, feed rate and pH was put forward.

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2. Materials and methods

2.1. Materials

The phenolic wastewater was taken from a plant of Beijing Yanshan Petroleum & Chemical Corporation (China). The phenol concentration was 500–2,000 mg·L^{-1}. The experimental wastewater was prepared by deionized water and the industrial wastewater to meet the initial concentration of phenol, and the pH was adjusted by HCl solution or NaOH solution.

The performance of the macroporous resins used in this work was showed in Table 1. The new macroporous resins were pretreated with immersion cleaning (ethanol, HCl 5%wt, NaOH 5%wt and deionized water, respectively) before experiment.

2.2. Experimental methods

Static adsorption experiments can be used to evaluate the equilibrium adsorption capacity of the resin. The pretreated resins were put into flasks with phenolic wastewater, respectively. Keeping stir (150 rpm) and solution temperature steady, the phenol concentration was measured by UV spectrophotometry (270 nm). The adsorption capacity Q can be calculated by Eq. (1) [16] according to mass balance.

$$Q = \frac{(C_0 - C)V}{M} \tag{1}$$

where C_0 is the initial concentration of phenol; C is the concentration of phenol in the residual solution; V is the volume of wastewater; M is the dosage of macroporous resin.

Dynamic adsorption experiments were put forward with an adsorption column which was filled with resin. The phenolic wastewater was fed into the column in a certain flow velocity, and the effluent with phenol concentration was analyzed. Keep feeding wastewater until the breakthrough point was coming. The removal rate of phenol η can be estimated according to Eq. (2), where C_a is the average concentration of phenol in the residual solution.

$$\eta = \frac{C_0 - C_a}{C_0} \times 100\% \tag{2}$$

Table 1
Performance of macroporous resins

Species	Specific surface area ($m^2 \cdot g^{-1}$)	Average pore size (nm)
H-103	1,000–1,100	8.5–9.5
CAJ	1,100	8.4–9.3
860021	160–200	14.5–15.5
CAC	700–800	8–9
LK-001	500–600	11.0
AB-8	500–550	9–10

3. Results and discussion

3.1. Effect of operation conditions on the static adsorption process

Operation time and temperature are the important conditions in the processes of static adsorption. Under the experimental conditions (C_0 = 877 mg·L^{-1}, T = 298 K and pH 7), the relationships between the adsorption capacity of resin Q and operating time t are shown in Fig. 1.

It can be seen from Fig. 1 that the adsorption capacity of different resins was all increased significantly at the beginning. However, the value of Q raised slowly after 0.5 h and turn to absorption equilibrium after 2.5 h. In this case, CAJ resin was obviously superior on the phenol adsorption capacity, which coincide with the specific surface area results of the macroporous resins.

Adsorption was an exothermic process, so that raising temperature was a disadvantage for phenol adsorption. Moreover, higher temperature can cause phenol ionization and enhance the solubility of phenol, which will led to further decrease of the equilibrium adsorption capacity. The effect of operation temperature on the equilibrium adsorption was investigated with different macroporous resins (C_0 = 877 mg·L^{-1}, pH 7, t = 2.5 h).

It can be seen from Fig. 2 that the equilibrium adsorption capacity of the macroporous resins Q_e decreased near linearly with the operation temperature increasing. Under the experimental conditions, CAJ resin shows the best adsorption performance and can be selected as the preferred macroporous resin. Moreover, the operation temperature can be determined as room temperature (298 K) considering the condition of the real wastewater and the energy consumption.

3.2. Static equilibrium adsorption isotherm of CAJ resin

The equilibrium adsorption isotherm of CAJ resin was investigated under the static experimental conditions (T = 298 K, pH 7 and t = 2.5 h). Under the equilibrium state, the relationships between Q_e and C_e are shown in Fig. 3.

As can be seen from Fig. 3, the equilibrium adsorption capacity of CAJ resin increased with the phenol equilibrium concentration increasing. The fitted line between C_e/Q_e and C_e according to Eq. (3) is plotted in Fig. 3. The linear relationship indicated that phenol adsorption of CAJ resin can be

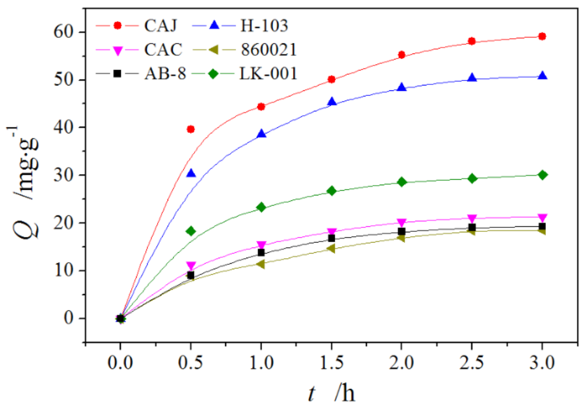

Fig. 1. Relationships between the adsorption capacity Q and operating time t (C_0 = 877 mg·L^{-1}, T = 298 K and pH 7).

described by the Langmuir isotherm model [10], where the adsorption coefficient was $K_L = 0.003$ L·mg^{-1} and maximum adsorption capacity was $Q_m = 125$ mg·g^{-1}.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

3.3. Column adsorption and process optimization

When it comes to the industry application, adsorption column will be the preferential equipment, and then the dynamic adsorption process should be studied thoughtfully to meet the requirements from application. In this case, CAJ resin was selected as the preferred resin to remove phenol from the wastewater.

3.3.1. Relationship between the adsorption amount and the phenol concentration in feed

Here the bed volume (BV) of the resin in the adsorption column was marked as b, and the feed rate of the solution in the adsorption column was marked as v. Under the operation conditions (CAJ resin, $b = 0.1$ L, $v = 3$ BV·h^{-1}, $T = 298$ K, pH 7), the dynamic adsorption processes were put forward with different phenol concentration in feed C_0 as Fig. 4.

It can be seen from Fig. 4 that the effluent volume at the breakthrough point V_e decreased with C_0 increasing proportionally. In the adsorption process before breakthrough point, if the concentration of phenol in the effluent was negligible, the process adsorption amount q can be calculated as the product of b, V_e and C_0 (Eq. (4)):

$$q = bV_eC_0 \quad (4)$$

Under the experimental conditions, the lower the initial phenol concentration, the more the wastewater volume can be treated. However, substituting the equation of $V_e = 40.26225 - 0.01473\, C_0$ and $b = 0.1$ L (Fig. 4) into Eq. (4), Eq. (5) is derived as follows:

$$dq / dC_0 = 0 \quad (5)$$

The extreme value of the adsorption amount q can be obtained at $C_0 = 1{,}366.68$ mg·L^{-1} according to Eq. (5), which is coincide with the experiment results in Fig. 4.

3.3.2. Treatment efficiency and feed rate optimization

Treatment efficiency is an important parameter to evaluate the treatment process. Under the batch column adsorption mode and the conditions (CAJ resin, $C_0 = 1{,}000$ mg·L^{-1}, $b = 0.1$ L, $T = 298$ K, pH 7), the effect of feed rate v on adsorption amount q and effluent volume V were investigated. The results are shown in Fig. 5.

As can be seen in Fig. 5, when it comes to the breakthrough point, both V_e and q were decreased linearly with v increasing (equation of $q - v$ marked in Fig. 5). Under the batch operation mode, feed quickly can do help to shorten the treatment time, but the adsorption amount will reduce. Marked the

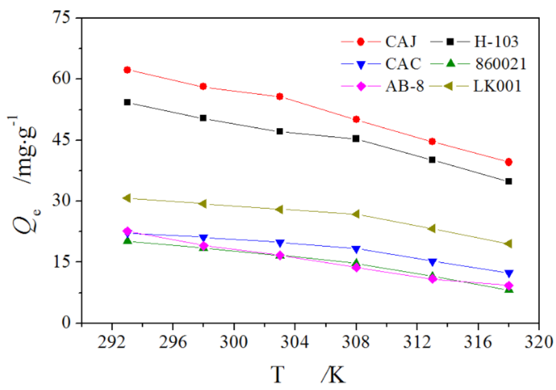

Fig. 2. Relationships between the equilibrium adsorption capacity Q_e and operation temperature T ($C_0 = 877$ mg·L^{-1}, $t = 2.5$ h and pH 7).

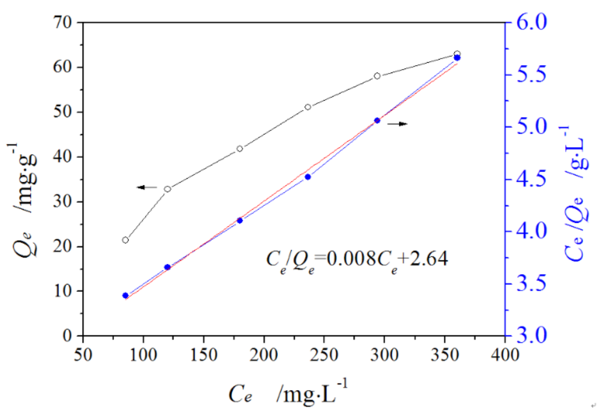

Fig. 3. Equilibrium adsorption isotherm curve of CAJ resin ($T = 298$ K, pH 7 and $t = 2.5$ h); Q_e, the equilibrium adsorption capacity of the resin; C_e, the equilibrium concentration of phenol in the residual solution.

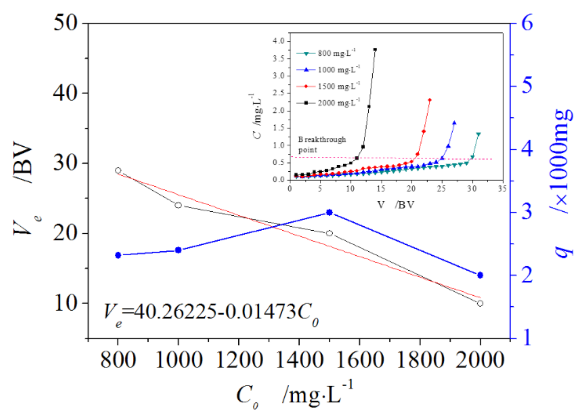

Fig. 4. Relationship between the adsorption amount q and the phenol concentration in feed C_0 (CAJ resin, $b = 0.1$ L, $v = 3$ BV·h^{-1}, $T = 298$ K and pH 7); V_e, the effluent volume at the breakthrough point; C, the phenol concentration in effluent; V, the effluent volume.

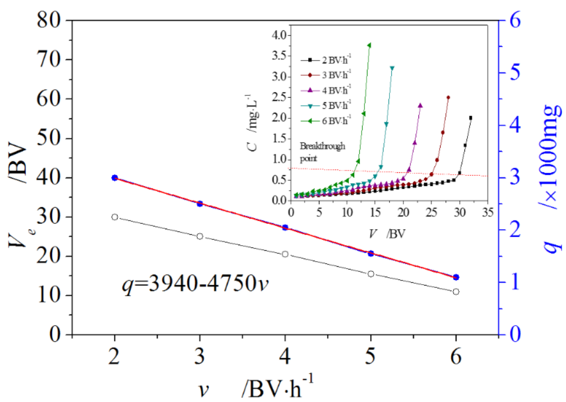

Fig. 5. Adsorption amount under different feed rate (CAJ resin, $b = 0.1$ L, $C_0 = 1{,}000$ mg·L^{-1}, $T = 298$ K and pH 7); V_e, the effluent volume at the breakthrough point; q, the process adsorption amount; C, the phenol concentration in effluent; V, the effluent volume; v, the feed rate of the solution in the adsorption column.

total amount of the phenol in the wastewater which need to be removed as m, the intermission time between every batch (include the regeneration time of the resin) as a, and then the total time of wastewater treatment t can be calculated by Eq. (6) as follows:

$$t = \frac{ma}{q} + \frac{m}{C_0 bv} \tag{6}$$

Substituting the equation of $q - v$ (Fig. 5) into Eq. (5), the extreme value of t can be obtained under the condition of Eq. (7).

$$\mathrm{d}t/\mathrm{d}v = \frac{4750ma}{(3940-4750v)^2} - \frac{m}{C_0 bv^2} = 0 \tag{7}$$

Discard the negative result, the optimized value of v can be estimated as Eq. (8):

$$v = \frac{3940}{4750 + \sqrt{4750abC_0}} \tag{8}$$

In the case of $a = 2$ h, $b = 0.1$ L and $C_0 = 1{,}000$ mg·L^{-1}, the minimal value of the total treatment time t can be obtained at $v = 0.688$ BV·h^{-1}, where the treatment efficiency come to maxmum. Based on the theoretical and experiment results, the treatment process can be optimized upon the semi-empirical equations.

3.3.3. Effect of the feed solution pH on breakthrough point

As a weakly acidic compound, phenol can exist as ionic state ($C_6H_5O^-$) and non-ionic state (C_6H_5OH) in the solution. Non-ionic phenol molecules show higher hydrophobicity, and hydrogen bonds were formed easily on the surface of the non-polar CAJ resin. In this case, phenol molecules can be adsorbed easily. In the wastewater, lower pH can decrease the ionization of phenol molecules, while higher pH can cause phenol ionization. Fig. 6 shows the relationships between the concentration of phenol in effluent C and the effluent volume under different pH of feed solution (CAJ resin, $v = 3$ BV·h^{-1}, $b = 0.1$ L, $C_0 = 1{,}000$ mg·L^{-1}, $T = 298$ K).

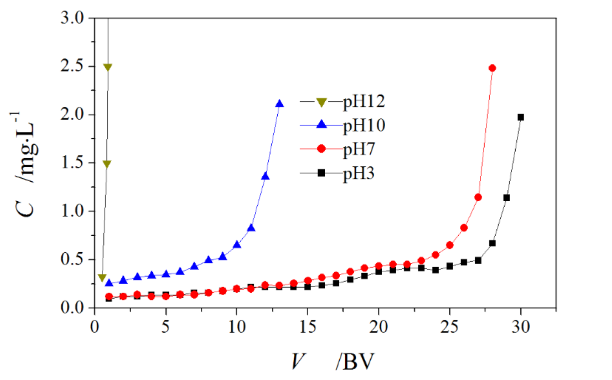

Fig. 6. Kinetic curve of phenol adsorption under different pH (CAJ resin; $v = 3$ BV·h^{-1}; $b = 0.1$ L; C_0 1,000 mg·L^{-1} and $T = 298$ K); C, the phenol concentration in effluent; V, the effluent volume.

It can be seen from Fig. 6 that the adsorption capacity of CAJ resin was promoted in acidic solution, while it was sharply decreased in alkaline solution. The adsorption amount at pH 7 is 2.3 times than that at pH 10, while the adsorption amount at pH 7 is 0.9 times than that at pH 3. In particular, the breakthrough point of phenol appeared directly when the solution was pH 12. When it comes to the industry application, keeping the feed solution in alkaline pH range was an important condition for the removal of phenol from the wastewater, which indicated that the pH of the feed wastewater should be controlled properly. In case of alkaline wastewater, adjusting the feed solution to pH 6–7 was appropriate considering the cost and operation.

4. Conclusions

The adsorption optimization for phenolic wastewater treatment was studied with macroporous resins. Under the experimental conditions, CAJ resin showed obvious superiority on the phenol adsorption capacity. Phenol adsorption on CAJ resin was a monolayer adsorption, and the equilibrium adsorption isotherm can be described by Langmuir isotherm model ($K_L = 0.003$ L·mg^{-1}, $Q_m = 125$ mg·g^{-1}, under the conditions $T = 298$ K, pH 7 and $t = 2.5$ h).

The column adsorption process can be optimized based on the model development work. The semi-empirical equations were put forward based on the theoretical and experimental results. Under the optimized conditions (CAJ resin; $C_0 = 1{,}000$ mg·L^{-1}; $a = 2$ h, $b = 0.1$ L, $T = 298$ K and pH 7), the minimal value of the total treatment time can be achieved at $v = 0.688$ BV/h, where the treatment efficiency achieves maximum.

Acidic solution can decrease the ionization of phenol molecules, and the adsorption capacity of resin can be promoted. The breakthrough point in kinetic curve indicated that the pH of the wastewater should be controlled properly. Usually adjusting pH to 6–7 was appropriate for the alkaline wastewater.

Acknowledgments

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Symbols

C_0	—	Phenol concentration in feed solution, mg·L^{-1}
C	—	Concentration of phenol in the residual/effluent solution, mg·L^{-1}
C_a	—	Average concentration of phenol in the residual/effluent solution, mg·L^{-1}
C_e	—	Equilibrium concentration of phenol in effluent solution, mg·L^{-1}
M	—	Dosage of resin, g
η	—	Removal rate of phenol, %
Q	—	Adsorption capacity of the resin, mg·g^{-1}
Q_e	—	Equilibrium adsorption capacity of the resin, mg·g^{-1}
Q_m	—	Theoretical maximum adsorption capacity, mg·g^{-1}
V	—	Volume of solution, BV
V_e	—	Effluent volume at the breakthrough point, BV
K_L	—	Constant coefficient, L·mg^{-1}
T	—	Operation temperature, K
m	—	Total amount of the phenol in the wastewater which need to be removed, mg
a	—	Intermission time between every batch (include the regeneration time of resin), h
b	—	Bed volume (BV) of the resin in the adsorption column, L
q	—	Process adsorption amount of the resin, mg
t	—	Total time of wastewater treatment, h
v	—	Feed rate of the solution in the adsorption column, BV·h^{-1}

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