

Research Article

Adsorption of Monobutyl Phthalate from Aqueous Phase onto Two Macroporous Anion-Exchange Resins

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As new emerging pollutants, phthalic acid monoesters (PAMs) pose potential ecological and human health risks. In the present study, adsorption performance of monobutyl phthalate (MBP) onto two macroporous base anion-exchange resins (D-201 and D-301) was discussed. It was found that the adsorption isotherms were best fitted by the Langmuir equation while the adsorption kinetics were well described by pseudo-first-order model. Analyses of sorption isotherms and thermodynamics proved that the adsorption mechanisms for DBP onto D-201 were ion exchange. However, the obtained enthalpy values indicate that the sorption process of MBP onto D-301 is physical adsorption. The equilibrium adsorption capacities and adsorption rates of DBP on two different resins increased with the increasing temperature of the solution. D-301 exhibited a higher adsorption capacity of MBP than D-201. These results proved that D-301, as an effective sorbent, can be used to remove phthalic acid monoesters from aqueous solution.

1. Introduction

Water pollution by phthalic acid esters (PAEs) has attracted increasing attention in recent decades. They are widely used as plasticizers in the manufacture of polyvinyl chloride [1]. Phthalic acid monoesters (PAMs) as degradation products of PAEs or synthetic intermediates for the preparation of PAEs have attained more attention. They are mutagenic endocrine disrupting compounds, posing the adverse reproductive effects on humans and wildlife equal to PAEs. Some studies have shown that the hydrolytic breakdown products of some PAEs have higher toxicity than PAEs [2]. Recently, many PAMs have been detected in surface water, sea water, and landfill leachate [3]. Previous research proved that some PAMs have greater solubility than corresponding PAEs, especially for monomethyl phthalate (MMP, 3721 mg/L), monobutyl phthalate (MBP, 409 mg/L), and mono-ethyl-hexyl-phthalate (MEHP, 1.85 mg/L). Thus, some polluted

aquatic environment may contain high concentration of PAMs [4, 5]. For instance, Jonsson found that, in landfill leachate, MBP appeared at a concentration of 2500 µg/L that was much higher than that of dibutyl phthalate (DBP) (50 µg/L) [6]. Therefore, as a new type of organic pollutants, how to effectively remove PAMs from aqueous solution is an important issue.

Many previous studies have reported that PAMs can be removed from aqueous environment through different methods, such as activated sludge process [7] and adsorption [8, 9]. In the active sludge process, PAMs can be further broken down to phthalic acid, benzoic acid, and finally carbon dioxide [10, 11]. However, this process was reported to be relatively slow and is not expected to be an effective method, because of the toxicity of PAMs to microorganism [12, 13]. Earlier research results indicated that PAMs can be adsorbed by chitosan, but the adsorption capability (0.015 mg/g) was too low to application in practice [10].

TABLE 1: Salient properties of polymeric adsorbents.

	D201	D301
BET surface area (m^2/g)	25.6	31.8
Particle size (mm)	0.4~0.7	0.4~0.6
Cross-link density (%)	8	8
Appearance	Ivory white	Ivory white
Functional groups species	Quaternary amine (-CHN ⁺ (CH ₃) ₃)	Tertiary amine (-CH ₂ N(CH ₃) ₂)
Amino content (m mol/g)	3.7	4.9

The primary objective of the present study is to find a new method for effective removal of PAMs from aqueous solution. MBP is chosen as a representative target contaminant because of its widespread occurrence in aqueous environment. The adsorption performance of MBP onto a macroporous strongly basic anion exchanger D-201 and a macroporous weakly basic anion exchanger D-301 was investigated.

2. Materials and Methods

2.1. Materials. Sodium hydroxide, hydrochloric acid, phosphoric acid, ethanol, methanol, and monobutyl phthalate (MBP) were used in this study. All chemicals are of analytic grade and were purchased from Nanjing reagent station. D-201 and D-301 were provided by Hangzhou Zhengguang Resin Co. Ltd. (Zhejiang Province, China). Physicochemical properties of the sorbents used in this study are presented in Table 1.

2.2. Resin Pretreatment. Prior to use, all the resins were packed in column and first rinsed with DI (deionized), and then with 50 bed volumes (BV) of 1.0 N NaOH followed by DI washing until neutral pH was achieved. After this, the column was subjected to acidic flushing by introducing 50 BV of 1.0 N HCl and again DI flushing to neutral pH. Finally, the resin was washed with ethanol using the same method and desiccated at 308 K for 24 h before use [14].

2.3. Sorption Experiments. Batch sorption tests were carried out in 100 mL glass bottles. To start the experiment, 0.050 g of sorbent was introduced into 50 mL solution containing a known concentration (50, 100, 150, 200, 250, and 300 mg/L) of MBP. The flask then was transferred to a G24 model incubator shaker with thermostat (Jintan Medical Instrument Factory, Jiangsu Province, China) and shaken under 150 rpm for 24 h at desired temperature (288 K, 298 K, and 313 K) to ensure equilibrium of the adsorption process. A series of parallel kinetics experiments were carried out at different conditions: the concentration and volume of MBP solutions, mass of resins, agitated speed (DF-101B model stirrer, Nanjing Yuhua Instrument Co. Ltd., Jiangsu Province, China), and temperature (TH-10 model intelligence electrothermostatic water cabinet, Ningbo Tianheng instrument factory, Zhejiang Province, China) were 20 mg/L, 2000 mL, 1 g, 400 rpm, and 288 K, 298 K, and 313 K, respectively. With MBP sorption at

different time intervals, 1 mL solution of MBP was extracted for detecting.

2.4. Analysis. Measurements of the BET surface area were based on N₂ adsorption data from an Autosorb-IQ-AG-MP Sorptomatic apparatus (Quantachrome Instruments, USA).

Concentrations of MBP in the solution were analyzed by HPLC (Agilent, 1200, USA) equipped with a reverse phase column (Agilent, TC-C18, 3.19 mm × 150 mm) and a UV detector. The mobile phase was composed of 68% methanol and 32% purified water and the detective wavelength was 228 nm [15]. Prior to analysis, the phosphorous acid was used to adjust the sample solution to acidity [16] (about pH = 4.0).

The anion-exchange capacity of D-201 and D-301 was determined by the literature method [17].

The rate of MBP adsorption, q_t (mg/g), was calculated using the relation

$$q_t = \frac{(C_i - C_t)V}{M} \quad (1)$$

with C_i (mg/L) being the initial concentration of MBP, C_t (mg/L) representing the concentration of time, V (L) being the volume of solution, and M (g) the mass of dry adsorbents [10].

3. Result and Discussion

3.1. Characterization of Sorbent. Some important physical-chemical properties of D-201 and D-301 are present in Table 1. As can be seen from Table 1, the two exchangers have low surface area (less than 40 m^2/g) and a large number of functional groups. For the strongly basic anion-exchange resin D-201, it contains 3.7 mmol/g quaternary amine; for the weak base anion exchanger, the exchangeable capacity of D-301 is 4.9 mmol/g. These two adsorbents show a similar particle size and cross-link density.

3.2. Adsorption Isotherms. Adsorption isotherms of MBP onto D-201 and D-301 (in Figure 1) are represented by Langmuir model and Freundlich model [18]:

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}, \quad (2)$$

$$q_e = K_f C_e^{1/n},$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_e (mg/L) represents the solute concentration in equilibrium, K_f and n are the Freundlich constants to be determined, q_m (mg/g) is the maximal sorption capacity, and K_L (L/mg) is a binding constant.

It can be observed from Figure 1 that the amounts adsorbed of MBP on D-201 and D-301 are increased with the increase of equilibrium concentrations, indicating the spontaneous process. Results in Table 2 show that the Langmuir model and the Freundlich model representing the MBP adsorption isotherms were different by the value of R-square (R^2). The Langmuir model may be more reasonable

TABLE 2: Adsorption isotherm parameters of D-201 and D-301.

Adsorbent	T/K	q_m (mg/g)	Langmuir		Freundlich		
			K_L (L/mg)	R^2	K_F	n	R^2
D-201	288	284.6	0.043	0.994	51.1	3.137	0.916
	298	287.8	0.050	0.990	57.0	3.283	0.913
	313	288.3	0.098	0.943	82.1	4.014	0.942
D-301	288	388.9	0.088	0.987	84.7	3.159	0.887
	298	390.7	0.107	0.987	98.7	3.462	0.901
	313	400.0	0.128	0.998	123.5	4.043	0.943

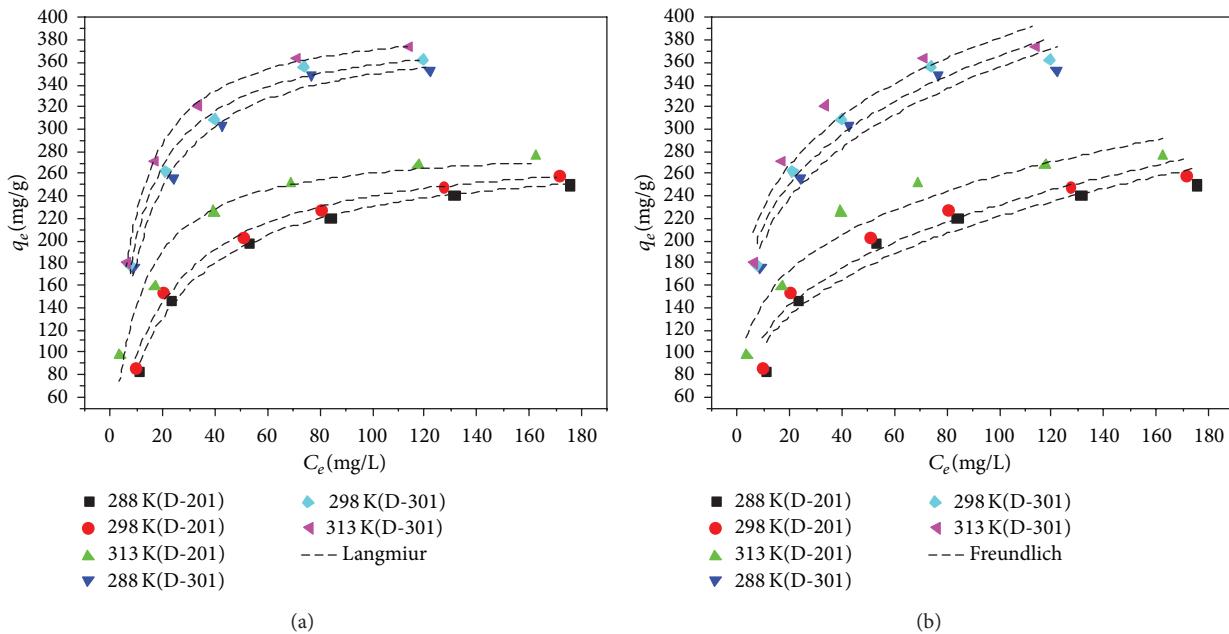


FIGURE 1: Equilibrium adsorption isotherms of MBP on D-201 and D-301. (a) Fitting by Langmuir equation. (b) Fitting by Freundlich equation.

than Freundlich model. q_m values increased by the rise of temperature, which may also indicate that the adsorption of MBP onto D-201 or D-301 was an endothermic process. In other words, higher temperature is more favorable for MBP adsorption onto D-201 and D-301. This result indicated that the function groups of D-201 and D-301 play an important role in the removal process of MBP from aqueous solution. As shown in Figure 1 and Table 2, the maximum adsorption capacity of MBP on D-301 is much higher than that on D-201. The more excellent adsorption property of D-301 than D-201 may be attributed to its large number of functional groups. In addition, all the values of n , the Freundlich parameter, are greater than one, which means that the adsorption of MBP on the two sorbents is the optimal adsorption [19].

3.3. Thermodynamic Analysis. Thermodynamic parameters for the adsorption process can be calculated as

$$\begin{aligned} \Delta G &= -RT \ln K_L \\ \ln K_L &= -\frac{\Delta H}{RT} + A, \\ \Delta G &= \Delta H - T\Delta S, \end{aligned} \quad (3)$$

TABLE 3: Thermodynamic parameters of D-201 and D-301.

Adsorbent	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS (J/mol)
		288 K	298 K	313 K	
D-201	25.32	7.72	7.11	6.19	61.11
D-301	11.12	5.78	5.59	5.32	18.54

where T is the absolute temperature in K and K_L is the Langmuir adsorption constant. R is the gas constant with a value of $8.314 \text{ J}/(\text{mol}\cdot\text{K})$, and A is a constant [20, 21]. The enthalpy change ΔH was determined by plotting $\ln K_L$ versus $1/T$ (Figure 2). Thermodynamic parameters of MBP adsorption onto D-201 and D-301 are listed in Table 3.

Generally, the enthalpy change due to chemical adsorption ($>20 \text{ kJ/mol}$) is considerably larger than that due to physical adsorption ($<20 \text{ kJ/mol}$). The adsorption enthalpies in Table 3 suggest that the adsorption process of MBP on D-201 might be considered to be ion exchange in nature. However, the agreement of MBP adsorption enthalpy with values for physisorption (0 to 20 kJ/mol) indicates that MBP was adsorbed onto D-301 via physical adsorption.

TABLE 4: Adsorption kinetic parameters of D-201 and D-301.

Temperature	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model	
	k_1 (1/min)	R^2	k_2 (g/kg·min)	R^2
D-201	0.016	0.996	185.5	0.979
D-301	0.016	0.998	189.4	0.990

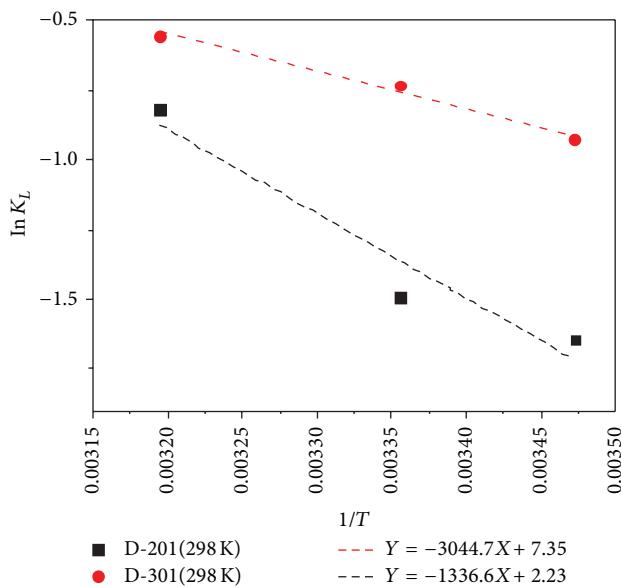


FIGURE 2: Van't Hoff plot for the adsorption of MBP onto D-201 and D-301.

The positive ΔS values in Table 3 imply that MBP adsorption onto D-201 and D-301 is entropy-driven process [22].

3.4. Adsorption Kinetic. Figure 3 shows sorption kinetics of MBP onto D-201 and D-301. It is clear that about 250 min was required to reach sorption equilibrium for the two adsorbents. Pseudo-first- and pseudo-second-order models were fitted to the kinetic data [23]:

$$\begin{aligned} \ln(q_e - q_t) &= \ln q_e - k_1 t, \\ \frac{1}{q_t} &= \frac{1}{k_2 q_e^2 t} + \frac{1}{q_e}, \end{aligned} \quad (4)$$

where k_1 and k_2 are the pseudo-first-order model and pseudo-second-order model constants to be determined. The kinetic parameters are determined and listed in Table 4.

From Table 4 we can see that the pseudo-first-order model gave a better representation of the data than the pseudo-second-order model. It is apparently clear that the values of the rate constant k_1 in Table 4 are similar to each adsorbent.

4. Conclusion

In summary, this work provides a new approach to remove MBP from an aqueous solution, using two macroporous

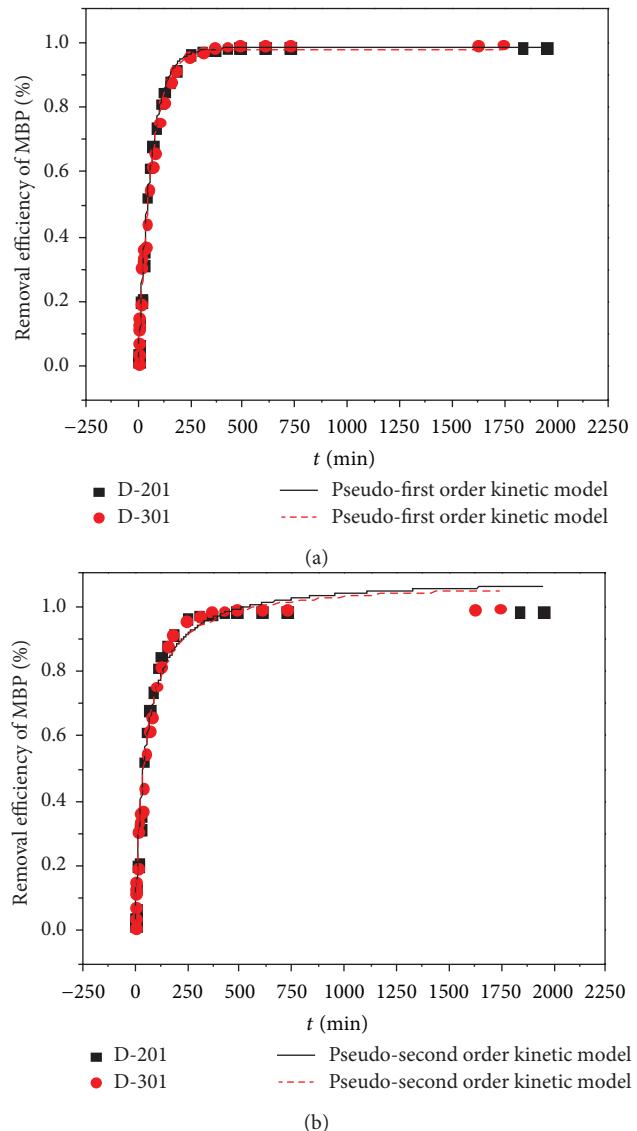


FIGURE 3: Adsorption kinetics of MBP onto D-201 and D-301 at 298 K. (a) Fitting by Pseudo-first-order equation. (b) Fitting by Pseudo-second-order equation.

anion-exchange resins. The results reported herein demonstrate that the macroporous weakly basic anion exchanger D-301 was a highly efficient material for MBP removal. The satisfactory adsorption capability of D-301 displays its potential for PAMs removal in aqueous environment.

Conflict of Interests

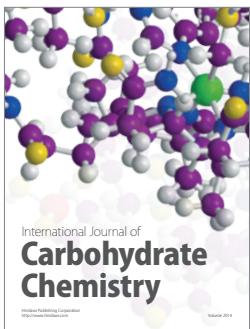
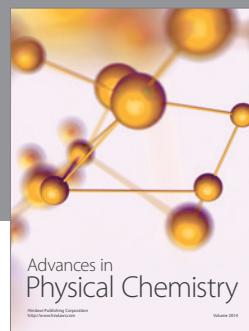
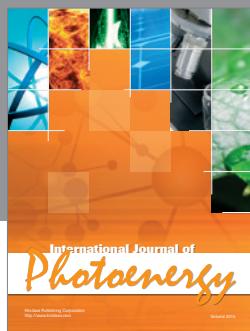
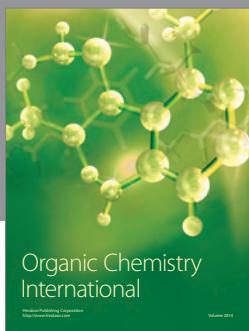
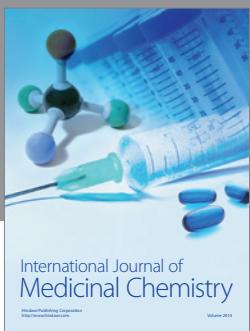
The authors declare that there is no conflict of interests regarding the publication of this paper.

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