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Research Article

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N-(phosphonomethyl)iminodiacetic acid adsorption onto D301 composite resin

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ABSTRACT

The nanoscale hydrated aluminium oxide composite resin (AlD301) was successfully synthesized through incorporation of nano hydrated aluminium oxide into the weakly basic resin D301 as supports. The adsorption behavior of weakly basic anion exchange composite resin AlD301 to N-(Phosphonomethyl)iminodiacetic acid (PMIDA) was studied. The influences of pH, initial concentrate of PMIDA, contact time and temperature on the adsorption process were investigated. The results showed that the adsorption capacity of AlD301 reached the maximum when the temperature was 303 K and the time was about 2.5 h. The adsorption experimental data fitted well to the Freundlich isotherm model. The second-order adsorption kinetics equation was described for this process, and the related parameters were showed in the paper. The results demonstrated that AlD301could be an idea adsorbent for removal PMIDA from aqueous solution.

Key words: composite resin; N-(Phosphonomethyl)iminodiacetic acid; adsorption

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INTRODUCTION

N-(Phosphonomethyl)iminodiacetic acid (PMIDA) was an important intermediate of herbicide glyphosate production of IDA method [1]. With the scale expanding of glyphosate production, the market demand of PMIDA was also growing. However, the production process of PMIDA can produce large amount of high concentrated organic wastewater. The wastewater is one of the most difficult industrial wastewater to deal with, including high salt content and non biodegradable. The removal of PMIDA from wastewater can be carried out by membrane filtration [2-5], evaporation crystallization [6, 7], microelectrolysis [8, 9], adsorption [10, 11]. Among the various methods of wastewater treatment, adsorption method has been more developed in the last decade for its advantages of high efficiency, economy and no-secondary contamination. It has been successful used in industrial wastewater treatment. Based on the characteristics of PMIDA wastewater, aluminium loading D301 composite resin was prepared and used for removal a PMIDA from wastewater.

EXPERIMENTAL SECTION

Chemicals and reagents

D301 resin was from Nankai Resin Co. Ltd. (Tianjin, China). PMIDA was from QiaoChang Chemical Co. Ltd. (Binzhou, China). All chemicals used were of analytical reagent grade and obtained from Shanghai Chemical Reagent Station (Shanghai, China). AlD301 resin was prepared by soaking dry D301 resin in mixed solution of $AlCl_3$, HCl and NaCl for 24 h at 298 K.

Experiment methods

Batch adsorption experiments were performed by mixing 0.05 g of AlD301 resin particles with 50 mL of different PMIDA concentration in a 250 mL glass flask. The samples were shaked continuously in constant temperature bath shaker (120 $r \cdot min^{-1}$) for 24 h to achieve equilibrium. The effect of temperature (288, 303 and 318 K) was investigated at pH 2.0 at the different initial concentrations. The adsorption kinetics of PMIDA on AlD301 resin

were conducted using samples withdrawn at pre-determined times at different concentrations. The concentration of PMIDA was analyzed by a high performance liquid chromatograph (Waters 2695, Waters Corp, America) and a UV-Vis spectrophotometer (Waters 2996, Waters Corp, America). Separation was performed on a C18 analytical column (150 ×4.6 mm i.d., particle size 3.5 μm). The mobile phase was water containing 0.5 % KH_2PO_4 as pH regulator. The mobile phase flow rate was 1.0 mL·min^{-1}, and the detector wavelength was 200 nm. All samples were filtered through 0.45 μm membrane filters before detection.

RESULTS AND DISCUSSION

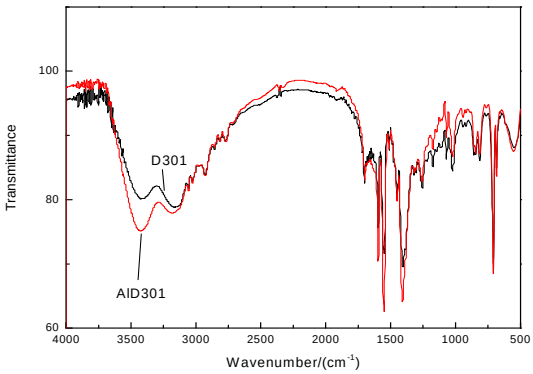

Figure 1 FT-IR spectrum of resin AlD301 and D301

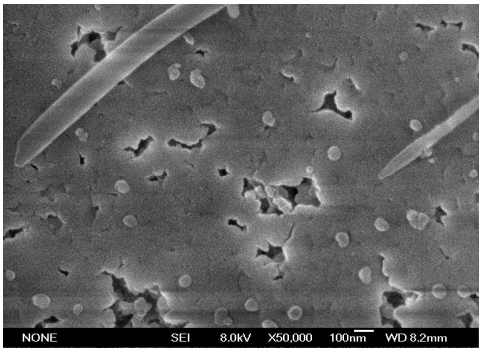

Figure 2 Morphology of resin AlD301

Absorbent characterization

The FT-IR spectra of D301 and Al D301 are shown in Figure 1. The FT-IR spectrum of AlD301 shows a broad absorption band around 3300 cm^{-1}, which may be attributed to the O-H group. The bands near 1370 cm^{-1} corresponded to the characteristic C–N stretching vibration of amine groups in the resin. The bands at 1600 cm^{-1} can be assigned to the stretching vibration of Al-O in AlD301. Figure2 shows the SEM micrograph of the AlD301 resin. It clearly shows that crystallites of hydroxy-aluminium are well dispersed on the surface of D301. Hydroxy-aluminium exhibited an irregular morphology by rod-shape particles.

Effect of pH value

pH is one of the most important factors affecting adsobate adsorption on adsorbent. Because the PMIDA species and the surface charge sites of adsorbent depend on the pH of solution. The effect of pH on PMIDA adsorption is illustrated in Figure 3. As shown in Figure 3, the Al D301 adsorption capacity to PMIDA was clearly pH dependent and it obtained the maximum adsorption capacity at low pH value. It's mainly due to the fact that pH could change the surface charge sites of absorbent by changing the protonation of AlD301. With the increase of pH value, amino groups were free from the protonation, and so the adsorption capacities decrease. But if the pH was low, it will enhance the surface polarity of AlD301 resin and reduce the hydrophobicity of AlD301 by occupying adsorption pores of the resin. The maximum adsorption capacity on PMIDA appeared at pH 2.0, so other adsorption experiments were performed at pH 2.0.

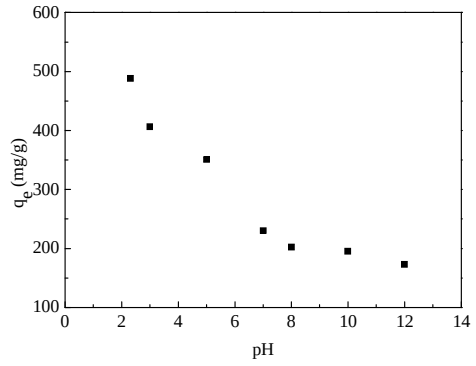

Figure 3 Effect of pH on adsorption of PMIDA onto AlD301

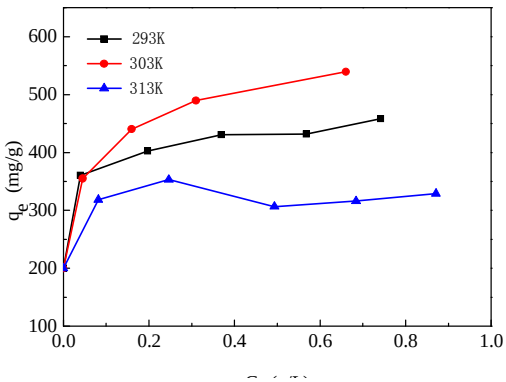

Figure 4 Effect of temperature on adsorption of PMIDA onto AlD301

Adsorption isotherm

The effect of different temperature on PMIDA adsorption on AlD301 was performed from 293 to 313 K. Figure 4 shows the PMIDA adsorption isotherms at 293, 303 and 313 K, respectively. The results indicated that the

equilibrium adsorption capacity increased first and then decreased with an increase of temperature. This may be due to PMIDA molecular thermal motion enhances with increasing temperature in the lower temperature range. Because contact opportunity of PMIDA molecular and the activity adsorption site of AlD301 increasing, the adsorption quantity of PMIDA molecules increase. At the same time, the adsorption capacity increased with equilibrium concentration increasing is a preferential adsorption. The adsorption isotherm is very important for describing adsorption behavior to a solid liquid system. The equilibrium data were then fitted using three different isotherm models including the Langmuir and Freundlich, Temkin models. Three models can be expressed as equations (1), (2) and (3) respectively.

Langmuir model $$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

Freundlich model $$q_e = K_F C_e^{1/n} \quad (2)$$

Temkin $$q_e = B\ln A + B\ln C_e \quad (3)$$

The correlation coefficients (R^2) along with other parameters for two different models are listed in Table1. As shown in Table 1, the 1/n lied in the range from 0.1 to 0.5 indicating that PMIDA adsorption on AlD301 is wonderful. It also can be seen from Table 1 that the experimental data for PMIDA adsorption show a better correspondence with the Freundlich model under the experimental conditions. This shows that the adsorption of PMIDA on AlD301 was monolayer

Table 1 Isothermal parameters and correlation coefficients (R^2) obtained from the three models

model		293 K	303 K	313 K
Langmuir	q_{max}/(mg·g^{-1})	443.53	538.21	330.91
	b/(L·mg^{-1})	102.10	39.21	37.19
	R^2	0.7923	0.9028	0.8860
Freundlich	k/(mg·g^{-1})	461.61	580.23	329.64
	1/n	0.0784	0.1547	0.0912
	R^2	0.9565	0.9931	0.9761
Temkin	A	2281.75	3.78	199.68
	B	31.35	69.02	26.93
	R^2	0.9500	0.9994	0.9691

To describe the thermodynamic behavior of adsorption of PMIDA onto AlD301, the changes in free energy, ΔG, enthalpy, ΔH, and entropy, ΔS, of adsorption were calculated from the experiments carried out at different temperatures by the following equations:

$$\log C_e = \frac{\Delta H}{2.303R}\frac{1}{T} - \log K_0 \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The thermodynamic parameters for the adsorption of PMIDA onto AlD301 at different temperatures were summarized in Table 2. Table 2 shows Gibbs free energy (ΔG) was negative. So the PMIDA adsorption from solution onto adsorption agent surface was spontaneous and favorable. The calculated enthalpy (ΔH) value showed the adsorption process was an exothermic reaction. The positive values of ΔS suggested a higher randomness tendency between the solid and solution interface during the adsorption of PMIDA on the AlD301.

Table 2 Values of thermodynamic parameters evaluated for PMIDA adsorption

Adsorbent	*T* (K)	*ΔG* (kJ·mol^{-1})	*ΔS* (kJ·(mol·K)$^{-1}$)	*ΔH* (kJ·mol^{-1})
AlD301	298	-14.943	0.0138	-10.891
	313	-16.023	0.0170	
	323	-15.088	0.0134	

Adsorption kinetics

Figure5 shows the adsorption capacity of PMIDA onto AlD301 as a function of contact time at different initial concentration. Results indicated the adsorption capacity increased rapidly during the starting stage then gradually increased until equilibrium at about 2.5 h. The adsorption kinetic data can be analyzed using different kinetic models. In our finding, four kinetic models including the pseudo-first-order, pseudo-second-order equation, intraparticle diffusion and Elovich were applied to find out adsorption mechanism. Four models can be written as equations (6) and (7), (8), (9), respectively.

Pseudo-first-order model $$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

Pseudo-second-order model $$\frac{t}{q} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad (7)$$

intraparticle diffusion $$q_t = k_{id} t^{1/2} + C \quad (8)$$

Elovich $$q_t = \frac{\ln \alpha\beta}{\beta} + \frac{\ln t}{\beta} \quad (9)$$

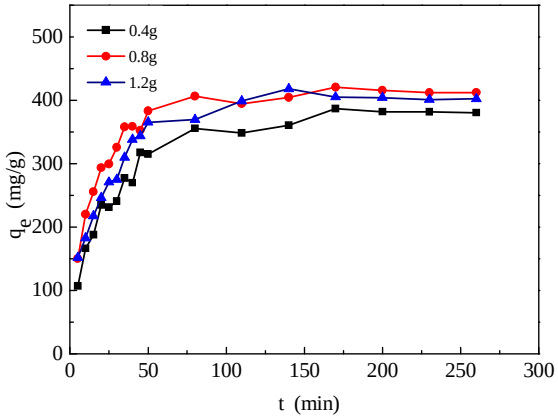

Figure 5 Effect of contact time on adsorption of PMIDA onto AlD301

The k_1, k_2, K_{id}, β, q_e and correlation coefficients R^2 of AlD301 under different conditions were calculated and given in Table 3.

Table 3 Kinetics parameters and correlation coefficients (R^2) obtained from four models

model	parameter	C_0/(g·L^{-1})		
		0.4	0.8	1.2
Pseudo-first-order model	k_1/(min^{-1})	0.01670	0.02146	0.03224
	q_e/(mg·g^{-1})	225.2942	191.9862	303.8086
	R^2	0.9070	0.9188	0.9522
Pseudo-second-order model	k_2/(g·(mg·min)$^{-1}$)	0.0500	0.1139	0.0836
	q_e/(mg·g^{-1})	500	434.7826	427.3504
	R^2	0.9984	0.9993	0.9981
Intraparticle diffusion	K_{id}	37.1244	38.2493	37.3370
	R^2	0.9500	0.9099	0.9260
Elovich	β	0.0123	0.0125	0.0115
	R^2	0.9566	0.9286	0.9636

It can be seen from Table 3 that the values of the correlation coefficients (R^2) of the pseudo-second-order model for the adsorption of PMIDA were higher than other models. Furthermore, the theoretically calculated values of q_e by pseudo-second-order model were much closer to experimental values at different temperatures. Therefore, the pseudo-second-order model could accurately describe the adsorption of PMIDA onto AlD301. And it suggested that the adsorption process was controlled by chemical adsorption. From values of kinetic parameter k_2, it can be seen that the adsorption of PMIDA is divided into fast and slow reactions. When the initial concentration was 0.4, 0.8 and 1.2 g·L^{-1} of PMIDA solution, the k_2 was 0.0500, 0.1139 and 0.0836 g·(mg·min)$^{-1}$, respectively. And it suggested

this adsorption process was mainly controlled by the slow reaction.

CONCLUSION

An efficient composite resin (AlD301) was successfully synthesized using the weakly basic resin D301 by a incorporation reaction. When the temperature is 303 K at low pH value, AlD301 can obtain the maximum adsorption capacity. The adsorption of PMIDA on AlD301 was fitted well to the Freundlich isotherm model. The thermodynamics of PMIDA adsorption onto AlD301 resin confirmed the adsorption process was exothermic and spontaneous. The kinetic results show that the pseudo-second-order equation fitted the experimental data very well. The adsorption process is mainly controlled by the slow reaction, belonging to two stages reaction process.

Acknowledgments
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