Journal of Hazardous Materials B124 (2005) 173–180

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Adsorption characteristics of aniline and 4-methylaniline onto bifunctional polymeric adsorbent modified by sulfonic groups

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Received 1 February 2005; received in revised form 29 April 2005; accepted 4 May 2005
Available online 31 May 2005

Abstract

In this paper a new bifunctional polymeric resin (LS-2) was synthesized by introducing sulfonic groups onto the surface of the resin during the post-crossing of chloromethyl low crosslinking macroporous poly-styrene resin, and the comparison of the adsorption properties of LS-2 with Amberlite XAD-4 toward aniline and 4-methylaniline in aqueous solutions was made. The study focuses on the static equilibrium adsorption behaviors, the adsorption thermodynamics, and the column dynamic adsorption and desorption profiles. Freundlich model gives a perfect fitting to the isotherm data. Although the specific surface area of LS-2 is lower than that of Amberlite XAD-4, the adsorbing capacities for these two adsorbates on LS-2 are higher than those on Amberlite XAD-4 within the temperature range 288–318 K, which is contributed to microporous structure and the polar groups on the network of LS-2 resins. The adsorption for aniline or 4-methylaniline on LS-2 was proved to be an endothermic process and increasing temperature was favorable. From the studies on the adsorption thermodynamics, static equilibrium adsorption, and the desorption conditions, an important conclusion can be drawn that the adsorption for aniline or 4-methylaniline on the LS-2 is a coexistence process of physical adsorption and chemical transition.

Keywords: Adsorption; Bifunctional polymeric adsorbent; Aniline; 4-Methylaniline; Hypercrosslinked adsorbent; Sulfonic groups

1. Introduction

Aniline and its derivatives, as one of the most important organic intermediates, are widely used for the manufacture of pesticides, rubber, drugs, varnishes and dyestuffs; as a result, more and more aniline-containing wastewater has been introduced into water bodies. For their high toxicity, the efficient removal of these organic compounds from water has drawn significant concern.

Presently, various methods of wastewater treatment have been developed such as catalytic oxidation, liquid membrane separation, biological degradation and adsorption [1–5]. Due to the high concentrating ability of typical adsorbents [6,7], adsorption is proved to be one of the most attractive and effective techniques for purification and separation in wastewater treatment. Activated carbon, as a porous material with large specific surface area and predominant proportion of micropores, has been widely used in industrial adsorptive processes efficiently [8,9].

In recent years, polymeric adsorbents have increasingly been viewed as an alternative to activated carbon for efficient removal of specific organics from contaminated water due to their good properties and mechanical strength. Among them the commercially available Amberlite XAD-4 resin was reported to be an ideal adsorbent for a wide variety of organic compounds, especially for phenols. However, the extreme hydrophobic surface of XAD-4 lowers its adsorbing capacity for polar organic compounds [10,11]. To overcome the limitation, chemically modified polymeric adsorbents with functional groups such as phenolic hydroxyl, acetyl, benzoyl and

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doi:10.1016/j.jhazmat.2005.05.001

hypercrosslinked polymers have been synthesized recently [12–14]. There are also reports that some hypercrosslinked resins were used in sorption of aniline compounds from aqueous solution [15].

The purpose of present work was to prepare a new chemically modified bifunctional adsorbent (LS-2) for the removal of the two aniline compounds (aniline, 4-methylaniline) from their aqueous solutions, and to compare the adsorption properties of the adsorbent with those of the commercial Amberlite XAD-4 resin.

2. Materials and synthetic methods

2.1. Chemicals

Acetone, ethanol, nitrobenzene, zinc chloride, sulfuric acid, hydrochloric acid, dibenzoyl peroxide, aniline and 4-methylaniline were used in this study. All these chemicals are of analytical grade and were purchased from Shanghai Chemical Reagent Plant (Shanghai, China). Photographic-grade gelatin was obtained from Yancheng Dafeng Gelatin Plant (Yancheng, China). Styrene and divinylbenzene (purity: 50.4%) were purchased from Dongda Chemical Co. Ltd. (Shandong province, China). Chloromethyl methylether was obtained from Langfang Chemical Co. Ltd. (Hebei province, China). The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). Physicochemical properties of the adsorbates and adsorbents used in this study are presented in Tables 1 and 2. Aniline and 4-methylaniline were dissolved in deionized water without pH adjustment.

Table 1
Typical properties of the studied adsorbents

Polymeric resins	Amberlite XAD-4	LS-2
Polarity	Nonpolar	Moderate polar
BET specific surface area (m^2/g)	880	506
Average pore diameter (nm)	5.8	4.5
Particle size (mm)	0.4–0.6	0.4–0.6
Pore volume (mL/g)	1.05	0.57
Micropore area (m^2/g)	3.1	280.4
Residual chloride content (%)	0	7.78
Strong acidic exchange content	0	1.2
Color	White	Deep gray

2.2. Synthesis of LS-2 adsorbent

The synthesis of low-crosslinked macroporous styrene–divinylbenzene copolymer and its chloromethylation were carried out as the literature [17].

The bifunctional polymeric adsorbent LS-2 was prepared through the following post-crosslinking step. In a 500 mL round-bottomed flask, 50 g chloromethylated styrene–divinylbenzene copolymers (the chlorine content 19.5%) were swollen in 300 g nitrobenzene. Under mechanical stirring, 7.5 g zinc chloride was slowly added into the flask at room temperature. Then, 10 mL sulfuric acid (mass percentage: 98%) was added. The mixture was further stirred for 12 h at 383 K. Finally, the mixture was poured into an acetone bath containing 1% (mass percentage) hydrochloric acid. The filtered polymers were extracted by ethanol for 8 h in Soxhlet apparatuses and dried under vacuum at 333 K for 8 h.

2.3. Characterization of adsorbents

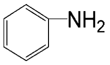
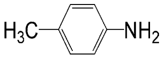
The specific surface area and the pore distribution of the adsorbents were calculated, respectively by BET and BJH methods via the nitrogen adsorption and desorption curves at 77 K using a Micromeritics ASAP-2010 automatic surface area analysis instrument (Micromeritics Instrument, Norcros, USA). Infrared spectra of the polymeric adsorbent before and after the post-crossing reaction were obtained from a Nicolet 170 SX IR spectrometer (USA) with a pellet of powdered potassium bromide and resin. The chlorine content was measured according to the method of Volhard [18]. And the strong acidic exchange content was measured by chemical titration.

3. Experimentation

3.1. Static adsorption experiment

Equilibrium adsorption of two aniline compounds was performed at four different temperatures: 288 K (risen from 275 K), 303, 318 and another 288 K (fallen from 318 K). Dry LS-2 resin (0.1 g) was weighed accurately and introduced into a 250 mL conical flask directly, while the XAD-4 resin should be wetted in 0.5 mL methanol and rinsed with deionized water for more than three times before use. Then, 100 mL aqueous solution of the adsorbates of certain concentration (C_0, mg/L) ranging from 200 to 1000 was added to each flask.

Table 2
Properties of the adsorbates

Adsorbates	Molecular formula	Molecular weight	pK_a[a]	Solubility (g/100 g H_2O)[a]
Aniline		93	4.58	3.7
4-Methylaniline		107	5.08	0.7

[a] Data from [16].

The flasks were completely sealed and shaken in a G25 model incubator shaker (New Brunswick Scientific Co. Inc.) at a presettled temperature under 130 rpm until equilibrium reached. The concentration (C_e, mg/L) of the residual aqueous phase was determined using HPLC (Nov-Pak C_{18} column, flow phase: methanol:5% ammonia = 70:30, wavelength: 275 nm, flow rate: 1 mL/min) assembled by Waters 600 controller, Waters 600 pump and Waters 2487 Dual Absorbance Detector (Waters Assoc., USA). Thus, the concentration of the adsorbent-phase solute, Q_e (mmol/g), is calculated by Eq. (1):

$$Q_e = \frac{V_1(C_0 - C_e)}{MW} \quad (1)$$

where V_1 is the volume of solution (L), W is the weight of dry resin (g), and M is the molecular weight of corresponding adsorbate.

3.2. Selection of desorption condition

100 mL aqueous solution (10.0 mmol/L) of the aniline compounds was added to each 250 mL conical flask containing 0.1 g of dry resins. The flasks were tightly sealed and shaken in a G25 model incubator shaker at 303 K under 130 rpm. After adsorption equilibrium reached, all the resins were filtered and again introduced, respectively into the flasks. Hundred milliliters of the different desorption solvents were added into the flasks at 313 K and shaken continually. Twenty-four hours later, the concentration of solution was determined by HPLC, and the removal efficiency was evaluated.

3.3. Dynamic adsorption and desorption

Dynamic adsorption was conducted using a 10 cm × 4.6 mm i.d. stainless-steel column packed with the new prepared polymeric adsorbent LS-2 and connecting with a 6672 reciprocating pump (Beijing Analytical Instrument Plant) at room temperature. Aniline solution of 14.8 mmol/L was passed through the column at a flow rate of 6 BV/h (BV is bed volume), and the solvent (5% hydrochloric acid) was used for desorbing at the temperature of 313 K. Dynamic adsorption capacities of resins were evaluated in two ways: (1) the breakthrough capacity, which was based upon the total amount of adsorbed aniline until the effluent concentration reached 5% of initial concentration, (2) the total capacity, which was based upon the total amount of adsorbed aniline until the concentration reached 100% of the initial concentration. The effluents from the column were analyzed quantitatively by HPLC in every 5 min and the adsorption capacities Q_c (mmol/mL resin) were calculated with following Eq. (2):

$$Q_c = \frac{V_2(C_0 - C_a)}{V_3} \quad (2)$$

where C_0 is the concentration of initial solution (mmol/mL), C_a is the average concentration of the effluents (mmol/mL), V_2 is the volume of solution (mL), and V_3 is the volume of wet resin (mL).

4. Result and discussion

4.1. Characterization of the polymeric adsorbents

The two adsorbents (Amberlite XAD-4 and LS-2) are quite different in the BET surface area, chemical composition, and the pore structures as listed in Table 1. The distribution of pore sizes of the two adsorbents is shown in Fig. 1. LS-2 exhibits a wider distribution (<120 nm, not shown) than XAD-4 (<18 nm) in pore sizes. The micropore (<2 nm) dominates the pore structure of LS-2, while mesopore (2–18 nm) plays the main role in the XAD-4 resin.

After the reaction, the strong band of 671.8 cm^{-1} (chloromethyl group) in LS-2 was weakened, and the bands of about 3420 cm^{-1} (hydroxyl group), 1680 cm^{-1} (carbonyl group), 1360 and 1170 cm^{-1} (sulfonic groups) were strengthened, as shown in the IR spectrum 2, which indicated the existence of other polar groups besides sulfonic groups Fig. 2.

4.2. Static equilibrium adsorption

Equilibrium data concerning the adsorption of the adsorbates from aqueous solutions onto the two adsorbents were presented in Fig. 3(a–d). It is well known that increasing temperature was disadvantageous for a physical adsorption process, and the process has the reversible character [19]. The equilibrium adsorption capacities of aniline and 4-methylaniline on Amberlite XAD-4 decrease with the increase of temperature, and have no differences at the same temperature of 288 K whether it is fallen from 318 K or risen from 275 K, which is the characteristic of physical adsorption process. As for LS-2, the equilibrium adsorption capacities increase with the rise of temperature and the adsorption capacities on LS-2 at 288 K fallen from 318 K are the highest,

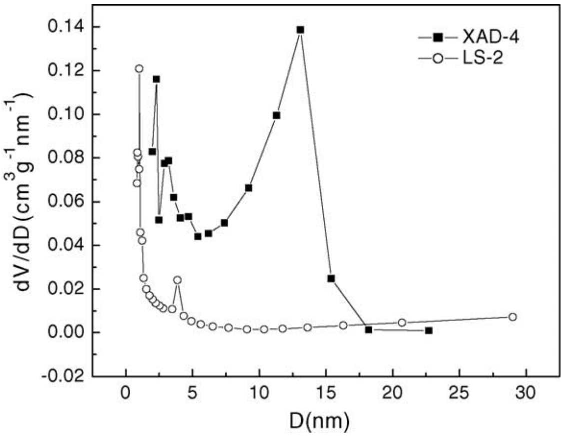


Fig. 1. Plot of pore size distributions vs. pore diameter for Amberlite XAD-4 and LS-2.

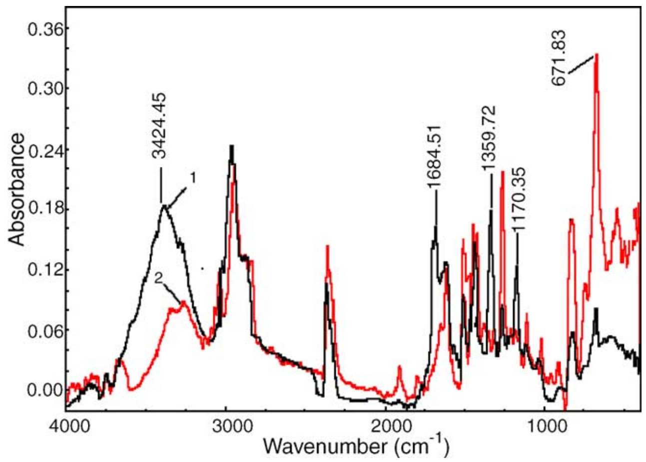


Fig. 2. IR spectra of the chloromethylated copolymer of styrene and divinylbenzene before and after the reaction, 1 is the LS-2 resin and 2 is chloromethylated macroporous copolymer of styrene-divinylbenzene.

which may ascribe to the coexistence of irreversible chemical process and the reversible physical process.

The equilibrium adsorption isotherms of aniline and 4-methylaniline on Amberlite XAD-4 and LS-2 resins at 303 K were shown in Fig. 4(a and b). The adsorbing capacities for aniline and 4-methylanilinethe on the bifunctional polymeric adsorbent LS-2 are significantly higher than those on Amberlite XAD-4, which may be contributed to its high micropore area and sulfonic functional groups on the networks.

Freundlich model was used to fit the equilibrium adsorption data. The model was rearranged and expressed as Eq. (3) [20,21]:

$$\text{Freundlich equation}: \quad \ln Q_\mathrm{e} = \ln K_\mathrm{F} + \frac{1}{n}\ln C_\mathrm{e} \qquad (3)$$

where C_e is the equilibrium concentration (mmol/L), Q_e is the equilibrium adsorption capacity (mmol/g), K_F and n are the characteristic constants.

The correlative parameters of Freundlich isotherm equations at 303 K are listed in Table 3. The Freundlich adsorption model can give a perfect fitting for all the correlative factors $R^2 > 0.99$.

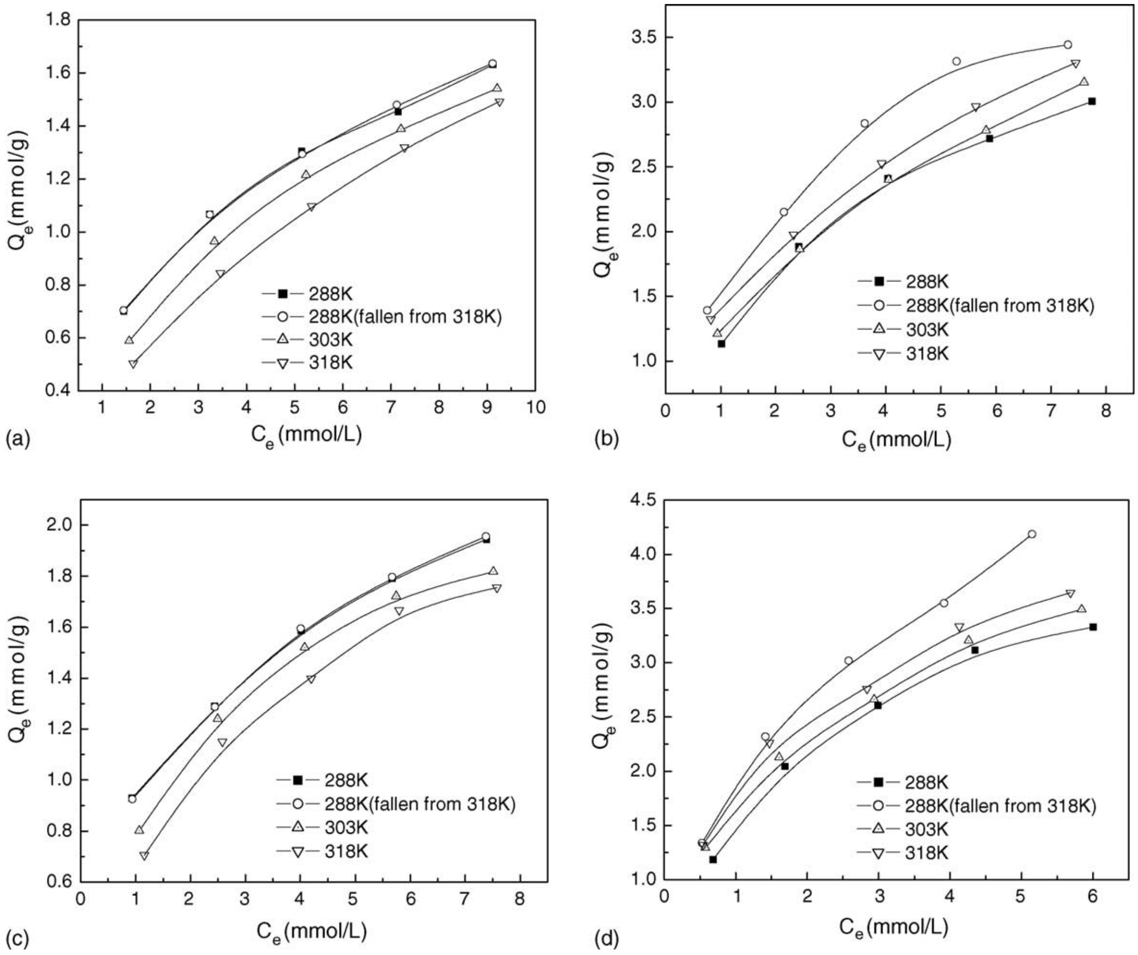


Fig. 3. (a) The equilibrium adsorption isotherms of aniline on Amberlite XAD-4 at different temperature. (b) The equilibrium adsorption isotherms of aniline on LS-2 at different temperature. (c) The equilibrium adsorption isotherms of 4-methylaniline on Amberlite XAD-4 at different temperature. (d) The equilibrium adsorption isotherms of 4-methylaniline on LS-2 at different temperature.

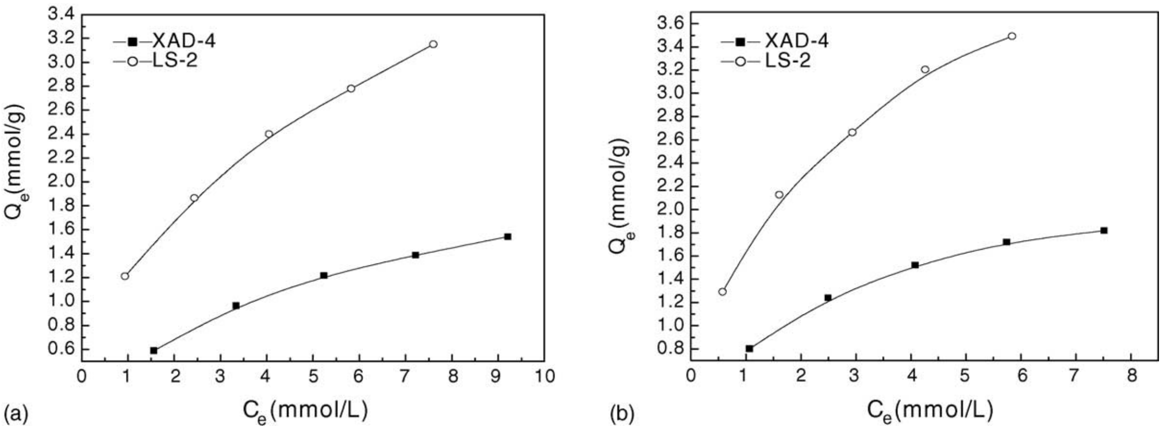


Fig. 4. (a) The equilibrium adsorption isotherms of aniline on Amberlite XAD-4 and LS-2 at 303 K. (b) The equilibrium adsorption isotherms of 4-methylaniline on Amberlite XAD-4 and LS-2 at 303 K.

Table 3
Correlative parameters of aniline and 4-methylaniline on Amberlite XAD-4 and LS-2 resins at 303 K

Adsorbent	Adsorbate	Freundlich parameters			
		Equation	K_F	*n*	R^2
XAD-4	Aniline	$\ln Q_e = -0.736 + 0.542 \ln C_e$	0.479	1.844	0.990
	4-Methylaniline	$\ln Q_e = -0.214 + 0.427 \ln C_e$	0.807	2.341	0.996
LS-2	Aniline	$\ln Q_e = 0.220 + 0.459 \ln C_e$	1.246	2.181	0.999
	4-Methylaniline	$\ln Q_e = 0.515 + 0.447 \ln C_e$	1.673	2.235	0.998

The correlative parameters of Freundlich adsorption isotherm equations for aniline and 4-methylaniline at different temperatures are listed in Table 4, respectively. Based on the Freundlich theory, coefficient K_F is an indication of the adsorbing capacity and R^2 denotes the degrees of deviation from isotherm linearity. According to K_F in Table 4, the obviously higher adsorbing capacities toward aniline and 4-methylaniline on LS-2 can be expected.

The specific surface area of LS-2 is lower than that of Amberlite XAD-4, but the adsorbing capacities for these two adsorbates on LS-2 are higher than those on Amberlite XAD-4 within the temperature range 288–318 K, which further proved that besides specific surface area, adsorption capacity will be effected by several other factors, including adsorbent polarity, active groups and pore structures, and so on.

Although XAD-4 has a high specific area, its micropore area is much lower. In contrast, the micropore area of LS-2 is nearly 50% of total specific surface area (Table 1), which favors a solute–solute interaction for the adsorbates according to the capillary condensation theory. This expression is in good agreement with other reports, which refer that the micropores of resins affect the sorption proceeds via pore filling mechanism [22,23]. Moreover, the networks of LS-2 contain several different groups such as sulfonic groups, carbonyl groups, hydroxyl groups and chloromethyl residues as shown in Fig. 2. These polar groups enhance the surface contact with aqueous solutions. Furthermore, the acidic active groups on LS-2 will interact with the basic amino groups of aniline compounds easily, which is helpful for the adsorption and also is a factor for the increase of adsorption capacities when the temperature increases. So it is quite obvious that

Table 4
Correlative parameters of Freundlich model for aniline and 4-methylaniline on the two resins at different temperatures

Adsorbent	Temperature (K)	Aniline Freundlich parameters			4-Methylaniline Freundlich parameters		
		K_F	*n*	R^2	K_F	*n*	R^2
Amberlite	288[*]	0.606	2.202	0.994	0.948	2.756	0.999
	303	0.479	1.844	0.990	0.807	2.341	0.996
XAD-4	318	0.376	1.587	0.997	0.682	2.028	0.985
	288[*]	1.172	2.078	0.986	1.482	1.946	0.995
LS-2	303	1.246	2.181	0.999	1.673	2.235	0.998
	318	1.422	2.384	0.999	1.784	2.311	0.989

[*] Risen from 275 K.

Table 5a
Thermodynamic values of aniline adsorption on the two adsorbents

Adsorbent	Q_e (mmol/g)	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS (J/mol K)		
			288 K	303 K	318 K	288 K	303 K	318 K
Amberlite XAD-4	0.6	−19.41	−5.27	−4.65	−4.20	−49.10	−48.71	−47.83
	0.8	−14.90				−33.43	−33.83	−33.65
	1.0	−11.41				−21.32	−22.31	−22.67
LS-2	0.6	18.83	−4.98	−5.49	−6.30	82.67	80.26	79.03
	0.8	16.04				72.99	71.06	70.25
	1.0	13.88				65.49	63.93	63.46

the microporous structure and the polar groups of LS-2 are considered to be the predominant factors affecting adsorption capacities.

4.3. Thermodynamics of the adsorption

Estimations of the isosteric adsorption enthalpy change, free energy change, and entropy change were calculated using the well fitting Freundlich equations. The isosteric adsorption enthalpy change can be easily calculated with a derivative Van't Hoff equation [24]:

$$\ln\left(\frac{1}{C_e}\right) = \ln K_0 + \left(-\frac{\Delta H}{RT}\right) \tag{4}$$

where C_e is the equilibrium concentration of solute at the absolute temperature T (mol/L), ΔH is the isosteric enthalpy of adsorption when Q_e is a fixed value (kJ/mol), T is the absolute temperature (K), and R is the gas constant and K_0 is the Van't Hoff equation constant.

C_e was obtained from the Freundlich isotherms at a definite Q_e value (0.6, 0.8 and 1.0 mmol) at different temperatures (288, 303 and 318 K). And ΔH was calculated from the slope of the line plotted by $\ln(1/C_e)$ versus $1/T$ if ΔH is independent of temperature.

The free energy change of adsorption can be calculated using an expression derived from the Gibbs adsorption isotherm, and the following equation was obtained at low solute concentration [25]:

$$\Delta G = -RT\int_0^x q\frac{\mathrm{d}x}{x} \tag{5}$$

where ΔG is the free energy change of adsorption (kJ/mol), q is the number of moles of solute adsorbed per unit mass of adsorbent (mol/g), x is the mole fraction of adsorbed solute in solution.

The use of Freundlich isotherm model would lead to a value of the free energy change per mole of solute adsorbed which is independent of Q_e in the following form:

$$\Delta G = -nRT \tag{6}$$

where n represents the Freundlich exponent.

Entropy change values associated with adsorption can be calculated using previously obtained ΔH and ΔG values by Gibbs–Helmholtz equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7}$$

The thermodynamics values of the two adsorbates on the two adsorbents are summarized in Tables 5a and 5b.

The isosteric adsorption enthalpy change of the two adsorbates on Amberlite XAD-4 are negative and in the range of 10–25 kJ/mol, which indicates a physical adsorption process. This is in good agreement with the above conclusion, that is, the equilibrium adsorption capacities of aniline and 4-methylaniline on Amberlite XAD-4 decrease with the increasing temperature, and have no differences at the same temperature of 288 K fallen from 318 K or risen from 275 K. However, the values of enthalpy change of the two aniline compounds adsorption on LS-2 are positive and in the range of 10–30 kJ/mol. So the processes are endothermic and the values are comparatively low, which suggests the coexistence of physical adsorption and chemical transition. The heat released in the physical adsorption process is lower than the heat needed in the chemical transition process, which results in the endothermic character of the whole adsorption process.

The negative ΔG values indicate all these adsorptions are spontaneous. The absolute ΔG values of adsorption of the

Table 5b
Thermodynamic values of 4-methylaniline adsorption on the two adsorbents

Adsorbent	Q_e (mmol/g)	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS (J/mol K)		
			288 K	303 K	318 K	288 K	303 K	318 K
Amberlite XAD-4	0.6	−25.39	−6.60	−5.90	−5.36	−65.24	−64.32	−62.99
	0.8	−20.06				−46.74	−46.73	−46.23
	1.0	−15.94				−32.43	−33.14	−33.27
LS-2	0.6	19.38	−4.66	−5.63	−6.11	83.47	82.54	80.16
	0.8	16.69				74.13	73.66	71.70
	1.0	14.60				66.88	66.77	65.13

Table 6
The desorption efficiency of different solvents

Adsorbent	Desorption solvent	Desorption efficiency (%)	
		Aniline	4-Methylaniline
XAD-4	Acetone	88.5	88.1
	Acetone:5% hydrochloric acid = 1:1	87.8	86.9
	5% hydrochloric acid	86.4	85.3
LS-2	Acetone	60.6	61.5
	Acetone:5% hydrochloric acid = 1:1	82.4	80.6
	5% hydrochloric acid	87.1	86.4

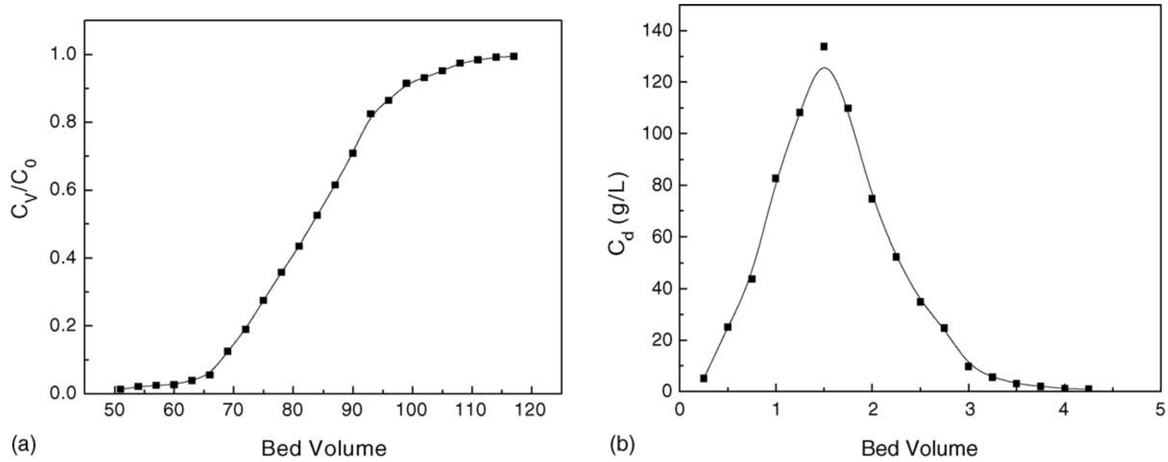


Fig. 5. (a) Adsorption curve of aniline on LS-2 at room temperature. (b) Desorption curve of LS-2 adsorbed aniline at 313 K.

two adsorbates on Amberlite XAD-4 decrease with the increase of temperature, which elucidates the decreasing tendency of adsorption spontaneity and further confirms the physical character of the adsorption. On the contrary, the absolute ΔG values of adsorption of the two adsorbates on LS-2 increase with the increasing temperature, which manifests that rise of temperature is helpful for the adsorptive system. And this confirms the existence of chemical transition.

The negative ΔS values of the two adsorbates adsorption on Amberlite XAD-4 indicate that more ordered arrangement of solute molecules is shaped on the surface of the adsorbent. While the positive ΔS values of the two adsorbates adsorption LS-2 indicate increased randomness at the solid/solution interface during the adsorption of the two adsorbates onto the adsorbent, which may attribute to the water molecules from the chemical transition.

4.4. Comparison of desorption conditions

Different solvents were used to desorb the static equilibrium adsorbents, and the results are shown in Table 6.

The aniline compounds adsorbed on XAD-4 can be desorbed easily with the three different solvents, and all the desorption efficiencies are above 85%, while acetone could desorb only about 60% of adsorbed compounds from LS-2. Once the solvents are acidized, the desorption efficiencies could be improved greatly, which is an additional proof of chemical transition when aniline or 4-methylaniline is adsorbed on LS-2.

4.5. Dynamic adsorption and desorption

Due to the satisfactory adsorption capacity for the aniline compounds on LS-2 in our research, it is hopeful for LS-2 to be developed as a polymeric adsorbent for the removal of organic pollutants from drinking water and for the recovery of organics from wastewater. So it is necessary to test the dynamic adsorption and desorption. The results of mini-column dynamic adsorption of aniline by LS-2 are shown in Fig. 5(a), where C_V is the concentration at different bed volume of the effluent (M). The breakthrough adsorption capacity and the total adsorption capacity, calculated by Eq. (2), were 0.96 and 1.24 mmol/mL resin, respectively.

Considering the results of desorption with different solvents, 5% hydrochloric acid was used for desorbing aniline from LS-2. At the flow rate of 1.5 BV/h, nearly 100% regeneration efficiency for the adsorbent was achieved. Fig. 5(b) shows the desorption curve.

5. Conclusions

A new bifunctional polymeric adsorbent (LS-2) for adsorbing aniline and 4-methylaniline from their aqueous solutions was synthesized. The equilibrium adsorption capacities for the two aniline compounds on LS-2 are higher than those on XAD-4, which attributes to its microporous structure and the polar functional groups. The Freundlich isotherm model can perfectly fit the experimental data in the temperature range of 288–318 K.

The results of static equilibrium adsorption manifest that the adsorption of the two aniline compounds on Amberlite XAD-4 is an exothermic physical process, while the adsorption of the adsorbates on LS-2 is a coexistence process of physical adsorption and chemical transition, which is further confirmed by the thermodynamics values.

The dynamic adsorption studies towards aniline by LS-2 show the breakthrough capacity and the total capacities are 0.96 and 1.24 mmol/mL resin, respectively, which further elucidates its higher adsorbing capacity, and the resin can be desorbed easily by 5% hydrochloric acid.

Acknowledgements

The work was financially supported by the Science & Technology Council, Jiangsu Province, PR China (Grant Code GB2003030), Natural Science Foundation of Jiangsu Province, PR China (Grant Code 2004088), Major Projects of Environment Protection Office of Jiangsu Province PR China (Grant Code 2004001) and State Key Laboratory of Pollution Control and Resources Reuse, PR China (PCRRF 05007). We gratefully acknowledge the analytical center at Changzhou Petro-Chemical College for the measurement of surface area and pore diameter, and the analytical center at Yancheng Teachers College for the analysis of IR spectra.

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