Enhanced removal of *p*-chloroaniline from aqueous solution by a carboxylated polymeric sorbent

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Abstract

In the present study a carboxylated styrene-divinylbenzene (St-DVB) polymeric sorbent (CSPS) was prepared for enhanced removal of *p*-chloroaniline from aqueous solution. A commercial styrene-divinylbenzene polymeric sorbent Amberlite XAD-4 was selected as the reference sorbent to evaluate the performance of CSPS. Characterization of CSPS was determined by infrared spectroscopy and pore size distribution. A *p*-chloroaniline sorption enhancement on CSPS at capacity about twice of Amberlite XAD-4 was observed, which was mainly attributed to the carboxyl group added on the polymeric matrix. Different pH-dependent sorption property of *p*-chloroaniline onto XAD-4 and CSPS was observed partly due to the role of carboxyl group. Sorption isotherm of *p*-chloroaniline on CSPS could be represented by Freundlich model reasonably, and that on XAD-4 was more suitable for Langmuir model. Kinetic studies demonstrated that the uptake of *p*-chloroaniline on CSPS and XAD-4 followed the pseudo-second order model. Moreover, breakthrough curves on CSPS further demonstrated its better performance towards *p*-chloroaniline removal from aqueous solution. Complete regeneration of the spent sorbent CSPS was achieved by dilute hydrochloric acid for its repeated use, implying its potential application in associated chemical wastewater treatments.
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1. Introduction

Water pollution by chemical wastewater has been of great concern in many developing countries such as India and China [1]. Accordingly, many practical processes, such as adsorption by activated carbon [2,3] and low-cost sorbents [4–6] have been developed to treat chemical wastewater before discharging into the receiving water. However, poor mechanical strength and demanding regeneration of activated carbon hinders its wider application. Low-cost sorbents based on red mud and other industrial wastes [4–6] seems more attractive in the specific field, but many valuable organic compounds cannot be readily recovered for further use after sorption. In recent years polymeric sorbents have been emerging as a potential alternative due to its better mechanical strength, feasible regeneration under mild conditions, and potential recovery of chemical pollutants by further treatment of the concentrated eluate, the typical ones being of styrene-divinylbenzene (St-DVB) matrix [7,8]. In general, many hydrophobic organic pollutants can be readily removed from wastewater by the St-DVB polymeric sorbents [9], which mainly results from van der Waals interaction between the solute and sorbent phase [10]. However, many hydrophilic or water-soluble organic compounds cannot be readily removed by those sorbents partly due to the strong solute–water interaction [11], and how to improve the adsorption performance of the polymeric sorbents is of particular significance.

In review of literatures, chemical modification of polymeric matrix is a potential pathway to enhance sorption of the hydrophilic compounds from aqueous solution [12,13]. For example, the aminated polymeric sorbents exhibited better performance for removal of acidic compounds such as phenols, aromatic carboxylic acids and sulfuric acids [14]. However, little
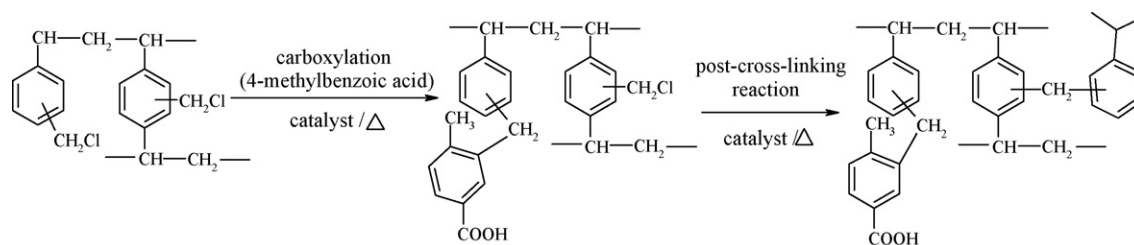
Scheme 1. Preparation procedures of the carboxylated polymeric sorbent CSPS.

was available in open literature on how to enhance sorption of amine compounds from aqueous solution, among which aromatic amines should gain more attention because most of them are ubiquitous in chemical wastewater and listed as priority pollutants in aquatic systems [15,16].

In the current study we aimed at preparing a new polymeric sorbent to gain sorption enhancement of aromatic amines. *p*-Chloroaniline was chosen as a target solute because it was widely used as a chemical intermediates for manufacturing of dyes, pharmaceuticals and other compounds. Moreover, *p*-chloroaniline is a well-known priority pollutant in terms of its hematoxicity, splenotoxicity, hepatoxicity, and nephrotoxicity [17,18], and its presence in water even at a low level (mg/l) would be harmful to aquatic life and human health. This was achieved by carboxylation of a St-DVB polymeric matrix followed by post-cross-linking of the carboxylated derivative. Batch sorption runs including isotherm, kinetics and column sorption tests were performed to evaluate the new sorbents.

2. Materials and methods

2.1. Materials

Zinc chloride, 4-methylbenzoic acid, ethanol, 2,4-dichlorobenzene, nitrobenzene, *p*-chloroaniline (A.R.) were purchased from Shanghai Chemical Reagent Plant (Shanghai, China) and used without further purification. *p*-Chloroaniline was dissolved in double-distilled water for batch sorption runs. A macroporous St-DVB sorbent Amberlite XAD-4 was obtained from Rohm–Haas (Philadelphia, PA, USA). The chloromethylated St-DVB copolymer (denoted CSC, the chloro content in mass is 17.3%) beads were kindly provided by Langfang Resin Co. (Hebei province, China).

2.2. Preparation of the new sorbent

As shown in Scheme 1, the new sorbent was prepared by carboxylation of the CSC particles followed by post-cross-linking of the carboxylated derivatives. First, 30.0 g of CSC beads were swollen overnight by 250.0 g of *o*-dichlorobenzene together with 28.0 g of 4-methylbenzoic acid in a 500 ml flask. Under a mild mechanical stirring (at about 60 rpm), 6.0 g of anhydrous zinc chloride was gradually added as catalyst into the flask at 298 K and the reaction lasted about 12 h. The reaction mixture was then filtered to remove the liquid moiety and the rest solid particles were extracted with ethanol for 4 h in a Soxlet apparatus. The

carboxylated particles (designated CCSC) were obtained for the following post-cross-linking reaction.

In the post-cross-linking procedure 30.0 g of CCSC particles (the chlorine percent content decreased to 12.6%) was swollen overnight in 100.0 g of nitrobenzene in a flask. Under mechanical stirring, 6.0 g of anhydrous zinc chloride was gradually added into the flask at 298 K, followed by an increase of the ambient temperature from 298 to 405 K within 1 h. After 8 h of the post-cross-linking reaction at 405 K, the mixture was treated by filtering and extracting in the similar manner for CCSC particles and we got the new sorbent CSPS.

2.3. Batch sorption runs

Batch sorption experiments were performed as follows: 0.100 g of each sorbent was introduced into a 250 ml conical flask containing 100 ml of the *p*-chloroaniline solution ranging from 100 to 500 mg l^{-1}. The flasks were sealed and shaken in a G25 model incubator shaker (New Brunswick Scientific Co. Inc.) at a preset temperature under 120 rpm for 24 h to ensure sorption equilibrium. The *p*-chloroaniline uptake was calculated by conducting a mass balance before and after adsorption using the following equation:

$$q_e = \frac{V_1(C_0 - C_e)}{W} \tag{1}$$

where V_1 (l) is the volume of solution and W (g) is the mass of dry sorbent; C_0 and C_e (mg l^{-1}) denote the initial and equilibrium concentration of *p*-chloroaniline in aqueous solution. As for the kinetic study, the amount of sorbent and solution was determined as 0.50 g and 500 ml, respectively, and 0.5 ml solution at various time intervals was sampled from the flasks to determine sorption kinetics.

2.4. Fixed-bed sorption

Column experiments were carried out with a glass column (12 mm diameter and 230 mm length) equipped with a water bath to maintain a constant temperature. A HL-2B pump (China) was used to assure a constant flow rate. All column runs were performed under the same hydrodynamic conditions: the superficial liquid velocity (SLV) and the empty bed contact time (EBCT) were identical and equal to 1.0 m/h and 4 min, respectively.

Concentrations of *p*-chloroaniline were determined spectrophotometrically by using a Helious Betra UV–vis spectrometer (Unicam Co., UK) at wavelengths of 238 nm.

Table 1
Characteristics of the polymeric sorbents in the present study

Sorbent	XAD-4	CSPS
Matrix	Polystyrene	
Polarity	Nonpolar	Moderate
BET surface area ($m^2\,g^{-1}$)	908	1000
Micropore surface area ($m^2\,g^{-1}$)	115	587
Micropore volume ($cm^3\,g^{-1}$)	0.033	0.27
Average pore diameter (nm)	5.64	2.31
Functional group	None	–COOH
Amount of functional group ($mmol\,g^{-1}$)	0	1.32

3. Results and discussion

3.1. Sorbent characterization

Table 1 listed some characteristics of XAD-4 and CSPS sorbents. No significant difference of both sorbents in the BET surface area was observed, however, micropore surface area and micropore volume of CSPS was much larger than that of XAD-4. It could also be concluded by comparison with the pore size distribution (PSD) of both sorbents (in supporting materials). The average pore diameter of the XAD-4 was almost twice of CSPS. The presence of carboxyl groups on CSPS was further proved by the strong band at 3446, 1607.5 cm^{-1} in the IR spectrum (in supporting materials). The strong absorbance band of 673.9 cm^{-1} (chloromethyl group) in CSPS was weaker than CSC because of the decrease of chlorine content after carboxylation, and the bands of about 3446 (hydroxyl group), 1607.5 (carbonyl group), 1510.5 and 1450.2 cm^{-1} (carboxyl ester group) were strengthened accordingly, which further testified the existence of carboxyl groups.

3.2. Effect of solution pH

Fig. 1 illustrated the effect of solution pH on *p*-chloroaniline sorption onto XAD-4 and CSPS at 298 K. Maximum sorption capacities of both sorbents was observed at neutral pH (about 6), but they exhibited different pH-dependent sorption properties. Sorption capacity of XAD-4 approached to a plateau when the
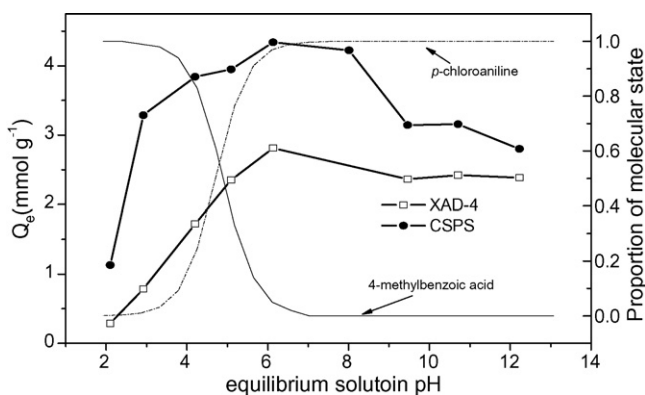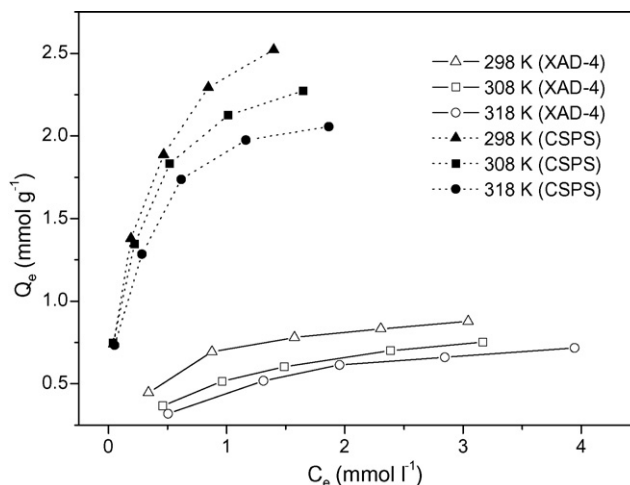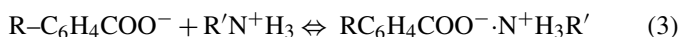

Fig. 2. Sorption isotherms of *p*-chloroaniline onto XAD-4 and CSPS at different temperatures.

solution pH values were larger than 6, and decreased as the solution pH decreased. It was consistent with the protonation curve of *p*-chloroaniline as shown in Fig. 1. In fact, *p*-chloroaniline sorption onto XAD-4 was driven mainly by van der Waals interaction and the protonated *p*-chloroaniline cannot be effectively loaded on the surface of XAD-4. On the other side, sorption capacity of CSPS decreased whether solution pH was less or larger than 6. In general, effect of carboxyl group on amine sorption can be inferred from the following equation [11,19] (Figs. 2 and 3):

$$R–C_6H_4COOH + R'NH_2 \Leftrightarrow RC_6H_4COOH \cdot NH_2R' \qquad (2)$$

$$R–C_6H_4COO^- + R'N^+H_3 \Leftrightarrow RC_6H_4COO^- \cdot N^+H_3R' \qquad (3)$$

where R represents the polymeric matrix, and R' is the *p*-chlorobenzyl group. Effective sorption of *p*-chloroaniline can occur simultaneously on the introduced carboxyl group by formation of acid–base complex [20] or electrostatic interaction [21]. Effective interaction depicted in Eq. (2) required the acidic and basic compounds both at molecular state while that in Eq. (3) required both at ionization state. In fact both requirement

Fig. 1. Correlation of solution pH with sorption capacity in equilibrium (Q_e) of XAD-4 and CPCS (left) and the proportion of the molecular state of *p*-chloroaniline and 4-methylbenzoic acid (right).
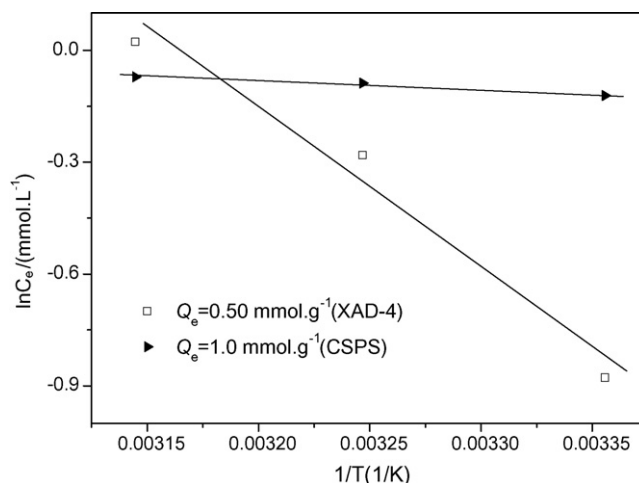

Fig. 3. Determination of isosteric enthalpy of *p*-chloroaniline sorption on sorbent CSPS and XAD-4.

could not be met simultaneously and a maximum sorption would be reached under a specific condition As illustrated in Fig. 1, solution pH larger or less than the optimal one (around 6) was unfavorable for one or both interactions and therefore resulted in a decrease of sorption capacity. Anyway, different pH-dependent sorption onto CSPS by comparison with XAD-4 indicated that the carboxyl group introduced on the polymeric sorbent takes an important role in p-chloroaniline removal from aqueous solution.

3.3. Sorption isotherm

Sorption isotherms of PCA on XAD-4 and CSPS at 298 K are shown in Fig. 2. It is very clear that sorption capacity of CSPS is much larger than the typical polystyrene sorbent XAD-4. The semi-empirical Freundlich equation and Langmuir equation [22] were employed to describe the sorption isotherms of p-chloroaniline on CSPS and XAD-4:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m C_e} + \frac{1}{Q_m} \tag{5}$$

where K_F and n is the Freundlich constants for a heterogeneous sorbent, Q_m (mmol g^{-1}) is the maximal sorption capacity, and K_L (l mmol^{-1}) is a binding constant. The constant K_F is always taken as a relative indicator of sorption capacity, n is related to the magnitude of the sorption driving force and to the sorbent site energy distribution. All the related parameter values were listed in Table 2. It can be seen that the Langmuir equation fit the sorption on XAD-4 well while the Freundlich equation is more representative for that on CSPS sorbent, which depends upon their different sorption mechanism. In general, the Langmuir equation originates from the ideal sorption model onto a homogeneous sorbent, an example being XAD-4 of a uniform styrene-divinylbenzene matrix and pore structure. On the contrary, CSPS presented a heterogeneous surface property resulting from the uneven functional group and its pore size distribution. Another observation is that sorption on both sorbents is an exothermic process inferred from the effect of ambient temperature on sorption. Detailed thermodynamic properties will be discussed in the forthcoming section.

3.4. Thermodynamic aspects

The free energy change for sorption process is given by

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

At low solute concentration, $\Delta G_{overall}$ can be determined as follows [23]:

$$\Delta G = \frac{-RT \int_0^{C_e} Q(C_e) d \ln C_e}{Q(C_e)} \tag{7}$$

where x is the mole fraction of the sorbate in the solution. When the sorption capacity Q (C_e) follows the Freundlich equation, incorporating Eq. (4) into Eq. (7) yields [11]:

$$\Delta G = -nRT \tag{8}$$

On the other side, when Q (C_e) follows the Langmuir equation, we can get the following equation by incorporating Eq. (5) into Eq. (7):

$$\Delta G = \frac{-RT(1 + K_L C_e)}{K_L C_e}[\ln(1 + K_L C_e)|_0^{C_e}] \tag{9}$$

If isosteric sorption enthalpy change (ΔH) can be assumed to be approximately constant, the van't Hoff equation gives:

$$\frac{d(\ln C_e)}{d(1/T)} = \frac{\Delta H}{R} \tag{10}$$

where T is the absolute temperature in K. The enthalpy change can be computed from the slope of the $\ln C_e$ versus $1/T$ plot (Fig. 3). Previous study indicates that enthalpic change thus determined agrees well with that obtained independently using microcalorimetric technique [24]. The free energy change can be obtained from Eqs. (8) and (9), and the entropic contribution can be subsequently determined according to Eq. (6). It should be noteworthy that different Q_e values selected in Table 3 mainly lay on their distinct sorption capacity onto both sorbents. However, the thermodynamic results listed there could still be taken for comparison because XAD-4 could be assumed to be a homogenous sorbent, implying its capacity-independent enthalpy changes. Higher absolute enthalpy change of p-chloroaniline sorption onto XAD-4 than CSPS was possibly attributed to their different sorption mechanisms. Generally, part sorption of p-chloroaniline onto CSPS driven by electrostatic interaction was an endothermic process [25,26], which

Table 2
Isotherm parameters of p-chloroaniline sorption onto XAD-4 and CSPS

Sorbent	T (K)	Freundlich model			Langmiur model		
		K_F	n	R^2	K_L (l mmol^{-1})	Q_m (mmol g^{-1})	R^2
XAD-4	298	0.85	2.49	0.967	2.43	0.995	0.998
	308	0.63	1.59	0.873	1.72	0.885	0.997
	318	0.49	2.02	0.996	1.31	0.873	0.999
CSPS	298	2.34	3.02	0.986	2.38	2.38	0.980
	308	2.06	3.57	0.978	2.11	2.11	0.969
	318	1.83	3.70	0.976	1.96	1.96	0.969

Table 3
Thermodynamic parameters of p-chloroaniline sorption onto XAD-4 and CSPS under different conditions

Sorbent	Q_e (mmol g^{-1})	T (K)	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
CSPS	1.5	298	−4.59	−7.53	9.87
	1.5	308		−9.14	14.8
	1.5	318		−10.5	14.3
XAD-4	0.5	298	−35.6	−3.50	−108
	0.5	308		−2.56	−103
	0.5	318		−2.15	−100

required absorption of heat and resulted in a lower value of enthalpy change. Similarly, the positive entropy change value of CSPS sorption was also possibly related to the sorption driven by electrostatic interaction, where the p-chloroanilne and the functional group on the polymeric matrix may be partly dehydrated before the effective sorption occurs. Additionally, the free energy changes for XAD-4 decreased but that for CSPS increased as the ambient temperature increased, which might also be related to their different sorption mechanism.

3.5. Sorption kinetics

The influence of contact time on p-chloroaniline sorption by XAD-4 and CSPS were illustrated in Fig. 4. Sorption equilibrium of PCA on XAD-4 was achieved in a shorter time than CSPS, depending upon the larger average pore diameter of XAD-4 than CSPS (in Table 1). Here the widely used pseudo-first order and pseudo-second order model were employed to fit the experimental data

$$\text{Pseudo-first order model}: \quad \ln\frac{Q_e}{Q_e - Q_t} = k_1 t \qquad (11)$$

$$\text{Pseudo-second order model}: \quad \frac{1}{Q_t} = \frac{1}{k_2 Q_e^2 t} + \frac{1}{Q_e} \qquad (12)$$

where Q_e is the equilibrium sorption capacity (mmol g^{-1}), Q_t is the sorption capacity (mmol g^{-1}) at the contact time t (min), k_1 is
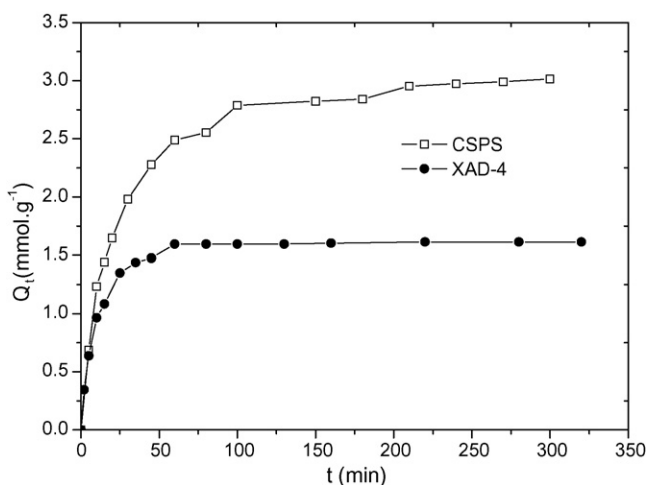
Table 4
Kinetic parameters of p-chloroaniline sorption onto CSPS and XAD-4 for the pseudo-first order model and the pseudo-second order model

Sorbents	Pseudo-first order model		Pseudo-second order model	
	k_1 (min^{-1})	R^2	k_2 (g mmol^{-1} min^{-1})	R^2
XAD-4	0.0159	0.731	0.0740	0.998
CSPS	0.0107	0.970	0.0184	0.995

the pseudo-first order rate constant(min^{-1}), and k_2 is the pseudo-second order rate constant(g mmol^{-1} min^{-1}). Results in Table 4 indicated that the pseudo-second order model could represent the PCA sorption kinetics onto CSPS and XAD-4 better than the pseudo-first order model. The K_2 value of XAD-4 four times than that of CSPS was also consistent with their average pore size order.

3.6. Column sorption tests

It is necessary to test the column sorption and desorption behavior of PCA on CSPS before its application. Fig. 5 depicted a complete effluent history of a fixed-bed column packed with either XAD-4 or CSPS for a feeding solution containing 500 mg l^{-1} PCA at pH 6.0. Earlier breakthrough occurred expectedly for XAD-4 than CSPS demonstrated the sorption enhancement of p-chloroaniline onto the carboxylated sorbent, which is consistent with their different sorption behaviors in batch runs. After column sorption both spent sorbents
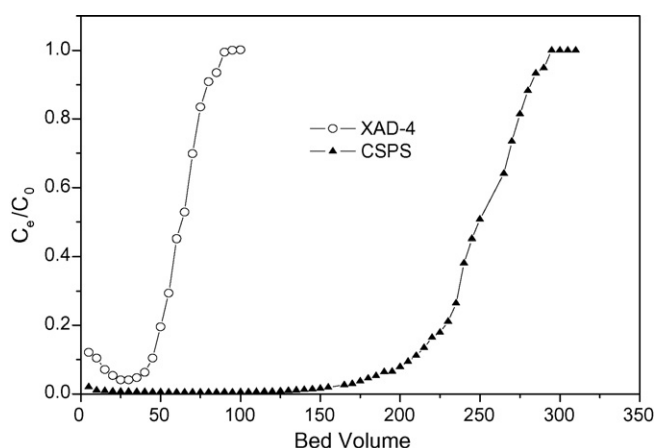

Fig. 4. Effect of contact time on p-chloroaniline sorption onto CSPS and XAD-4 at 298 K.

Fig. 5. Breakthrough curves of p-chloroaniline on XAD-4 and CSPS at 298 K.
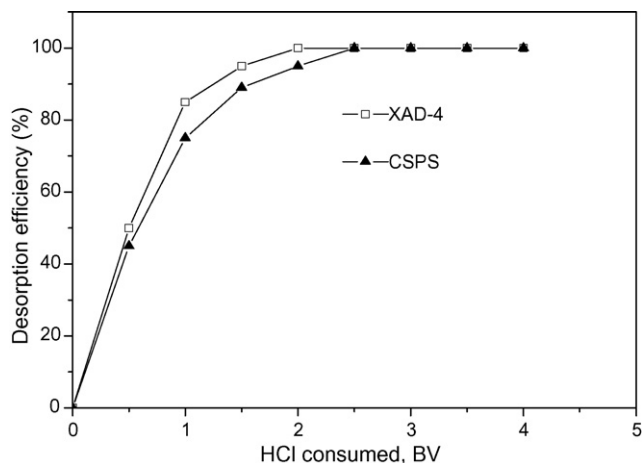
Fig. 6. Desorption curves of the spent XAD-4 and CSPS loaded with *p*-chloroaniline.

were subjected to a separate elution using 1 bed volume (BV) of hydrochloric acid (2 M) followed by 1.5 BV of deionized water at 333 K. Similarly to XAD-4, an entire elution efficiency of more than 99% indicated that the sorbent CSPS could be employed for repeated use after regeneration (Fig. 6). The satisfactory sorption and regeneration behavior of CSPS promoted us to believe it is a potential candidate for treatment of chemical wastewater containing aniline compounds.

4. Conclusion

A new carboxylated polymeric sorbent (denoted CSPS) was prepared for enhanced removal of *p*-chloroaniline from aqueous phase. *p*-Chloroaniline sorption onto CSPS was a pH-dependent process and the optimal solution pH is around 6. The carboxyl group introduced on the polymeric matrix takes a positive role in *p*-chloroaniline sorption enhancement by comparison with a typical polymeric sorbent XAD-4. Sorption isotherms of *p*-chloroaniline onto CSPS followed Freundlich model well and a satisfactory sorption kinetic property of the new sorbent was observed, which could be represented by the pseudo-second order model. Column test results suggested that sorption enhancement of *p*-chloroaniline on CSPS was validated by comparison with a typical polystyrene sorbent Amberlite XAD-4. The spent CSPS beads could be readily regenerated by dilute hydrochloride solution for repeated use. All the above results demonstrated that CSPS is a potential candidate for *p*-chloroaniline removal from industrial wastewater.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2006.09.052.

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