Adsorptive removal of phenol from aqueous phase by using a porous acrylic ester polymer

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Abstract

The removal of phenol from aqueous solution was examined by using a porous acrylic ester polymer (Amberlite XAD-7) as an adsorbent. Favorable phenol adsorption was observed at acidic solution pH and further increase of solution pH results in a marked decrease of adsorption capacity, and the coexisting inorganic salt NaCl exerts positive effect on the adsorption process. Adsorption isotherms of phenol were linearly correlated and found to be well represented by either the Langmuir or Freundlich isotherm model. Thermodynamic parameters such as changes in the enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) indicate that phenol adsorption onto XAD-7 is an exothermic and spontaneous process in nature, and lower ambient temperature results in more favorable adsorption. Kinetic experiments at different initial solute concentrations were investigated and the pseudo-second-order kinetic model was successfully represented the kinetic data. Additionally, the column adsorption result showed that a complete removal of phenol from aqueous phase can be achieved by XAD-7 beads and the exhausted adsorbent was amenable to an entire regeneration by using ethanol as the regenerant. More interestingly, relatively more volume of hot water in place of ethanol can also achieve a similar result for repeated use of the adsorbent.
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1. Introduction

Phenolic compounds which are generated by petroleum and petrochemical, coal conversion, and phenol-producing industries, are common contaminants in wastewater and suspected as toxic and carcinogenic. Therefore, phenol and phenolic compounds were listed as priority pollutants by the EPA of the United States and other countries [1]. Accordingly, various technical processes such as oxidation, biodegradation, solvent extraction, incineration, reverse osmosis and adsorption have been proposed to remove phenolic compounds from contaminated waters, among which adsorption is one of the most effective techniques in either laboratory or industrial scale. As a widely used adsorbent, activated carbon always exhibits satisfactory performance for phenol removal [2–4], however, its wider application is restricted due to the high operation costs and relatively poor mechanical strength. In recent years, considerable attention has also been devoted to the study involving different types of low-cost materials [5–9].

More recently, polymeric adsorbents have attracted increasing interest for removal of phenolic compounds from industrial effluents [10–12]. Their excellent performances for phenol removal are tightly associated with their high capacity, satisfactory mechanical strength and feasible regeneration under mild conditions [13,14], the most widely used ones being polystyrene adsorbent such as Amberlite XAD-4, CHA-101 and NDA-701 [10–12]. In China these polymeric adsorbents have been widely used in industrial settings for removal and even recovery of organic pollutants including phenolic compounds from chemical effluents [10–12]. As a family of polymeric adsorbents, acrylic ester polymer has been demonstrated for effective removal of phenolic compounds from the organic mixtures mainly through the hydrogen bonding interaction between the hydroxyl group of phenolic compounds and the carboxyl group fixed in the

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matrix of the polymeric adsorbent [15,17]. However, we have little knowledge of any studies involving the removal of phenolic compounds from aqueous phase by using an acrylic ester sorbent as adsorbent [18].

In the current study, batch and column adsorption tests were performed to elucidate the behavior and evaluate the feasibility of phenol removal from aqueous solution onto an acrylic ester polymer (Amberlite XAD-7). Effect of solution pH, ionic strength and temperature, isotherms and kinetics were included in the study as well as column adsorption and regeneration tests.

2. Experimental

2.1. Materials

The porous acrylic ester polymer (Amberlite XAD-7) was purchased from Rohm & Haas Co. Ltd. (USA) and sieved at 0.4–1.0 mm for further study. Other chemicals such as phenol and NaCl (all in A.R. grade) were provided by Shanghai Chemical Reagent Station (Shanghai, China) and used without further purification. The adsorbent beads were conditioned by extracting with ethanol for 8 h in a Soxhlet apparatus and desiccated in vacuum at 325 K for 24 h.

2.2. Batch experiments

Batch adsorption tests were carried out in 250-mL glass bottles. To start the experiment, 0.100 g of polymeric beads was introduced to a 100-mL solution containing a known phenol concentration. The flask was then transferred to a G25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) and shaken under 200 rpm for 24 h at desired temperature to ensure that the adsorption process reached equilibrium. HCl or NaOH solution (8% in mass) was employed for pH adjustment and NaCl was used to adjust the ionic strength of solution when necessary. A 0.5 mL aliquot of solution was sampled from the flasks at various time intervals to determine adsorption kinetics. The equilibrium solid-phase concentration of the adsorbate, q_e, was quantified based on a mass balance of the solute between the two phases.

2.3. Column adsorption runs

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. 4.0 g of XAD-7 beads (about 12 mL in wet volume) were packed with the column for the specific purpose. A Lange-580 pump (China) was used to ensure a constant flow rate. The column adsorption run was performed under the hydrodynamic conditions: the superficial liquid velocity (SLV) and the empty bed contact time (EBCT) were equal to 0.50 m/h and 30 min, respectively.

2.4. Analysis

Phenol content in aqueous solution was determined by using a Helious Betra UV-VIS spectrophotometer (UK) at the wave-
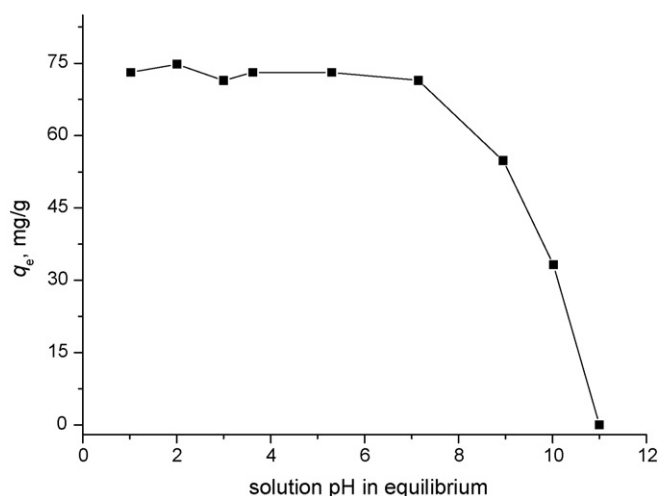

Fig. 1. Effect of solution pH on the phenol uptake onto XAD-7 at 298 K (0.100 g of XAD-7 was added into 100-mL solution with initial phenol concentration of 1000 mg/L).

length of 271 nm. Characterization of the polymeric adsorbents was performed by nitrogen adsorption on an ASAP-2010C Micromeritics Instrument (Micromeritics Instrument, Norcros, USA). Elemental analysis of the adsorbent was conducted by using a Perkin-Elmer 240C Elemental Analytical Instrument (Wellesley, MA, USA).

3. Results and discussion

3.1. Characterization of the acrylic ester polymer

The main characteristics of the acrylic ester polymer (Amberlite XAD-7) are listed in Table 1. Unlike the widely used polystyrene-divinylbenzene adsorbents such as Amberlite XAD-4 of nonpolar nature, the ester groups covalently bound on the polymeric matrix of Amberlite XAD-7 are expected to improve the hydrophilicity of the inner surface of the adsorbent, which avoid the prewetting process before adsorption from aqueous solution [19]. In addition, taken into account the small size of phenol molecule (0.57 nm × 0.42 nm × 0.02 nm) [20], its relatively high BET surface area and pore width are expected to favor the phenol adsorption from aqueous solution, as proved by the batch and column test results below.

3.2. Effect of solution pH

The effect of solution pH on phenol removal by XAD-7 was examined and the results are presented in Fig. 1. In general the phenol uptake onto XAD-7 keeps constant under acidic pH conditions and descends dramatically when solution pH turns to alkaline. Note that the pK_a value of phenol is 9.89 at 298 K [21], the pH-dependent trend could be explained by the fact that only the phenol molecules adsorb effectively onto the acrylic ester polymer through van der Waals interaction, while the phenolate anions do not due to their hydrophilic nature. Previous studies demonstrated that selective separation of phenolic compounds from their hexane solution can be achieved

Table 1
Salient properties of an acrylic ester polymer XAD-7

Matrix structure [15]	BET surface area (m² g⁻¹)	Micropore area (m² g⁻¹)	Pore volume (cm³ g⁻¹)	Average pore diameter (nm)	Oxygen content (%)	Particle size (mm)
	550	73	0.98	5.7	30.4	0.4–1.0

onto Amberlite XAD-7 primarily through the intermolecular hydrogen bond formed between the phenolic hydroxyl group and the carbonyl group on the polymeric matrix [15,16]. Such specific interaction may play a positive role in phenol adsorption from aqueous solution [22], however, it will be effectively weakened in aqueous solution due to the competitive effect of water [17].

3.3. Effect of ionic strength

The effect of ionic strength on phenol adsorption onto XAD-7 is shown in Fig. 2, where NaCl was used to control the ionic strength in solution. The phenol uptake was found to gradually increase, which can be explained by the so-called *salting-out* effect [23]. Turner and Rawling [23] have demonstrated that aqueous solubility of neutral organic compounds generally displays an inverse dependency on ionic strength, which is generally favorable for adsorption. In case of adsorption of organic solutes from aqueous solutions onto polymeric or other adsorbents, the coexisting salts in solution always play a positive role in adsorption capacity [24].

3.4. Adsorption dynamics

Adsorption dynamics of phenol by the acrylic ester adsorbent was investigated at different initial solute concentrations and the results are described in Fig. 3. A fast adsorption kinetics was observed and the adsorption equilibrium can even be reached within the contact time of only about 30 min, while that for other polymeric adsorbents such as Amberlite XAD-4 or ZCH-101 needs several hours [20]. Both pseudo-first-order and pseudo-second-order kinetic models were used to correlate the adsorption data [25,26]

$$\log\left(1 - \frac{q_t}{q_e}\right) = -\frac{k_1}{2.303}t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{2}$$

where q_t is the amount adsorbed at time t, k_1 and k_2 are the kinetic parameters to be determined. The kinetic parameters are determined and listed in Table 2. Higher correlation coefficients of the pseudo-second-order model and the calculated q_e values close to the experimental data indicated that phenol adsorption onto XAD-7 can be approximated more favorably by the pseudo-second-order model than the pseudo-first-order
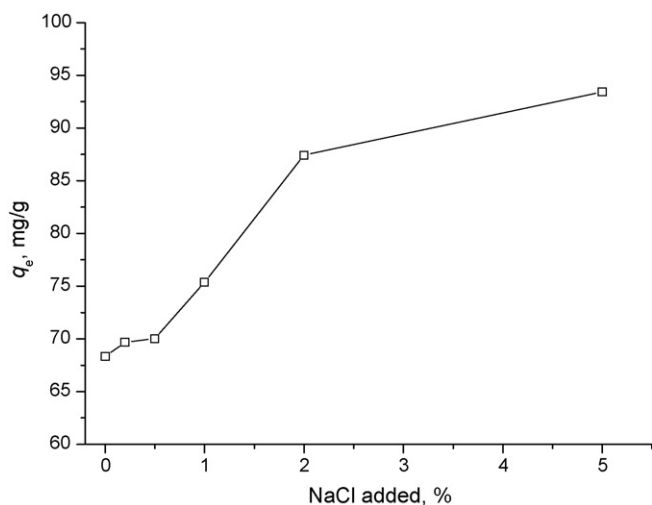

Fig. 2. Effect of ionic strength (NaCl) on phenol adsorption onto XAD-7 particles at 298 K (0.100 g of XAD-7 was introduced into 100-mL solution with initial phenol concentration of 1000 mg/L and varying content of NaCl).
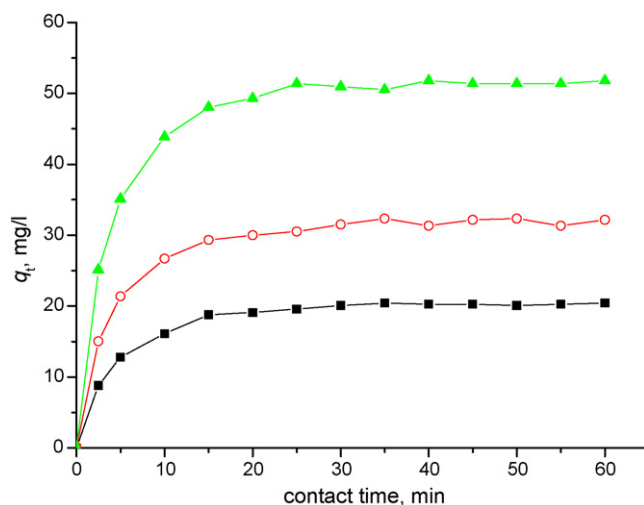

Fig. 3. Phenol adsorption kinetics onto XAD-7 at different initial phenol concentrations and 298 K (0.200 g of adsorbent was added into 500-mL solution, initial phenol concentrations: (■), 200 mg/L; (○), 400 mg/L and (▲), 800 mg/L).

Table 2
Kinetics parameters calculated for phenol adsorption on XAD-7 at 298 K

Initial Concentration (mg/L)	k_p (mg/g min$^{1/2}$)	R^2	Pseudo-first-order			Pseudo-second-order		
			k_1 (min^{-1})	R^2	k_2 ($\times 10^{-2}$ g/mg min)	R^2	q_e (mg/g)	
							Calculated	Experimental
200	5.1	0.983	0.266	0.970	1.63	0.999	21.5	20.5
400	8.3	0.987	0.210	0.902	1.19	0.999	33.6	32.5
800	14.7	0.991	0.388	0.957	0.86	1.000	53.8	51.8

one. Similar results were reported elsewhere on adsorption of phenolic compounds onto other polymeric adsorbents [27]. Additionally, though initial phenol concentration poses a negligible effect on the equilibrium time, the second-order rate constants decrease with increasing initial concentration. Similar results were also reported elsewhere for adsorption of dyes onto sepiolite [28] or mesoporous hybrid xerogel [29].

Considering the pseudo-second-order model cannot identify the diffusion mechanism, intraparticle diffusion model based on the theory proposed by Weber and Morris [30] was then tested as:

$$q_t = k_p t^{1/2} \tag{3}$$

where k_p (mg/g min$^{1/2}$), the intraparticle diffusion rate constant, is obtained from the slope of the straight line of q_t versus $t^{1/2}$. As shown in Fig. 4, the plot of the square root of time ($t^{1/2}$) versus the uptake (q_t) for the initial adsorption results in a linear relationship passing through origin, implying that the rate-limiting step of the adsorption may be due to the intraparticle diffusion. The k_p values increases as the increasing initial solute concentration, partly because they are proportional to the adsorption capacity [30]. Subsequently, the intraparticle diffusion starts to slow down due to the low adsorbate concentrations in solution and the final equilibrium stage was then reached.

3.5. Adsorption isotherm and thermodynamic assays

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Graphic presentations of the adsorption isotherms of phenol onto XAD-7 at different temperatures ranging from 298 to 323 K are illustrated in Fig. 5. It is obviously seen that the increase in temperature from 298 to 323 K decreases the adsorption capacity. These results confirm the exothermic nature of the adsorption process. The equilibrium data were then analyzed using the Freundlich and Langmuir isotherms given by Eqs. (4) and (5):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{5}$$

where q_m is the maximum amount of adsorption (mg/g), K_L is the affinity constant, K_f is a constant as a measure of adsorption capacity and n is a measure of adsorption intensity. The values of isotherm constants are presented in Table 3. It was observed that the equilibrium data fitted both the Freundlich and Langmuir isotherms well with correlation coefficient values larger than 0.98. q_m and K_f values dependent upon the ambient temperature further indicates the exothermic nature of phenol adsorption.
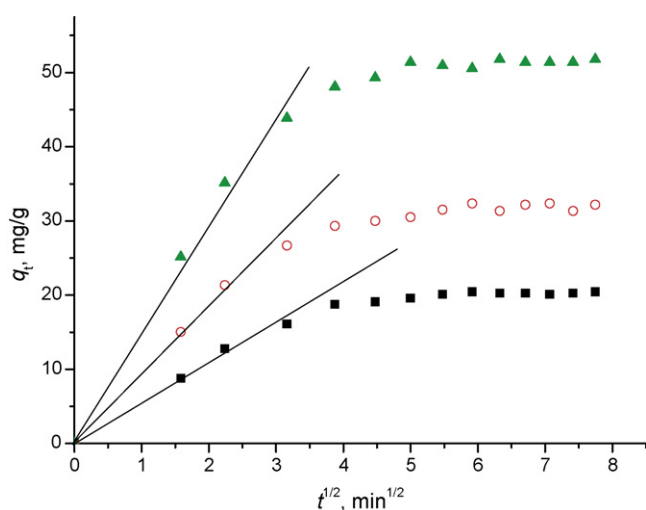

Fig. 4. Test of intraparticle diffusion model for phenol adsorption onto XAD-7 at 298 K. (Experimental data shown in Fig. 3; initial phenol concentrations: (■), 200 mg/L; (○), 400 mg/L and (▲), 800 mg/L.)
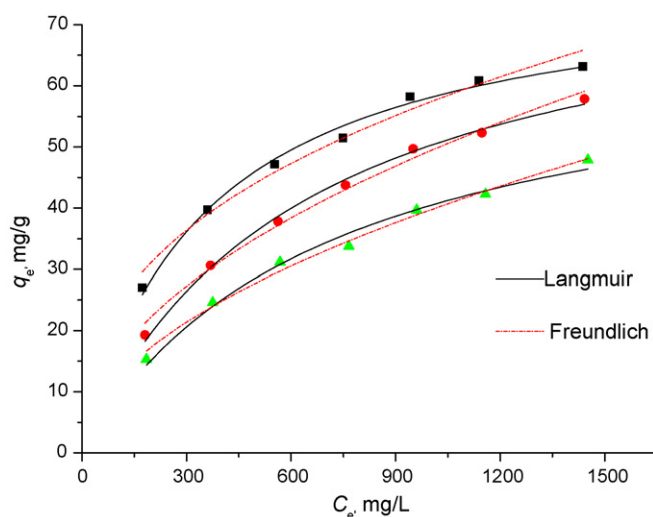

Fig. 5. Adsorption isotherms of phenol onto XAD-7 at different temperatures (XAD-7: 0.100 g, solution: 100 mL, (■) 298 K, (●) 313 K and (▲) 328 K).

Table 3
Isotherm parameters for phenol adsorption onto XAD-7 beads

T (K)	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/g)	R^2	K_f	$1/n$	R^2
298	78.7	2.76	0.992	3.51	0.406	0.982
313	72.3	1.86	0.996	1.31	0.526	0.991
328	62.9	1.73	0.996	0.96	0.540	0.990

Table 4
Thermodynamic parameters for phenol adsorption onto XAD-7

T (K)	ΔH (KJ/mol)	ΔG (KJ/mol)	ΔS (J/mol K)
298	−12.8	−13.3	1.68
313		−13.0	0.64
328		−13.4	1.83

Thermodynamic parameters such as changes of free energy of adsorption (ΔG), the heat of adsorption, and standard entropy changes (ΔH and ΔS) can be evaluated with the following equations [31,32]:

$$\Delta G = -RT \ln(K_L) \tag{6}$$

$$\ln K_L = -\frac{\Delta H}{RT} + A \tag{7}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}$$

where K_L is adsorption equilibrium constant in L/mol, R the universal gas constant, 8.314 J/mol K, T the absolute temperature, and A is a constant. The enthalpy change was determined by plotting $\ln K$ versus $1/T$. The negative value of ΔH and ΔG in Table 4 confirms that the process is essentially an exothermic and spontaneous one.

3.6. Column adsorption and regeneration test

Column adsorption of phenol onto XAD-7 beads was also performed and the breakthrough curve is illustrated in Fig. 6. Results indicated that phenol can be efficiently removed by the XAD-7 beads till the significant breakthrough occurs, and the adsorbent exhibited a sharp breakthrough at the point of ∼20 bed volumes (BV) under the experimental conditions.

Regeneration of the exhausted XAD-7 by phenol was also tested using ethanol and water separately at different temperatures. Results in Fig. 7 shows that the exhausted adsorbent is amenable to a complete regeneration by using limited volumes of ethanol (about 2 BV). Meanwhile, hot water at 353 K in the place of ethanol can also result in a similar regeneration efficiency, but larger volume (more than 10 BV per run) of water than ethanol was required to achieve the same goal. Such specific property may result in a more economic alternative and should not be ignored despite larger volume of water required. Further study on how to minimize the volumes of hot water is currently on the way.

Continuous adsorption-regeneration runs of an identical XAD-7 bed were also performed to test its applicability. The
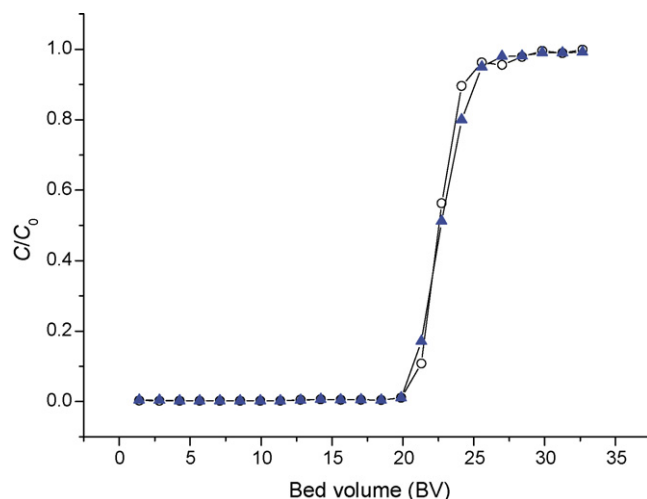

Fig. 6. The breakthrough curves of phenol adsorption onto XAD-7 at 298 K, the initial concentration of phenol is 500 mg/L and the pH is 6.2 ((○) the 1st run, and (▲) the 4th run, SIV: 0.2 m, EBCT: 30 min. The identical column was employed for continuous runs after regeneration with 2 BV ethanol at 323 K under the identical conditions in Fig. 7).

superposition of phenol breakthrough curves in the 1st and 4th run (Fig. 6) indicated that XAD-7 can be effectively regenerated for repeated use with negligible capacity loss.

3.7. Comparison of various adsorbents for phenol removal

Up to now various adsorbents have been prepared for phenol removal from aqueous media, most of which can be grouped as activated carbons [33,36], polymeric adsorbents [20,21,37], and low-cost adsorbents [6,38,40] (including inorganic adsorbents [6]). The typical adsorbents and their properties are presented in Table 5. As compared to other adsorbents, XAD-7 displays the best kinetic performance for phenol adsorption, and its adsorption capacity is higher than the low-cost adsorbents but lower than other polymeric adsorbents and activated carbons. Taken into account the fact that the exhausted XAD-7 beads
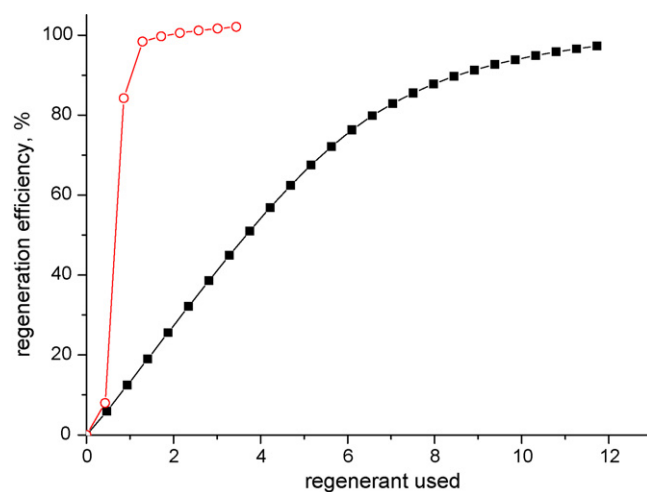

Fig. 7. A column desorption history of phenol loaded onto XAD-7 by using ethanol or water ((■) water at 353 K, (○) ethanol at 323 K; SLV: 0.1 m/h, EBCT: 60 min).

Table 5
Comparison of various adsorbents for phenol removal from aqueous media

	Adsorbent	Capacity (mg/g)	Equilibrium time (min)	Refs.
Activated carbon	Acid treated	~240	~1500	[33]
	Olive stone-based	~190	~180	[34]
	Eucalyptus wood-based	~80	~2000	[35]
	Waset tires-based	~180	NA	[36]
Polymeric adsorbents	Acrylic ester polymer	~100	~30	The present study
	Macroprous, polystyrene	~82	200–400	[37]
	Hypercrosslinked, polystyrene	~240	~250	[20]
	Aminated, polystyrene	~200	NA	[21]
Low-cost adsorbents	Surfactant modified silica	~40	NA	[38]
	Carbonized beet pulp	~90	~100	[39]
	Pinus pinaster bark	~50	~3000	[40]
	Activated bentonites	4–16	~600	[6]

are amenable to an entire regeneration for repeated use, XAD-7 can be taken as an ideal adsorbent for phenol removal from contaminated water.

4. Conclusions

From the current study we can conclude that phenol can be effectively removed by an acrylic ester polymer (Amberlite XAD-7) from aqueous phase, and acidic solution pH as well as coexisting inorganic salt was favorable for the adsorption. Adsorption isotherms were found to be well correlated by either the Langmuir or Freundlich isotherm and phenol adsorption onto XAD-7 is an exothermic and spontaneous process in nature. The pseudo-second-order kinetic model reasonably fits the adsorption process, and the intraparticle diffusion may be the rate-controlling step. Moreover, the exhausted adsorbent is amenable to an entire regeneration by using ethanol or relatively more volume of hot water as the regenerant. The regenerated XAD-7 displays almost identical performance for phenol removal from water compared to the virgin adsorbent.

Acknowledgements

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