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Chemical Engineering Journal 138 (2008) 194–199

Chemical Engineering Journal

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Hybrid gel reinforced with coating layer for removal of phenol from aqueous solution

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Received 27 December 2006; received in revised form 7 June 2007; accepted 27 June 2007

Abstract

Following our preceding results of fabricating phenol adsorbing hydrogel, we aimed to complete adsorbent gel material for removal of phenol. As a practical requirement, it needs to be mechanically more durable for repeated use of adsorption and desorption. In earlier works, we succeeded in fabricating *N*-isopropylacrylamide (NIPAM) hydrogel incorporated with tributyl phosphate (TBP). This hybrid gel was shown to be effective for removal of phenol dissolved in water. In this work, we succeeded in sealing the above hybrid gel completely with poly(vinyl alcohol) (PVA) thin layer coating by repeated freezing and thawing. The coated hybrid gel was remarkably improved in its mechanical durability. In the performance of adsorption of phenol, the PVA thin layer coating hardly hindered the mass transfer of phenol. The mechanical durability was sufficiently improved for the desorption (stripping) of the adsorbed phenol by immersing the adsorbent gel in sodium hydroxide solution. The cycle of the adsorption and desorption could be repeated without loss of the phenol adsorbing ability.

Keywords: Phenol; Adsorption; Hydrogel; Reinforcement; Repeated use

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1. Introduction

Phenol is one of the most common pollutants in wastewater from industries producing resins, plastics, fibers, adhesives, iron, steel, aluminum, leather, rubber, etc. Phenol and its derivatives have been shown to be toxic to aquatic life even at a low level. The American Environmental Protection Agency (EPA) has regulated concentration of phenol in wastewater below 4 mg/l in order to protect human health from the potential toxic effects caused by exposure to phenol. In general, removal of phenol from wastewater is quite desirable. However, phenol is not easy to remove from its dissolved state in water due to its considerable molecular polarity which brings about its high solubility over 10 wt%. Therefore, efficient methods for removing phenol from its aqueous solution have been desired from the viewpoint of environmental protection.

Until now, many approaches have been explored for treating phenol in wastewater, for example, by adsorption [1–4], solvent extraction [5,6] and biodegradation [7,8]. Among them, biological degradation has been most conventionally employed in a large-scale process for treating phenol-containing wastewater. In particular, use of biologically activated sludge is advantageous for large processes. However, the use of activated sludge has some unavoidable drawbacks. Its continuous operation constantly generates excessive sludge which needs to be frequently removed by dredging. The most serious shortcoming is elimination of microorganism which unexpectedly occurs when the phenol concentration exceeds the critical condition.

From the engineering viewpoints, adsorption for removing phenol is considered as an important subject in phenol treatment for its remarkable advantages. Among these, adsorption on activated carbon has been most widely studied [1–3]. Conventional solvent extraction has been also proved to work well for removal of phenol. For example, an earlier work showed that use of extractant species greatly improves the performance of the removal of phenol [9]. As for the solvent extraction, a method to bypass a settling process has been desired for designing a more inexpensive process for removing phenol.

To circumvent the complication of the settling process, the extractant TBP (tributyl phosphate) should be immobilized in solid or solid-like matters. Based on this idea, the authors incorporated TBP in NIPAM (*N*-isopropylacrylamide) hydrogel and demonstrated its effectiveness in removing phenol from its aqueous solution [10]. The hydrogel medium to immobilize the

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doi:10.1016/j.cej.2007.06.025

extractant species (TBP) was revealed to work well because phenol molecules can easily go into the hydrogel as they diffuse in bulk water. This relatively rapid mass transfer is possible thanks to the small volume fraction of constituent poly-NIPAM chains at a fully swollen state. For further improvement, the mechanical durability of the hydrogel should be increased. Therefore, the hybrid hydrogel should be reinforced by some supporting structure. Here, the authors considered the use of coating of the hybrid hydrogel with a layer of another chemically stable gel species. For the present purpose, poly(vinyl alcohol) (PVA) was expected to be suitable because PVA forms stable physically cross-linked gel simply by repeating freezing and thawing as previously reported [11–13]. The mechanical reinforcement was considered to affect the adsorption or desorption behavior of the hybrid hydrogel. In particular, we should pay attention to whether it can be used repeatedly in the cycle of the adsorption and desorption. If we make a progress at this point, we can propose the use of hydrogel as an adsorbent medium of phenol. Particularly, a hydrogel can be expected to be superior to activated carbon in that it is free of irreversible adsorption of adsorbed species. This is because the hydrogel adsorbent examined in the present work is equipped with the adsorption ability by immobilized TBP which can completely switch the adsorption and desorption of phenol depending on pH. Therefore, the mechanically reinforced hydrogel incorporated with TBP is worth examining in its ability of repeated use of adsorption and desorption of phenol. The results of the study will be reported with a special attention to the effect of the repeated use on the performance of the hydrogel medium in removing phenol.

2. Experimental

2.1. Materials

All the chemicals used in the present work (phenol, tributyl phosphate, *N*-isopropylacrylamide, *N*,*N*′-methylenebisacrylamide, α,α′-azobis(isobutyronitrile), methanol, poly(vinyl alcohol), sodium alginate, calcium chloride, 1 mol/l sodium hydroxide solution and 1 mol/l hydrochloric acid solution) were purchased from Wako Pure Chemical Industries and used as provided. The water used for the sample preparation was purified by ion-exchange followed by distillation.

2.2. Preparation of hybrid hydrogel

The hybrid hydrogel of *N*-isopropylacrylamide (NIPAM) and tributyl phosphate (TBP) which will be referred to as NIPAM/TBP gel in the following text was prepared by free radical polymerization. For the preparation of the NIPAM/TBP gel samples, 1.975 g of NIPAM monomer and 0.333 g of cross-linker *N*,*N*′-methylenebisacrylamide (BIS) were dissolved in a mixed solution of 12.5 ml of methanol and 17.5 ml of TBP. To initiate the polymerization reaction, 0.5 g of α,α′-azobis(isobutyronitrile) (AIBN) was added. The homogeneous pre-gel solutions were kept at 60 °C for 24 h. Finally, the obtained gel was rinsed with distilled water for 24 h to remove dissociable unreacted reagents. The density of the obtained gel was almost the same as that of water as seen from the balance when it was immersed in water.

2.3. Reinforcement of NIPAM/TBP hybrid gel

Considering the convenience in handling, the obtained NIPAM/TBP hybrid gel (wet 0.4 g) was to some extent air-dried on its surface for more stable formation of the coating layer. Next, it was immersed in a mixed aqueous solution of poly(vinyl alcohol) (PVA) (7.5 wt%) and sodium alginate (1 wt%). Immediately after that, the above dipped gel was soaked in a calcium chloride aqueous solution (3 wt%) to immobilize PVA layer on the surface of the hybrid gel. A preliminary coating layer of PVA could be formed with the help of the instantaneous bivalent ion cross-linking of calcium alginate. This coating procedure was repeated for three times to have the hybrid gel completely sealed by the PVA layer. Subsequently, the sealed hybrid gel underwent four cycles of freezing at −12 °C and thawing at room temperature (≃25 °C). At this stage, the coating with physically cross-linked PVA gel was completed. Next, the PVA-coated hybrid gel was soaked in sodium hydroxide aqueous solution to remove the alginate moiety. Finally, the sample gel was rinsed with distilled water for 48 h, and the final weight of the hydrogel sample was approximately 0.6 g. The outside appearance of the sample gel apparently showed improved mechanical strength.

2.4. Adsorption and desorption experiments

The adsorption experiments were carried out as follows. A sample gel was immersed in a phenol aqueous solution which was 40 times larger in volume than the immersed sample gel. The concentration in the outside aqueous solution of the phenol solution was set at 30, 90 and 150 mg/l. The above solution with the sample gel was immediately shaken at 150 rpm. The time dependence of the phenol concentration was measured by UV–vis spectrophotometer (Shimazu, UV-1650PC) at the wavelength of 269 nm. The same measurement as above was also carried out for neat PVA gel piece to obtain the background absorbance. Special care was made to prevent the experimental error caused by evaporation of the solvent (water). The adsorption experiments were continued until the adsorption equilibrium was reached, which was indicated by the plateau in the phenol concentration in the outside aqueous solution.

The desorption experiments were carried out by the same procedure as above except that the solution immersing the sample gel was 0.1 mol/l of sodium hydroxide aqueous solution. In the desorption experiments, the concentration of phenol anion was measured by the UV–vis spectrophotometer at the wavelength of 288 nm. Phenol is considered to be in a completely dissociated state in the present condition of the desorption experiment.

3. Results and discussion

3.1. Appearance of sample gel

NIPAM/TBP hybrid has been used for removing phenol from its aqueous solution, in which the adsorption capacity increases

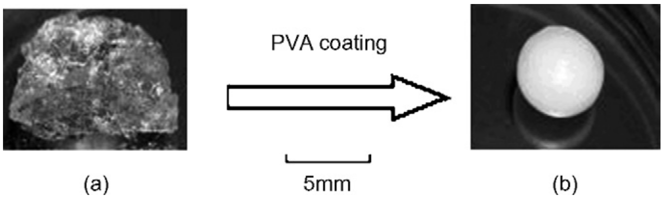

Fig. 1. Appearance of (a) as-polymerizied NIPAM/TBP hybrid gel and (b) PVA-coated NIPAM/TBP hybrid gel.

with the fraction of TBP in the gel [10]. Here, the hybrid gel was prepared at [TBP]/[NIPAM] = 3.5. This ratio is relatively large compared to those in our previous work [10].

Fig. 1 shows the appearance of the NIPAM/TBP hybrid gel before and after being coated with the PVA gel layer. The as-polymerized NIPAM/TBP hybrid gel [(a)] was fragile and had sticky surface, which makes its handling quite problematic. The PVA-coated sample gel [(b)] was much easier to deal with. As shown in Fig. 1(b), the PVA coating helped the hydrogel retain a well-defined shape and apparently improved the mechanical property of the hybrid gel.

3.2. Adsorption and desorption

Batch experiments were carried out both for the adsorption and desorption. The initial concentration of the outside phenol aqueous solution was set at 30, 90 and 150 mg/l. Fig. 2(a) shows the time dependence of the residual concentration of phenol in the outside solution. The concentration of phenol in the aqueous solution monotonously decreased for 50 h and asymptotically reached equilibrium. This type of the monotonous decrease in the adsorbate in the outside liquid phase is in accordance with the theoretical framework of Weber and Moris [14]. The adsorbed amount $Q(t)$ was theoretically given as follows [15]:

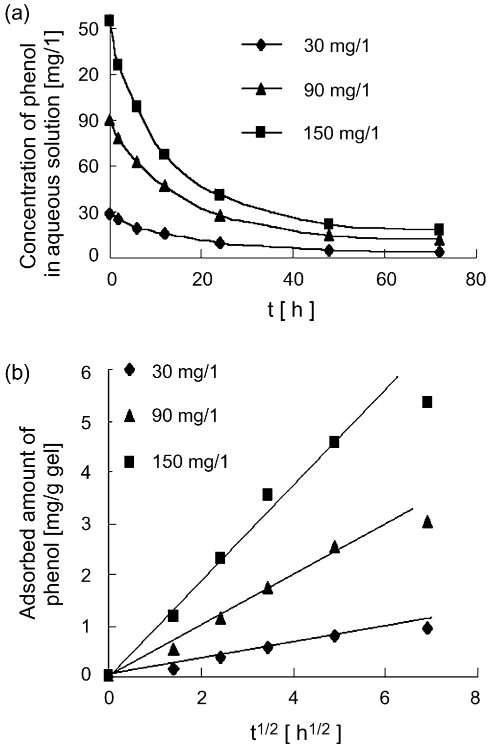

Fig. 2. Adsorption kinetics of phenol using the reinforced NTPAM/TBP hybrid gel as the adsorbent at 25 °C: (a) time dependence of the residual phenol concentration in the outside aqueous solution with initial concentration of 30, 90 and 150 mg/l; (b) adsorbed amount of phenol vs. square root of the lapse of time for the adsorption.

$$Q(t) = 2C_{A0}S\sqrt{Dt/\pi} = k_A t^{1/2} \tag{1}$$

where C_{A0}, D and S denote the initial concentration of phenol in the outside phase, diffusion coefficient of phenol in the gel and specific surface area of the adsorbent gel, respectively. k_A is the kinetic rate constant for the adsorption process rate-determined by the diffusion and given by $2C_{A0}S\sqrt{D/\pi}$. From Fig. 2(b), the value of k_A was evaluated as 2.78×10^{-6}, 8.77×10^{-6} and 1.45×10^{-5} s$^{1/2}$ by fitting Eq. (1) to the data for each initial concentration of phenol 30, 90 and 150 mg/l. Eq. (1) can be used only for the primary stage of the adsorption as obviously seen from $Q(t) \propto t^{1/2}$ which means phenol concentration $Q(t)$ is roughly in proportion to the diffusion depth from the surface of the adsorbent gel. It should be noted from Fig. 2(b) that the adsorption process can be well described by Eq. (1) in a certain region when the concentration of phenol steeply decreases. The diffusion coefficient D does not significantly depend on the initial concentration C_{A0}.

Having obtained the sample gels which reached the adsorption equilibrium in the above adsorption experiments, we carried out the desorption kinetic experiments using them.

For the desorption, 0.1 mol/l sodium hydroxide solution was used as the desorbing solution. Fig. 3(a) presents the time dependence of the concentration of desorbed phenol in the outside phase. It should be noted that the desorption occurred much faster than the adsorption and reached equilibrium in approximately 12 h. The faster desorption than the adsorption is explained by the assumable permeation of hydroxyl ion into the hydrogel in the case of the desorption. In the adsorption, phenol molecules need to diffuse into the adsorbent hydrogel themselves. In contrast, the stripping agent, sodium hydroxide, diffuses into the adsorbent hydrogel in the case of the desorption. Fig. 3(b) shows the dependence of the residual amount of phenol in the adsorbent gel plotted against the square root of the lapse of time for the desorption. The rate constant for the desorption in the initial stage can be obtained as we did for the adsorption from Fig. 2(b). They were evaluated as 4.55×10^{-6}, 1.53×10^{-5} and 2.50×10^{-4} s$^{1/2}$ for the initial concentration of 30, 90 and 150 mg/l, respectively. On the whole, the desorption occurs faster than the adsorption. Furthermore, it should be noted that the rate constant increases more steeply with the initial concentration of phenol for the desorption than adsorption. After being stripped, phenolic anions will be easily expelled out of the adsorbent hydrogel because of the greater hydrophilicity of the surrounding bulk aqueous phase.

The adsorption or desorption behavior of the present system has some features. First of all, these processes are likely to be rate-controlled by the diffusion in the hydrogel. In our previous work [10], the adsorption was terminated in the time scale in which the diffusion length reached the dimension of the hydro-

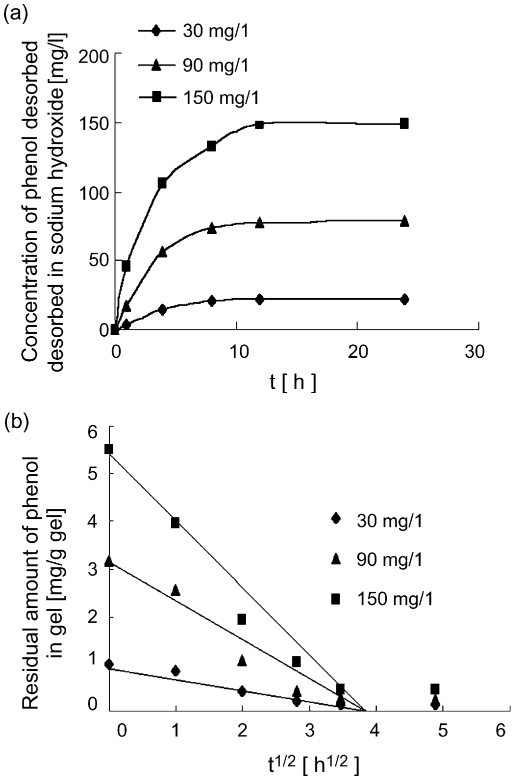

Fig. 3. Desorption kinetics of the adsorbed phenols using 0.1 mol/l sodium hydroxide solution as the desorbent at 25 °C; (a) time dependence of desorbed phenol concentration in the outside desorbing solution; (b) desorbed amount of phenol vs. square root of the lapse of time for the desorption.

gel. Quite similarly, those rate processes were terminated in the time scale of 10–20 h in the present cases. Therefore, the main rate-determining stage in the present experiments was also the diffusion in the hydrogel. Because the adsorption and desorption experiments were carried out under vigorous shaking at 150 rpm, the mass transfer in the outer vicinity of the surface of the hydrogel was not likely to be rate-controlling stage. The other feature is that the adsorption and desorption occurred more rapidly than in an activated carbon. Although the full reasoning cannot be given at present, the relatively rapid mass transfer seems to be related with the highly swollen structure of the hydrogel in which most volume is occupied with the solvent (water). In an activated carbon, the mass transfer is topologically hindered to some extent by the solid structure. Compared to that, the flexible structure of the swollen hydrogel weakly affects the mass transfer, and as the result, the diffusive process is relatively rapid in the hydrogel. Further evidence should be given to the above speculation.

3.3. Effect of initial phenol concentration

Table 1 lists the distribution ratios of phenol for three different initial concentrations. For comparison, the results obtained for neat PVA gel are shown together. Neat PVA adsorbed almost no phenol. Thus, the adsorption capacity is totally to be attributed to the incorporated TBP. The adsorbed amount of phenol at equilibrium was proportional to the initial concentration. This result is consistent to that of our previous work using uncoated NIPAM/TBP gel [10] and shows that the system reached the adsorption equilibrium with a common distribution ratio irrespective of the outside concentration of phenol. The common distribution ratios are considered as the result of the overwhelmingly larger number of the adsorption sites than that of phenol molecules which exist in the gel.

Table 1
Distribution ratios of phenol for different initial phenol concentrations

	Initial concentration (mg/l)		
	30	90	150
Hybrid adsorbent gel (mg/g)	1.006	3.16	5.49
Distribution ratio	78.02	84.64	83.85
Neat PVA gel (mg/g)	0.025	0.08	0.13

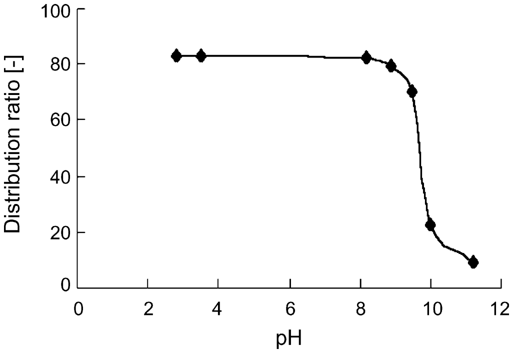

Fig. 4. Dependence of distribution ratio of phenol in two phases on the pH of the outside solution.

3.4. Effect of pH

The pK_a value of phenol at room temperature is 9.8–10.0. Fig. 4 presents the dependence of distribution ratio of phenol on pH of the outside aqueous solution. These experiments were carried out at the initial concentration of phenol at 150 mg/l. When the pH value is below the above pK_a, the distribution ratio was at approximately 80. Under this condition, phenol exists in the gel in the adsorbed state. The distribution ratio steeply decreased when the pH value exceeds pK_a, indicating that phenol tends to be out of the gel dissociated to phenolic anion. This understandable result is quite important in that the repeated adsorption and desorption take place when the pH value of the outside phase is below and above the pK_a value of the adsorbate phenol. Table 2 shows the desorbed amount at equilibrium in 0.1 mol/l sodium hydroxide solutions (pH > pK_a) for the three initial phenol concentrations. At least 85% of the adsorbed phenol at the adsorption equilibrium was removed at the desorption equilibrium.

Table 2
Desorbed amount of phenol at equilibrium in 0.1 mol/l sodium hydroxide solution for the saturated gel at the three initial concentrations

Initial concentration (mg/l)	Desorbed amount (mg/g)
30	0.865
90	2.909
150	5.04

Table 3
Adsorption capacity of the gel adsorbent in phenol aqueous solution at equilibrium after the desorption up to three times in 0.1 mol/l sodium hydroxide solution

	Initial concentration (mg/l)		
	30	90	150
I (distribution ratio)	75.00	76.30	83.42
II (distribution ratio)	73.17	75.56	79.50
III (distribution ratio)	79.00	74.39	82.22

3.5. *Effect of repeated adsorption/desorption cycle*

Table 3 presents the distribution ratios of phenol at the three different initial concentrations when the adsorption and desorption were repeated. I, II and III correspond to the second, third and fourth adsorption, respectively. These results show the phenol adsorbing ability of the adsorbent hydrogel is not deteriorated by repeating the adsorption/desorption cycles. Thus, the PVA coating was revealed to help the hydrogel retain not only the mechanical durability but also the phenol adsorbing ability. This retained adsorbing ability by the PVA coating is to be noticed in that it is an advantage of the present system to, for example, activated carbons.

3.6. *Type of adsorption isotherm*

The type of the adsorption can be deduced from the data fitting to model equations for the adsorption isotherm. Fig. 5 presents the adsorption isotherm obtained when the initial concentration of phenol in the outside solution was set at 150 mg/l. The fitted curves to the Langmuir and Freundlich models are also shown together. Q_e and C_e denote the adsorbed amount of phenol per unit weight of the adsorbent gel and outside concentration of phenol, respectively. The Langmuir model for Q_e is given by

$$Q_e = \frac{C_{Ae} b C_e}{1 + b C_e} \tag{2}$$

where C_{Ae} and b are the maximum adsorption capacity of the adsorbent of unit volume and Langmuir constant, respectively. The Freundlich model is as follows:

$$Q_e = k_F C_e^{1/n} \tag{3}$$

where k_F and n are the constants to be determined for each adsorption system. The parameters C_{Ae} and b for the Langmuir model in the present case were obtained as 20.92 mg/g and 0.092 l/mg, respectively. This value of the maximum adsorption capacity C_{Ae} was comparable with our previous result [10], showing that the gel layer coating for the mechanical reinforcement in the present work does not significantly affect the equilibrium adsorption. Those for the Freundlich model were $k_F = 3.4 \times 10^{-4}$ (l/mg)^n and $n = 1.37$. Since n exceeds unity for the present system, the adsorption state of phenol in the present adsorbent gel is considered to be thermodynamically favored.

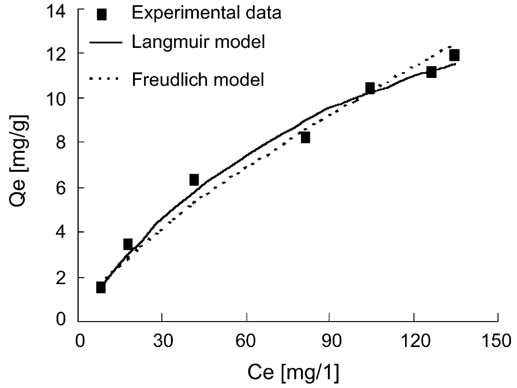

Fig. 5. Adsorption isotherm data for true adsorbent gel at 25 °C.

4. Conclusion

Adsorbent gel of phenol in an aqueous phase was prepared by incorporating tributyl phosphate (TBP) to *N*-isopropylacrylamide (NIPAM) gel. This hybrid gel was sealed with a thin layer of poly(vinyl alcohol) (PVA) gel by repeated freezing and thawing. In this sealing process, calcium alginate gel was used to form a preliminary layer of PVA prior to the freezing and thawing. The obtained adsorbent gel showed comparable performance in the adsorption of phenol to that of the hybrid NIPAM/TBP gel without the PVA thin layer. Therefore, the PVA coating does not induce significant hindrance in the mass transfer process of phenol. As a remarkable practical advance due to the PVA thin layer coating, desorption (stripping) of the adsorbed phenol could be stably and repeatedly carried out using a basic aqueous solution as the stripping liquid for phenol without deteriorating the adsorption ability of the adsorbent gel.

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