

Poly(ether sulfone)/Activated Carbon Hybrid Beads for Creatinine Adsorption

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ABSTRACT: Poly(ether sulfone)/activated carbon (PES-AC) hybrid beads, with various proportions of activated carbon (AC) or amounts of added propylene glycol (PG), were prepared with a liquid-liquid phase-separation technique. The specific surface area, porosity, diameter, and pore volume of the prepared beads were characterized. The adsorption of creatinine from a Tyrode buffer solution (pH 7.4) on different PES-AC hybrid beads was investigated through batch experiments at 25°C. The experimental results suggested that creatinine adsorption was enhanced by an increase in the AC or PG proportion added during the preparation of the PES-AC hybrid beads. The mass-

transfer model was applied to the experimental data for the analysis of the kinetic results. The experimental creatinine adsorption isotherms were adequately fitted with both Langmuir and Freundlich equations. Tests of the hemolysis ratio and protein adsorption were carried out. The results showed that the hemolysis ratio of the prepared beads was lower than 5%. The adsorption of creatinine was affected by the presence of serum albumin but not significantly enough to hinder its applications in blood purification. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1085–1092, 2007

Key words: adsorption; phase separation; poly(ether sulfones)

INTRODUCTION

Creatinine is a chemical waste molecule that is generated from muscle metabolism. The kidneys maintain blood creatinine in a normal range. Creatinine has been found to be a fairly reliable indicator of kidney function.¹ As the kidneys become impaired, the creatinine level in the blood will rise. Abnormally high levels of creatinine thus warn of possible malfunction or failure of the kidneys, sometimes even before a patient reports any symptoms. Powdered activated carbons (ACs) show excellent adsorption properties for creatinine. However, when the powdered ACs are used directly, especially in a liquid medium, fine carbon particles together with soluble organic compounds in the carbons will be eluted. Thus, when powdered ACs are used as adsorbents to remove creatinine, particularly when used in direct contact with blood, they should be coated with a polymer film outside to prevent the elution of fine carbon particles and soluble organic compounds.

To resolve the problems mentioned previously, AC adsorbent particles can be carbon encapsulated with a

polymer membrane, such as collodion (cellulose nitrate).² However, the cellulosic structure contains a high density of hydroxyl groups, which are known to cause complementary activation upon contact with blood. Moreover, it has been reported that adsorbents with a highly hydrophobic surface (e.g., resins prepared from styrene divinylbenzene copolymers) are characterized by significant bioincompatible responses such as complement activation, neutropenia, and thrombocytopenia.³

In our earlier reports,^{4,5} porous, DNA-loaded poly(ether sulfone) (PES) particles were prepared through liquid-liquid separation. The same technique can also be used in embedding powdered AC. Moreover, PES shows outstanding thermal and hydrolytic stabilities as well as good mechanical and film-forming properties. PES membranes also show good biocompatibility. Thus, PES is widely used in advanced separation technology and biomedical fields for artificial organs and medical devices used for applications such as blood purification, including hemodialysis, hemodiafiltration, hemofiltration, plasmapheresis and plasma collection, and scaffolding.^{6,7} Therefore, it is reasonable to predict that through the embedding of AC particles within PES, novel and useful adsorbents may be obtained.

In this study, poly(ether sulfone)/activated carbon (PES-AC) hybrid beads were prepared with a liquid-liquid phase-separation technique and then were used to remove creatinine. The levels of hemolysis and protein adsorption for the hybrid beads were also investigated.

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EXPERIMENTAL

Materials

PES (Ultrason E 6020P, Chemical Abstracts Service No. 25608-63-3) was purchased from BASF Chemical Co. (Ludwigshafen, Germany) and used to prepare the porous particles. Bovine serum albumin (BSA) was purchased from Sigma Chemical Co (St. Louis, MO). Healthy and fresh human blood (from a 35-year-old man) was collected with vacuum tubes (7 mL; Venoject II, Terumo, Co.) containing a citrate/phosphate/dextrose/adenine-1 mixture solution as an anticoagulant (anticoagulant/blood ratio = 1 : 7) and was used for the hemolysis testing. The other chemicals were supplied by Chengdu Chemical Reagent, Inc. (Chengdu, China). All the materials were analytical-grade and were used without further purification.

Preparation of the PES-AC hybrid beads

For comparison, a series of PES-AC hybrid beads were prepared with a liquid-liquid separation technique, which is described in detail in our earlier report.^{8,9} The required amount of PES with or without the corresponding amount of propylene glycol (PG) as a penetration enhancer was dissolved in *N,N*-dimethylacetamide (DMAc), and this was followed by stirring. After the homogeneous solutions were prepared, the required amounts of powdered ACs were added, and then the solutions were stirred sufficiently to obtain suspensions. Because of the difficulty of producing smooth beads when the proportion of AC was higher than 85% in beads without PG or higher than 75% in beads with PG, the two proportions were deemed the highest proportions for the preparation process. The ratios of the components are listed in Table I.

The resultant suspension was dropped into distilled water with a 1.2-mm-diameter syringe needle at room temperature to prepare hybrid particles. The injection speed was controlled at 60–100 drops per minute. The air gap from the syringe needle to the water was 5–10 cm. The particles were placed in ethanol for 15 min, and this was followed by incubation in boiling water

for over 24 h to elute the solvent as well as PG from the particles, which were then stored in distilled water until they were used.

Characterization of the PES-AC hybrid beads

For scanning electron microscopy (SEM) observations, the sample was dried at room temperature and then was cut with a single-edged razor blade, attached to the sample supports, and coated with a gold layer. The SEM images were recorded with an S-2500C microscope (Hitachi, Japan).

Mercury porosimetry (model 1300, Micromeritics, United States) was used to determine the specific surface area of the porous particles. The particles were dried at room temperature; about 0.1 g of dried particles was used as a sample. The reported data were obtained with Quantachrome Poremaster for Windows (version 4.02) (Boynton Beach, FL).

The diameter (D ; cm), porosity (P), and pore volume (PV) of the particles were calculated from the densities of PES ($\rho_P = 1.43 \text{ g/cm}^3$) and AC ($\rho_C = 2.2 \text{ g/cm}^3$), the ratio of AC to the polymer, and the sample weight change after drying with the following formulas:

$$\text{Diameter}(D) = \left\{ \frac{6[W_A(1 - C\%)/\rho_P + W_A \times C\%/\rho_C]^{1/3}}{\pi} \right\}$$

$$\text{Porosity}(P) = \frac{(W_B - W_A)/\rho_W}{W_A(1 - C\%)\rho_P + W_A \times C\%/\rho_C + (W_B - W_A)/\rho_W} \times 100\%$$

$$\text{Pore volume (PV)} = \frac{n\pi D^3 \times P}{6 W_A}$$

where W_B is the weight of the PES-AC hybrid beads before drying (g), W_A is the weight of the hybrid beads after drying (g), ρ_W is the density of water (1.0 g/cm^3), n is the number of beads (100), and $C\%$ is the mass percentage of AC in the PES-AC system.

TABLE I
Formulas for the Preparation of Different PES-AC Hybrid Carbon Beads

	DMAc/PES (w/w)	AC/PES (w/w)	PG/PES (w/w)
PES-AC0	9.0 : 1	0	0
PES-AC30	9.0 : 1	0.43 : 1	0
PES-AC50	9.0 : 1	1.00 : 1	0
PES-AC75	9.0 : 1	3.00 : 1	0
PES-AC85	9.0 : 1	5.67 : 1	0
PES-AC75-PG1.0	9.0 : 1	3.00 : 1	1.0 : 1
PES-AC75-PG1.6	9.0 : 1	3.00 : 1	1.6 : 1
PES-AC75-PG2.0	9.0 : 1	3.00 : 1	2.0 : 1

Adsorption experiments

The PES-AC hybrid beads were soaked in a Tyrode buffer (pH = 7.4),³ a solution mimicking the mineral composition and pH of blood, for over 24 h before being used in the creatinine adsorption experiments.

The creatinine was dissolved in a Tyrode buffer to prepare solutions with the required concentration. Batch experiments were carried out at a constant temperature of 25°C, and a fixed number (60) of PES-AC hybrid beads were brought into contact with 20 mL of the solution in conical flasks. The effects of the AC propor-

tion in the beads were observed for PES, PES-AC30, PES-AC50, PES-AC75, and PES-AC85 [in the hybrid codes, the number (e.g., 30 in PES-AC30) is equal to 100 times the ratio of the mass of AC to the total mass of PES and AC], for which the proportions of carbon in the spheres increased in that order. The influence of PG was evaluated for particles of PES-AC75, PES-AC75-PG1, PES-AC75-PG1.6, and PES-AC75-PG2. All the experiments were carried out to clarify the influence of the aforementioned factors and determine the optimum conditions for the preparation of PES-AC hybrid beads for the adsorption of creatinine.

An aliquot of the solution was sampled to determine the concentration of creatinine remaining in solution with a U-200A light-ultraviolet spectrophotometer at the wavelength of 235 nm. The calibration graph obeyed a linear Beer-Lambert relationship ($R^2 = 0.9999$) in the range of creatinine concentrations of 0–3 mg/dL. Dilution was required for the analysis of the samples at high concentrations.

The removal ratio and adsorbed capacity of creatinine were calculated with the following formulas:

$$R_t(\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \times 100\%$$

where R_t is the removal ratio of creatinine by the particles at time t (%), C_0 is the initial concentration of the creatinine solution (mg/dL), C_t is the concentration at time t (mg/dL), Q_t is the removal amount of the creatinine per gram of the hybrid beads at time t (mg/g), V is the volume of the creatinine solutions (dL), and m is the weight of the PES-AC hybrid beads (g).

Equilibrium adsorption isotherms for creatinine were established at 25°C with single-batch experiments, in which a fixed number (60) of PES-AC hybrid beads were mixed with solutions of creatinine in a Tyrode buffer (20 mL) in a range of concentrations (0–80 mg/dL). The data were fitted with Langmuir and Freundlich adsorption models of the following forms:

$$\text{Langmuir equation: } Q_e = Q_0 s C_e / (1 + s C_e)$$

$$\text{Freundlich equation: } Q_e = k C_e^{1/N}$$

where s , k , and n are constants; Q_e is the amount of creatinine adsorbed on the carbon at equilibrium (mg/g); Q_0 is the amount of the adsorbate sufficient to form a monolayer on the adsorbent surface (mmol/g); and C_e is the residual concentration at equilibrium (mg/dL).

Tests of hemolysis and protein adsorption

The procedure for the hemolysis ratio (HR) measurement is described in detail in ref. 10. The HR ratio was obtained with the following equation:

$$\text{HR} = (AS - AN)/(AP - AN)$$

where AS is the absorbance of the sample and AP and AN are the absorbances of the positive and negative controls, respectively. The absorbance was measured with a spectrophotometer at the wavelength of 542 nm.

BSA was dissolved in a Tyrode buffer to form a 0.1 g/dL solution. A fixed number of PES-AC hybrid beads for each sample (60), after soaking in a Tyrode buffer for over 24 h, were added to 20 mL of a BSA solution and incubated for over 8 h at room temperature. The concentration of BSA was measured with an ultraviolet-visible spectrophotometer at the wavelength of 280 nm.

To study the adsorption of creatinine in the presence of albumin, a mixture solution was prepared with 50 mg of creatinine and 100 mg of BSA per deciliter. PES-AC75 particles, which were chosen as the model sample, were added to a 20-mL mixture solution (60 beads). The wavelength used for this test was 235 nm.

RESULTS AND DISCUSSION

Sample characterization

The liquid-liquid phase-separation technique employed for the preparation of the beads results in a porous structure for the PES matrix. Figure 1 shows that beads with different AC proportions exhibit the following features. First, because of the rapid phase separation, a skin layer is formed on the outer surface of the beads. Second, in general, the pore size gradually increases from the outer surface to the internal region of the beads. Third, the mean pore diameter decreases, whereas the density of the beads increases, with an increase in the AC proportion; however, there is a very large pore in the center of the particle when AC is embedded in PES. The presence of the large pore in the hybrid particle is caused during the phase-separation process because AC cannot be dissolved in the solvent DMAc. Because the SEM pictures of the beads with AC proportions higher than 50% could not clearly show the internal structure, they are not presented in this article.

The data listed in Table II are adequate to supplement the SEM characterization and indicate the relationship between the structure of the beads and the adsorption property. As shown in Table II, the porosity and pore volume significantly decrease with an increase in the proportion of AC. This seems to be

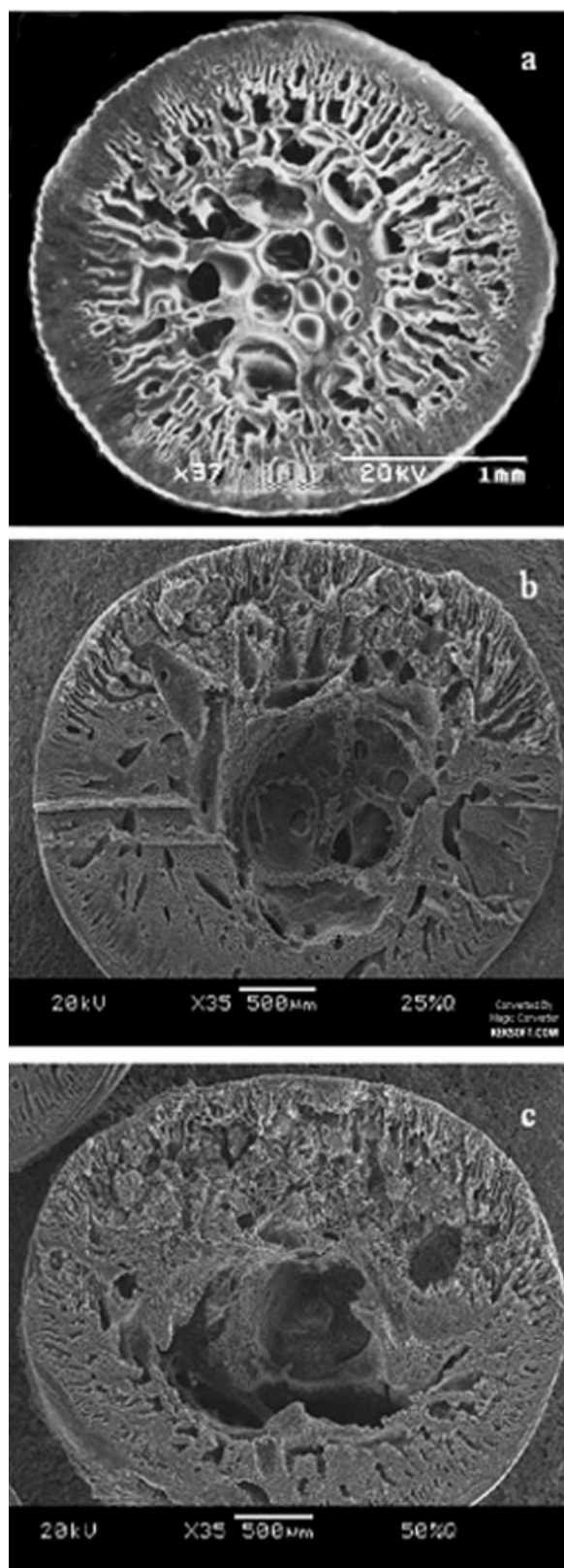


Figure 1 SEM pictures of different beads. The AC proportions for the beads were (a) 0, (b) 25, and (c) 50%.

inconsistent with the following facts. First, the specific surface area, determined with mercury porosimetry, increases with an increase in the AC proportion. Second, the adsorption results (presented in detail later in this article) suggest that creatinine adsorption is enhanced with an increase in the AC proportion. To address this problem, the parameters in Table II are under consideration in association with the SEM pictures (Fig. 1) and the pore size distribution results, which were obtained with mercury porosimetry.

For the pure PES beads, the pore diameter mainly ranges from 100 to 1000 nm, much larger than the pore size of powdered AC. The great amount of large pores greatly contributes to the porosity and pore volume but not to the specific surface area. For the PES-AC hybrid beads, the large pores formed by the PES matrix are filled with powdered AC, which mainly possesses pores less than 20 nm in size. This surely leads to a decrease in the porosity and pore volume. At the same time, the increase in the AC proportion in the particles leads to a significant increase in the specific surface area, which plays an intrinsic role in the adsorption properties.

It is also shown in Table II that the increase in the amount of PG used during the preparation process is accompanied by a slight increase in the porosity, pore volume, and specific area. This phenomenon then in turn affects the creatinine adsorption property as shown next. The diameter of all the beads appears to be about 2.95 ± 0.03 mm, which is suitable for column-packing applications.

Creatinine adsorption

The effect of the AC proportion in the particles on creatinine adsorption is presented in Figure 2. Beads with higher AC proportions adsorb more creatinine and adsorb it faster than their counterparts with lower AC proportions. The aforementioned phenomena may be explained as follows. For the PES-AC hybrid beads, the adsorption of creatinine is largely attributable to AC, whereas PES mainly functions as a matrix to immobilize AC. That is, the adsorption mechanism of the PES-AC hybrid beads should be primarily determined by the AC component. AC possesses a large quantity of pores larger than the molecular size of creatinine (0.54 nm^{11}). According to a study by Yang et al.,¹¹ the adsorption properties mainly depend on the active sites at which the adsorbate molecules are adsorbed for this small molecule. Therefore, the larger the specific area is, the higher the adsorbed amount of creatinine is. As discussed previously, the specific surface area increases with an increase in the AC proportion in the PES-AC hybrid beads. This consequently leads to a change in the removal ratio and kinetics, as shown in Figure 2. Creatinine can be effectively removed within 3–5 h,

TABLE II
Structural Properties of Different PES-AC Hybrid Carbon Beads

Sample	Specific surface area (m ² /g)	Porosity (%)	Pore volume (cm ³ /g)	Diameter (mm)
PES-AC0	28.13 ± 0.70	89.98 ± 2.00	5.47 ± 0.10	2.95 ± 0.05
PES-AC30	89.63 ± 2.00	87.13 ± 2.00	3.80 ± 0.10	2.95 ± 0.05
PES-AC50	134.72 ± 2.50	83.67 ± 2.00	2.65 ± 0.05	2.94 ± 0.05
PES-AC75	192.84 ± 4.00	78.67 ± 2.00	1.57 ± 0.05	2.97 ± 0.05
PES-AC85	218.76 ± 4.00	71.89 ± 2.00	1.11 ± 0.05	2.97 ± 0.05
PES-AC75-PG1.0	196.82 ± 4.00	78.99 ± 2.00	1.58 ± 0.05	2.98 ± 0.05
PES-AC75-PG1.6	198.46 ± 4.00	79.40 ± 2.00	1.94 ± 0.05	2.96 ± 0.05
PES-AC75-PG2.0	201.63 ± 4.00	80.21 ± 2.00	2.09 ± 0.05	2.92 ± 0.05
Powdered AC	456.38 ± 8.00	32.21 ± 1.00	0.38 ± 0.01	0.04 ± 0.01

The data are expressed as the mean plus or minus the standard deviation of three independent measurements.

which is the period that routine therapeutic processes involving creatinine removal last. Adsorption studies of creatinine by AC have been reported by other researchers,^{11,12} who used phenolic resin based, AC spheres or PAN-based, activated, hollow carbon fibers. Although the concentration of the creatinine, the volume of the solution, and the amounts of the adsorbents were different from those of this study, it is certain that the kinetic results for creatinine adsorption by pure AC are better than those shown in this study, and this is comprehensible for two reasons. First, the specific surface area is much larger for pure ACs (especially after a special treatment to enlarge the surface area) than PES-AC hybrid beads. Second, the matrix of PES can more or less affect the adsorption rate. However, the fact that fine carbon particles together with soluble or-

ganic compounds in the carbons would be eluted in practical use was not taken into account by the other researchers, and this is the first publication to propose the preparation of PES-AC hybrid beads for creatinine adsorption. Furthermore, the kinetic results, though not as sound as those of pure ACs, are adequate to prove that PES-AC hybrid beads should be a promising alternative for the application of creatinine removal; for example, they have attractive potential for clinical use.

Figure 3 illustrates the effect of the amount of PG added during the preparation of PES-AC hybrid beads on the creatinine adsorption. The removal ratio is only slightly affected by the PG amount after 7 h of adsorption, but it significantly increases with an increase in the PG amount within 5 h. That is, the PES-AC hybrid

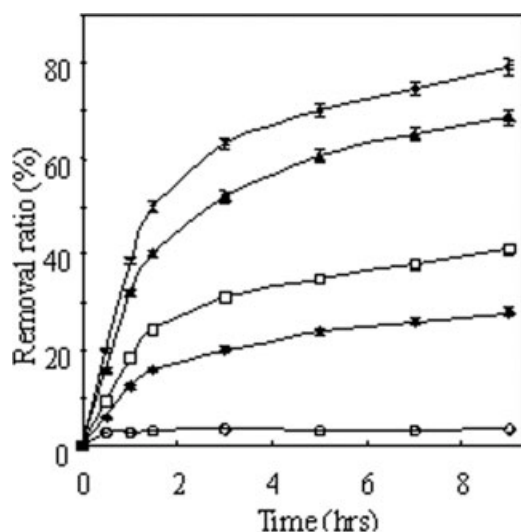


Figure 2 Creatinine adsorption kinetics on beads with different proportions of AC: (○) PES-AC0, (●) PES-AC30B, (□) PES-AC50B, (▲) PES-AC75B, and (×) PES-AC85B. The creatinine was dissolved in a Tyrode buffer (50 mg/dL). The batch experiments were carried out at a constant temperature of 25°C, and a fixed number (60) of PES-AC hybrid beads were in contact with 20 mL of a solution. The data are expressed as the mean plus or minus the standard deviation of three independent measurements.

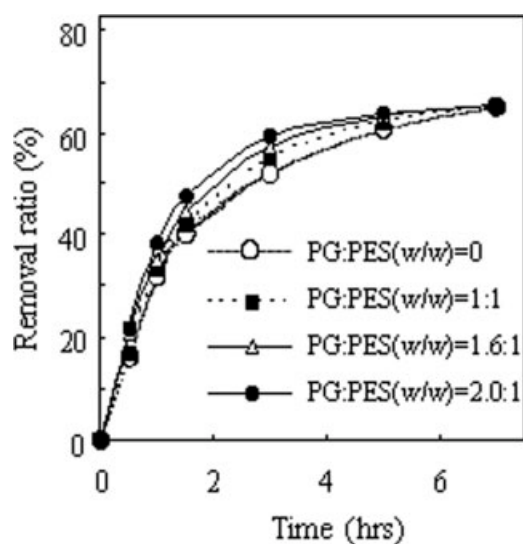


Figure 3 Creatinine adsorption kinetics on beads pretreated with different amounts of PG. The ratio of the mass of AC to the total mass of PES and AC was 75%. The creatinine was dissolved in a Tyrode buffer (50 mg/dL). The batch experiments were carried out at a constant temperature of 25°C, and a fixed number (60) of PES-AC hybrid beads were in contact with 20 mL of a solution. Duplicate experiments gave similar results.

TABLE III
Kinetic Parameters for Creatinine Adsorption on
PES-AC Hybrid Beads ($C_0 = 50$ mg/dL)

Sample	R^2	a
PES-AC30	0.99	0.7892 ± 0.0100
PES-AC50	0.99	0.7646 ± 0.0100
PES-AC75	0.99	0.7561 ± 0.0100
PES-AC85	0.99	0.7152 ± 0.0100
PES-AC75-PG1.0	0.99	0.7222 ± 0.0100
PES-AC75-PG1.6	0.99	0.6180 ± 0.0100
PES-AC75-PG2.0	0.99	0.5947 ± 0.0100

The data are expressed as the mean plus or minus the standard deviation of three independent measurements.

beads with more PG added have a higher rate for creatinine adsorption. It is especially interesting that the effect of PG is significant in the routine therapeutic period (3–5 h).

The creatinine adsorption results for PES-AC hybrid beads shown in Figure 3 are in agreement with the structural change mentioned previously. This is presumably due to the following mechanism. Tiny droplets of PG are first dispersed homogeneously in a PES-DMAc solution system and then eluted together with the solvent DMAc during and after the phase-separation process. The volume previously possessed by PG droplets is released, and so pores are left in the PES matrix. On the other hand, PG, which is a non-solvent of PES, affects the liquid-liquid phase-separation process during the preparation of the particles, thus affecting the structure of the particles. Further-

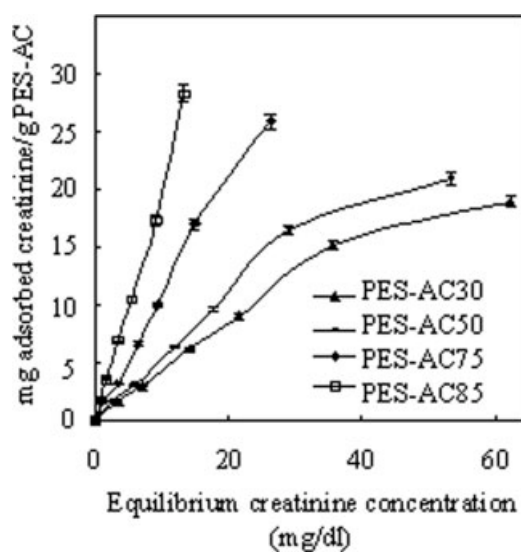


Figure 4 Creatinine adsorption isotherms from protein-free solutions with different PES-AC beads. The creatinine was dissolved in a Tyrode buffer (50 mg/dL). The batch experiments were carried out at a constant temperature of 25°C, and a fixed number (60) of PES-AC hybrid beads were in contact with 20 mL of a solution. The data are expressed as the mean plus or minus the standard deviation of three independent measurements.

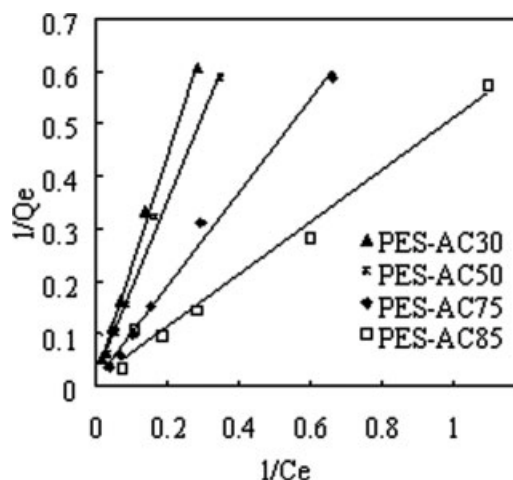


Figure 5 Langmuir isotherms for the adsorption of creatinine by different PES-ACs.

more, PG may function as a penetration enhancer (or sorption promoter or accelerant). PG was chosen for our work for two main reasons. First, it can be dispersed homogeneously in a PES-DMAc system in a comparatively large volume (the highest practical PG/PES ratio is 2 : 1 w/w) and thus can act more effectively as a pore-forming agent in the PES matrix. Second, it is basically nontoxic; this is demonstrated by its common use as a penetration enhancer for improving transdermal drug delivery.¹³

The mass-transfer model for the adsorption of creatinine to PES-AC hybrid beads can be expressed with the following formula:

$$Q_t = Q_e e^{-a/t}$$

where Q_t is the adsorbed amount at adsorption time t (mg/g), Q_e is the equilibrium adsorbed amount (mg/g), and a is a constant related to the creatinine concentrations and PES-AC hybrid beads. We took the re-

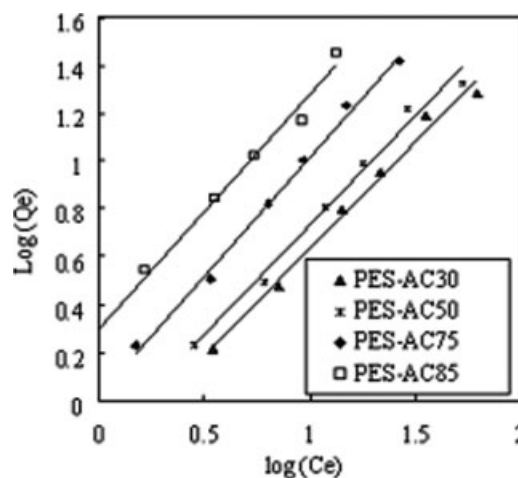


Figure 6 Freundlich isotherms for the adsorption of creatinine by different PES-ACs.

TABLE IV
Fitting of the Adsorption Isotherm with the Langmuir and Freundlich Equations

Sample	R^2	Langmuir model		Freundlich model		
		Q_0 (mg/g)	s	R^2	k	N
PES-AC30	0.99	53.8 ± 1.0	0.009 ± 0.001	0.99	0.55 ± 0.01	1.12 ± 0.02
PES-AC50	0.99	60.2 ± 1.0	0.010 ± 0.001	0.99	0.66 ± 0.01	1.10 ± 0.02
PES-AC75	0.99	82.6 ± 1.0	0.014 ± 0.001	0.99	1.07 ± 0.01	1.01 ± 0.02
PES-AC85	0.98	87.0 ± 1.0	0.023 ± 0.001	0.99	2.00 ± 0.01	1.02 ± 0.02

The data are expressed as the mean plus or minus the standard deviation of three independent measurements.

reciprocal of the adsorption time and the natural logarithm of the adsorbed amount (mg/g), and then the constants were obtained, as shown in Table III. According to the correlation coefficients, the adsorbed amount and time accord with this formula very well for different PES-AC hybrid beads.

The adsorption isotherms of four different types of PES-AC hybrid beads with different AC contents are presented in Figure 4. The adsorption isotherms for all four hybrid beads are smooth curves. The creatinine adsorption capacities are considerable, and the saturated capacities are not reached in the range of concentrations used in this work. An increase in the creatinine adsorption capacity with an increase in the creatinine concentration is a common phenomenon observed with all four types of beads. The amount of creatinine adsorbed increases with the proportion of AC. These adsorption isotherms have been fitted with Freundlich and Langmuir equations. Straight lines have been obtained (Figs. 5 and 6). The constants from these lines are listed in Table IV. The results show that the Langmuir and Freundlich equations adequately fit the creatinine adsorption isotherms for all four types of beads with different AC proportions. These tables and figures also show that the variety of AC proportions does not apparently change the adsorption mechanisms, and this also confirms that the adsorption mechanism should be mainly attributed to AC, rather than PES or a combination and interaction of the two.

When the potential clinical application of PES-AC hybrid beads is taken into account, the normal level of serum creatinine for adults is 0.8–1.3 mg/dL for men and 0.6–1.0 mg/dL for women. According to the pathophysiology, doubled serum creatinine implies 50% renal function, and creatinine increases by 1.0–1.5 mg/dL/day if there is no renal function. It can be inferred from this information that we should focus on the adsorption property at lower concentrations. That is why the results for high creatinine concentrations are not presented in this article.

Hemolysis and protein adsorption

HR is a parameter that represents the extent of red blood cells being broken by the sample when in con-

tact with blood. That is, the more broken cells there are, the greater the HR value is. In other words, the smaller the HR value is, the better the compatibility is of the blood-contacting material. For medical applications, the HR value of the blood-contacting material must be below 5%.¹⁰ The results of hemolysis testing (shown in Table V) show that HR is above 5% for powdered AC (HR = 8.9%), whereas the HR value of PES-AC hybrid beads is quite close to zero. The low value of HR is one of two pieces of evidence for the good blood compatibility of the PES-AC hybrid beads presented in this article.

The first event to occur when blood comes into contact with a foreign body is the adsorption of plasma proteins onto the surface. Deposited proteins on the surface of materials may initiate coagulation and thrombogenesis and complement activation. Therefore, prevention of protein adsorption is crucial for blood-contacting materials.¹⁴ Hydrophilicity is beneficial in reducing the protein adsorption. The protein adsorption ratios for all the samples were not more than 5% from a 100 mg/dL BSA solution within 10 h. The adsorbed amount of BSA was calculated to be less than 2 mg/g.

The influence of the presence of albumin protein on the creatinine adsorption has also been evaluated in this work. The presence of protein slightly affects the creatinine adsorption rate and capacity (the removal ratio decreases 5–10%), mainly because of the higher viscosity and lower diffusion rate of the solution. However, the effect is not significant enough to hinder the potential application of the PES-AC hybrid beads in blood purification.

TABLE V
HR Measurement Results

Sample	Absorbance	HR (%)
Powdered AC	0.135 ± 0.002	8.90 ± 0.13
PES-AC75	0.030 ± 0.002	0.00 ± 0.05
PES-AC75-PG2.0	0.044 ± 0.002	0.62 ± 0.04
AN	0.037 ± 0.002	—
AP	1.167 ± 0.002	—

The data are expressed as the mean plus or minus the standard deviation of three independent measurements.

CONCLUSIONS

This is the first time that the preparation of PES-AC hybrid beads through a liquid-liquid phase-separation technique has been proposed and that its creatinine adsorption properties and some properties related to their blood compatibility have been evaluated. The successfully prepared porous beads exhibit good performance in creatinine adsorption, hemolysis, and protein adsorption tests. As expected, the adsorption rate and capacity of creatinine increase with an increase in the proportions of AC and added PG during the preparation process. The mass-transfer model has been applied to the experimental data for the analysis of the kinetic results. The experimental creatinine adsorption isotherms are adequately fitted with both Langmuir and Freundlich equations.

Because the pore structure of AC is tailored and the surface chemistry can be modified, molecules of different sizes and chemical natures can be removed by corresponding types of AC. Thus, PES-AC hybrid beads can be further investigated for the further ascertainment of the blood compatibility and for improvements to the properties by, for example, changes in the types of ACs embedded in the polymer matrix, and in this way, the application field can be extended. It is expected that PES-AC hybrid beads may become promising materials used as adsorbents in devices such as

hemoperfusion columns for the purification of blood, plasma, or other biological media.

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