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MACROPOROUS POLYETHYLENIMINE GEL-COATED ON ACRYLONITRILE-DIVINYLBENZENE COPOLYMER: A GRANULAR SORBENT OF HIGH CAPACITY AND FAST KINETICS

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ABSTRACT

Gel coating of polyethylenimine (PEI) resin was performed on macroporous polyacrylonitrile (PAN) granules by a Cu(II)-mediated chemical process, which can be easily extended to any type of PAN substrate, including fibers, fabrics, and films. The process, named CR Process of Gel Coating, has been modified in the present work for imparting a high degree of macroporosity to the gel coat to enhance the sorption kinetics and to improve resistance to organic fouling. The process produces a thin, firm coating of PEI that is cross-linked with glutaraldehyde and rendered macroporous by acid decomposition of pre-deposited $CaCO_3$ on a PAN substrate that has been chemically modified a priori by limited hydrolysis with NaO-HH_2O_2. Designated as HYPAN(Na^+).. [PEI.XG], the gel-coated granular, macroporous sorbent affords nearly full at-

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tainment of the theoretical proton capacity of the coated resin and exhibits significantly faster attainment of equilibrium sorption than does the conventional bead-form ion exchanger. *p*-Toluenesulfonic acid (PTSA) and $CuSO_4$ were used as test sorbates for comparing the performance of the gel-coated sorbent with Reillex 425, a commercial poly(4-vinylpyridine) (PVP) resin. In sorbate solutions of relatively low concentration (<2 mmol/L), the gel-coated sorbent had 2 to 3 times higher sorption of PTSA and Cu(II) than did the PVP resin beads. Large differences were also observed in sorption rates of gel-coated beads and conventional whole-resin beads. Thus, under similar conditions, the initial rate of attainment of equilibrium sorption on HYPAN(Na^+)..[PEI.XG] was nearly twice that on PVP in both PTSA and $CuSO_4$ solutions. Application of the shell-core model equation to the initial sorption rate data yields for the gel-coated particles diffusivity values that are 2 to 3 times higher than those obtained for PVP resin beads.

INTRODUCTION

The important properties of ion-exchange resins that influence their applications are resin capacity, rate behavior, durability, and sorption selectivity. While selectivity is basically an attribute of the resin functional groups, the other 3 properties are largely determined by the physical characteristics and morphology of the sorbent. The inaccessibility of many sorption sites buried inside the resin matrix of conventional bead-form sorbents, especially those synthesized from functional group–containing polymers, e.g., poly(4-vinyl pyridine) and polybenzimidazole, often contribute to the measured sorption capacity being much less than the theoretical capacity (1,2), and this difference generally increases with the increase in the sorbent particle size. The inaccessibility of sorption sites in the interior of resin beads also contributes to slower kinetics. As the diffusion path in the resin matrix becomes longer and more tortuous with increasing conversion, the rate of sorption decreases, often necessitating that the sorbent be in prolonged contact with sorbate to reach the equilibrium capacity. The sluggishness of sorption may become acute in the case of large sorbate species, as has been demonstrated strikingly in the sorption of plutonium nitrate onto a weak-base anion-exchange resin, which required an excess of 500 hours to reach equilibrium (3).

Shell functionalization has been presented by several workers as a means to overcome the problem of relative inaccessibility of active sites in the resin-bead interior. Different approaches have been used to prepare shell-functionalized sorbents. In one approach (4), monomers were polymerized on cross-linked polymer particles and subsequently the outer polymeric shell was functionalized. Another approach (5) is based on preferential functionalization of the most readily accessible sites in the outer layers of the resin beads, such as through the use of a reagent system and a particulate resin in which the functionalization rate is faster than the rate of diffusion of the reagent and termination of the reaction when the most readily accessible sites are functionalized.

We developed (6–9) a simple process of making shell-functionalized sorbents in which prefunctionalized reactive resins were gel coated on a solid support, such as silica or nonreactive organic resin, using copper (II) as a transient host. This copper-mediated process, named CR process of gel coating, employs Cu(II) host ions preloaded on a solid substrate, such as silica (6,7) or macroreticular bead-form organic polymers (8) to build a surface layer of sorbent resin that is then stabilized through reactions with a suitable cross-linking agent before it leaches out the host copper ions. The process gives thin, uniform, firmly adherent coating of the sorbent polymer on a solid substrate of any physical shape and geometry. However, polymers that readily react with Cu(II) and can readily undergo cross-linking reactions with suitable reagents can be used for gel coating by this process, which yields sorbents of both high capacity and fast kinetics. Thus, a sorbent prepared through by gel coating poly(4-vinyl pyridine) on silica and the application of 1,4-dibromobutane as the cross-linking agent showed (6) a significant increase in the rate of sorption and elution compared to conventional bead-form resins in the sorption of UO_2SO_4 from dilute aqueous solutions at mildly acidic pH ($\geq$4). A similar process was later used for gel coating polyethyleneimine (PEI) on silica with glutaric dialdehyde (7) and a diepoxide (8) as cross-linking agents.

However, coating on inert organic base resin requires an initial surface functionalization to afford preloading of Cu(II), which acts as host ions to attract functionalized polymers from an aqueous solution onto the base resin. The formed outer gel layer is then stabilized by cross-linking and subsequent acid leaching to remove the Cu(II) host molecules. Thus, polystyrene resin beads have been partially oxidized, creating carboxyl groups to bind the copper (II) hosts (9). In the present work, polyacrylonitrile (PAN) was used as the base resin to make gel-coated sorbents, as it allowed us to explore the exciting possibility of producing a gel-coated sorbent as a fiber, film, or woven fabric for a wide variety of applications. The surface functionalization of PAN is easily carried out by hydrolysis (10) through NaOH and H_2O_2. In the present paper, we deal with PEI-coated particulate sorbents based on PAN. Sorbents made with PAN fiber and fabric as the base materials will be dealt with in a later communication.

While gel-type (or microporous) exchangers are essentially homogenous solid phases with closely spaced functional groups, a macroporous ion exchanger may be viewed as an ensemble of tiny microgels with an interconnected network of pores. Macroporous ion exchangers have greater durability, resistance to oxidation, and less susceptibility to fouling by neutral organic matters compared to gel-type exchangers. These exchangers are consequently gaining greater acceptance in environment applications. The CR process produces strongly adherent gel-type coating on organic core resin. The present paper describes a modification of the process that gives rise to a high degree of macroporosity in the surface-coated resin layer that enhances the kinetics and provides greater durability and resistance to organic fouling.

In our study, a granular, macroporous, copolymer of acrylonitrile (80%) and divinylbenzene (20%), prepared by suspension polymerization, was hydrolyzed to partially convert the nitrile groups to carboxylate functionality and then coated with macroporous, cross-linked PEI resin by the modified CR process. The performance of the resulting granular sorbent, in respect to sorption capacity and kinetics, was compared with that of the commercial resin Reillex 425, which was chosen because it is a macroporous weak-base resin, poly(4-vinylpyridine), and is derived from a monomer that itself carries the functional group. A strong organic acid, *p*-toluenesulfonic acid, and a common chelating ion, Cu(II), were used as test sorbates in this study.

EXPERIMENTAL

Sorbent

The macroporous acrylonitrile-divinylbenzene copolymer used in this work for making gel-coated sorbents was synthesized by suspension polymerization. A typical batch comprised of 80 g acrylonitrile (purified by distillation), 20 g divinylbenzene (Aldrich), 1.2 g AIBN, 200 mL ethyl acetate, 12 g sodium dodecyl sulfate, and 600 mL water was deoxygenated by passing nitrogen through the mixture which was heated to 60°C for 90 minutes and then to 80°C for 30 minutes. The suspension was sieved to collect 20–60 mesh particles. The elemental composition of this copolymer product is given in Table 1, and the

Table 1. Comparison of Elemental Compositions

	Elemental Composition, % (wt/wt)			
Resin	C	H	N	O
PAN[a]	72.3	5.9	20.6	N.A.
PEI.XG	56.6	9.2	16.4	17.1
HYPAN(H^+)[b]	70.4	6.2	16.9	7.1
HYPAN(Na^+)..[PEI.XG][c]	66.1	7.1	14.9	10.4

[a] Acrylonitrile-divinylbenzene copolymer.
[b] Partially hydrolyzed PAN in H^+ form.
[c] Hydrolyzed PAN-based gel-coated sorbent in free base form.

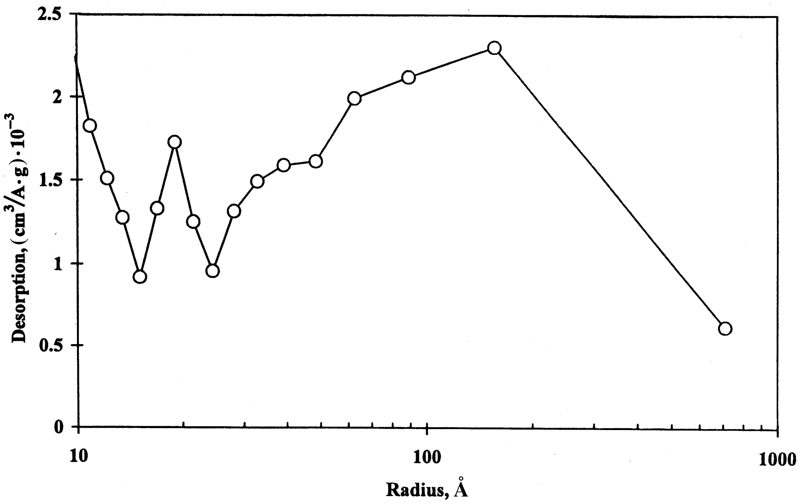

Figure 1. Pore size distribution in copolymer of acrylonitrile and divinylbenzene synthesized by suspension polymerization and designated as PAN.

pore size distribution of the dry resin is shown in Fig. 1, which reveals a reasonably high degree of macroporosity.

The nitrile group in PAN was partially converted to –CO_2Na by treatment with an aqueous NaOH solution that contained approximately 12% H_2O_2. In a typical procedure, 25 mL of 4 N NaOH and 20 mL of 30% H_2O_2 were mixed and added with continuous agitation to 40 g of PAN in a glass bowl placed on a steam bath. The reaction started quickly with considerable foaming. When the foaming subsided, the solution was decanted off and a fresh mixture of 25 mL NaOH and 20 mL H_2O_2 was added to the polymer while continuously stirred. The process was repeated 2 more times. The resin was washed with water and treated with excess 1N HCl. The carboxyl content of the partially hydrolyzed PAN in acid form, designated as HYPAN(H^+), was determined by treating a weighed amount with excess NaOH followed by estimation of the amount NaOH consumed. The carboxyl content thus determined was 2.1 mEq/g dry resin, which corresponds to approximately 14% hydrolysis of the –CN groups in PAN. The Fourier Transform Infrared Spectroscopy (FTIR) spectra of PAN and HYPAN(H^+) are compared in Fig. 2.

The procedure used for making a PAN-based sorbent with macroporous PEI coating is shown in Fig. 3. All the steps in this procedure, except Step 1 were performed at the ambient temperature. The partially hydrolyzed PAN in Na^+ form, designated as HYPAN(Na^+), was treated with a 5% $CaCl_2$ solution (Step 2) converting the resin to HYPAN(Ca^{2+}). After it was washed with water for removal of the residual $CaCl_2$ solution, HYPAN(Ca^{2+}) was treated with a 10% Na_2CO_3 so-

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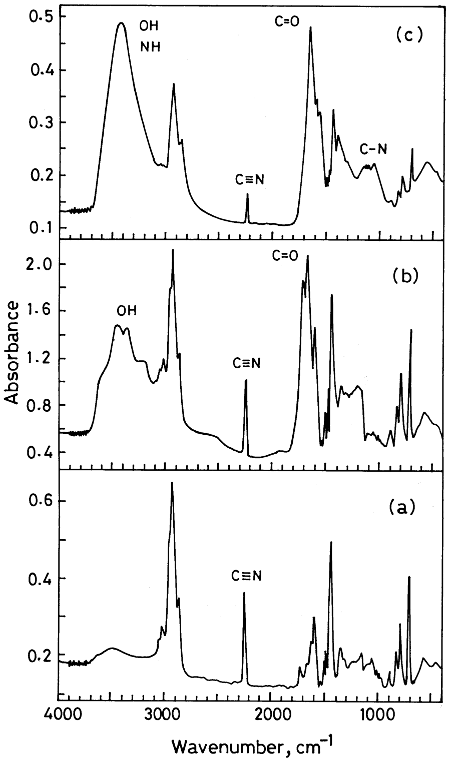

Figure 2. FTIR spectra of (a) PAN; (b) partially hydrolyzed product of PAN, designated as HYPAN(H^+); and (c) gel-coated sorbent PAN(Na^+)..[PEI.XG].

lution (Step 3), which resulted in instantaneous deposition of $CaCO_3$ on the macroporous resin and the resin was the simultaneously converted back to HYPAN(Na^+). The Na^+ form of the resin was then treated with 5% $CuSO_4$ solution (Step 4), which rapidly converted the HYPAN(Na^+) to HYPAN(Cu^{2+}) as could be seen from the blue appearance. The color became deeper on treatment (Step 5) of HYPAN(Cu^{2+}) with a 2% aqueous solution of PEI (Aldrich) of average M.W. = 25 000. The resin granules were quickly covered with a PEI gel layer as Cu^{2+} was anchored to the surface by the carboxylate functionality and, in the process, embedded the predeposited $CaCO_3$ fine solid. The PEI gel layer was then rendered acid-insoluble through treatment (Step 6) with 2% aqueous solution of glutaraldehyde for 4 hours. The granular product at this stage comprised partially hydrolyzed PAN coated with Cu^{2+}-mediated acid-insoluble PEI gel that contained the embedded fine precipitate of $CaCO_3$, which was then decomposed, generating

CO_2 by treatment (Step 7) with 4N HCl. Acid treatment imparted a high degree of porosity to the gel coat and caused Cu^{2+} to leach out of the gel layer. A final treatment with 0.5 N NaOH converted the PEI top layer into free-base form and the underlying carboxylic functionality to the NA^+ form. This final sorbent was designated HYPAN(Na^+)..[PEI.XG] in which PEI.XG represents the macroporous coating of PEI cross-linked with glutaraldehyde. The elemental composition of this sorbent shows higher oxygen content than does HYPAN(H^+) due to the coating of PEI.XG, while its IR spectrum, shown in Fig. 2, confirms the incorporation of imine groups.

To verify that macroporosity is imparted by the modified CR process of gel coating, we prepared a PEI.XG control resin by replacing HYPAN(Cu^{2+})($CaCO_3$) of Step 5 with SiO_2(Cu^{2+})($CaCO_3$) in the scheme shown in Fig. 3. The SiO_2(Cu^{2+})$CaCO_3$ was prepared through treatment with a $CaCl_2$-impregnated SiO_2 gel, of similar calcium content as HYPAN(Ca^{2+}), with Na_2CO_3 solution, after which the required amount of Cu^{2+} was loaded to match the Cu^{2+} content of

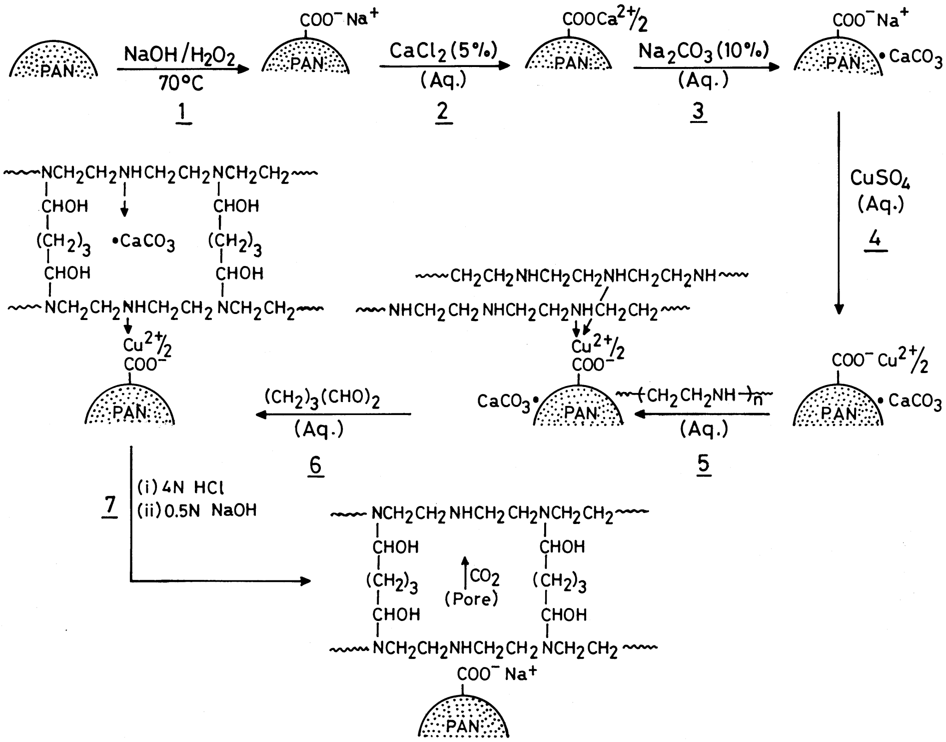

Figure 3. Procedure (schematic) of the modified CR process of gel coating to produce macroporous gel coat of PEI on partially hydrolyzed granular PAN.

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HYPAN(Cu^{2+})(CaCO$_3$). The control resin PEI.XG was recovered from the final product SiO$_2$..[PEI.XG] after the silica support was dissolved with NaOH. The pore size distribution in the control resin, measured with a Quantachrome Autosorb machine, is shown in Fig. 4. A large fraction of the pores in the dry resin was in the range of 40–400 Å. The pore size of the resin coating in the wet sorbent, as used in sorption experiments, would be expected to be much larger and the resin may thus be described as macroporous.

Because the sorbent HYPAN(Na$^+$)..[PEI.XG] has–$CO_2^-Na^+$ active groups that also contribute to sorption, a control sorbent HYPAN(Na$^+$) was prepared by following the same sequence of steps as outlined in Fig. 3, but we omitted the gel-coating steps nos. 5 and 6. The proton capacity of this control, determined by equilibration in 0.4 N HCl solution followed by estimation of the amount of acid consumed, was 1.50 mEq/g dry sorbent. The proton capacities of the sorbent HYPAN(Na$^+$)..[PEI.XG] and the control resin PEI.XG, also determined by this method, were found to be 2.52 and 8.25 mEq/g dry solid, respectively. The PEI.XG content of HYPAN(Na$^+$)..[PEI.XG] was thus estimated to be 100(2.52–1.50)/(8.25–1.50) or 15% (wt/wt). The nitrogen content (16.5%) of the sorbent, calculated on the basis of a 15% gel-coat content of the HYPAN(Na$^+$)..[PEI.XG] is in fair agreement with the nitrogen content (14.9%) determined by elemental analysis (Table 1).

For comparison of resin performance, Reillex 425 polymer, obtained from Reilly Industries, Inc (Indianapolis, Ind, USA), was used in this work. It is a spher-

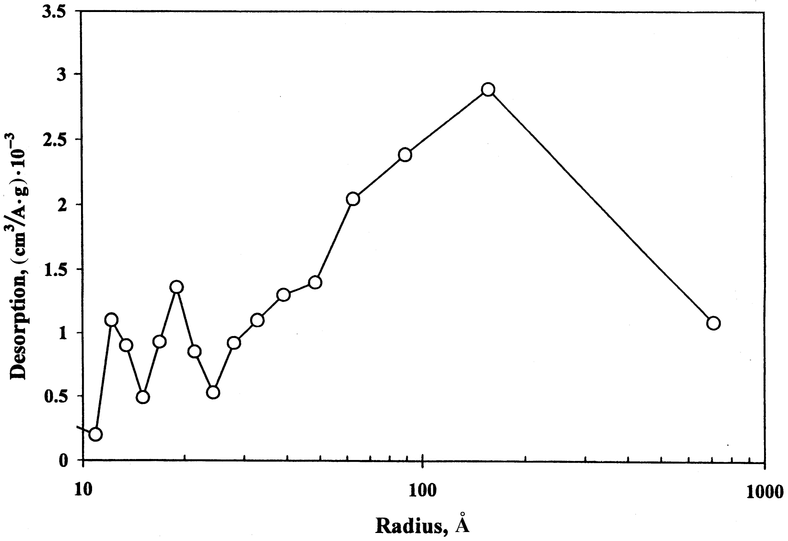

Figure 4. Pore size distribution in PAN(Na$^+$)..[PEI.XG].

Table 2. Properties of Sorbents Used for Comparison of PTSA and Cu(II) Sorptions

	Sorbent	
Properties	HYPAN(Na^+)..[PEI.XG]	PVP
Water content (g/g wet sorbent)	0.65	0.55
Particle diameter (mm)		
Wet	0.24–0.75	0.12–0.85
Dry	0.22–0.72	0.11–0.81
Surface Area (m^2/g dry)	121	90
Pore volume (cm^2/g dry)	1.86	1.22
Proton capacity (mEq/g dry)	2.52	4.90

Reillex 425 is the commercial name of the PVP used.

ical (18–50 US mesh) bead-form, macroporous poly(4-vinylpyridine) (PVP) resin of average pore size 600 Å with a divinylbenzene content of 25%. The resin was washed thoroughly with distilled water and partially dewatered and stored in wet condition with a moisture content of 55% (wt/wt). The capacity of the resin, determined by the conversion of a weighed amount into chloride salt by treatment with HCl and subsequent estimation of the amount of acid consumed, was 4.9 mEq/g dry resin.

The properties of the gel-coated free-base sorbent HYPAN(Na^+)..[PEI.XG] and the commercial free-base resin Reillex 425 are compared in Table 2.

Sorbates

Because the sorption capacity of the gel-coated resin in HYPAN(Na^+). .[PEI.XG] is due to the weakly basic chelating resin PEI, an acidic organic molecule and a chelating metal ion were used as test sorbates. *p*-Toluenesulfonic acid (PTSA) used in the work was a monohydrate of 99% purity (Aldrich), and copper sulfate pentahydrate was of 99.99% purity (Aldrich).

Analysis

The proton uptake of the sorbents was determined through measurements of the residual proton concentration in solution by titration with standard alkali. For analysis of PTSA in aqueous solution, visible spectroscopy (Varian Spectrophotometer Model Cary 219) was used. A simple and sensitive method (11) based on oxidation of the organic compound by dichromate in sulfuric acid medium and spectrophotometric measurement of the resulting Cr(III) was calibrated with standard solutions of PTSA in the concentration range employed in the work. For the estimation of Cu(II), a colorimetric method based on the development of a blue color with ammonia was used. For applying this method, a calibration chart was prepared using Cu(II) standard solutions and measuring absorbance at 612 nm of ammoniacal solutions of Cu(II) that contained a fixed concentration of NH_4OH.

Sorption Experiments

Sorption measurements were made separately with HYPAN(Na^+)..[PEI.XG], PVP, and the control sorbents HYPAN(Na^+) and PEI.XG using PTSA and Cu(II) as test sorbates. For equilibrium sorption measurements, a small-scale dynamic contact between the sorbent and the sorbate solution of specified composition was effected in tightly stoppered flasks at 25°C on a gyrotory shaker for 2 hours. The extent of sorption was calculated from the residual concentration of the sorbate in the equilibrated solution. A range of concentrations of the 2 sorbates was used.

For the measurement of sorption rates, wet-sieved sorbent beads of narrow size range were used. A rectangular basket (20 mm × 10 mm × 40 mm), made of polypropylene screen (0.45 mm opening), was used to hold the granular sorbent. The basket was rotated by attaching it to the shaft of a variable speed motor while the sorbate solution was brought into contact for a specified period. This arrangement allowed instantaneous separation of the sorbent from the sorbate solution at any specified time and analysis of the sorbate residual concentration for determining the rate of sorption. A fresh amount of sorbent from the same stock was used for each experiment.

Dynamic contacts between the sorbent and the solution were effected at different stirring speeds through use of a low solution concentration (2.0 mmol/L) to determine the minimum speed above which the sorption rate was not influenced by the degree of agitation and hence not controlled by film diffusion. All kinetic experiments were performed at stirring speeds (200–300 rpm) well above the minimum.

RESULTS AND DISCUSSION

Sorption Isotherm

The equilibrium sorptions of PTSA and Cu(II) by the gel-coated granular sorbent HYPAN(Na^+)..[PEI.XG] are compared in Figs. 5 and 6 with those of the commercial bead-form PVP resin Reillex 425, which were measured under simi-

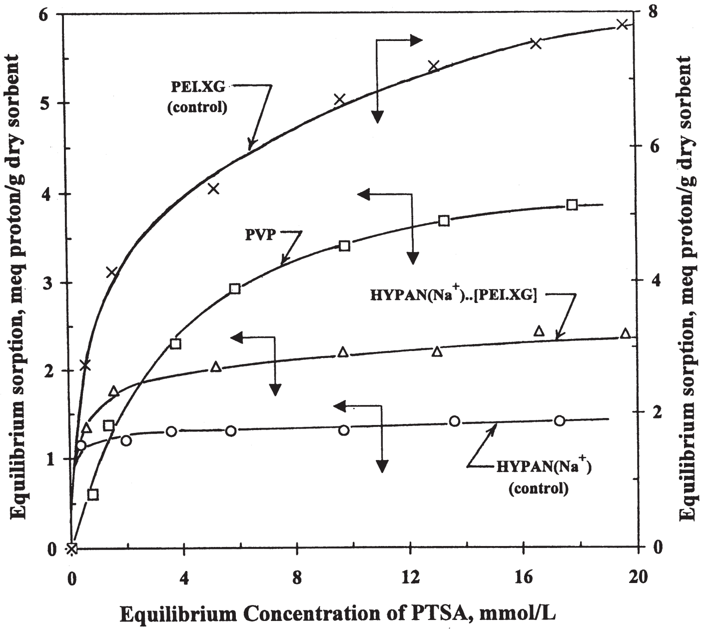

Figure 5. Sorption isotherms for PTSA on different sorbents. Sorbent loading 4.0 g(wet)/L; pH 2.0–2.6; temperature 25°C. Note that the control curve HYPAN(Na$^+$) represents uptake of only protons exchanged from PTSA (Eq. (1)) and HYPAN(Na$^+$)..[PEI.XG] both PTSA and protons exchanged from PTSA Eqs. (2) and (3) were adsorbed while the curves PVP and PEI.XG represent only the uptake of PTSA.

lar conditions. The figures also contain the sorption data measured on the control sorbents HYPAN(Na$^+$) and PEI.XG.

PTSA, a strong acid, can be represented by H$^+$ A$^-$, and the ion exchange on HYPAN(Na$^+$) can be written as

$$P\text{–CO}_2^-\text{Na}^+ + \text{H}^+\text{A}^- \leftrightarrow P\text{–CO}_2\text{H} + \text{Na}^+\text{A}^- \tag{1}$$

where *P* represents polyacrylonitrile base resin.

The curve labeled HYPAN(Na$^+$) in Fig. 5 represents the uptake of protons by the control sorbent, that is, only those protons exchanged from PTSA according to Eq. (1). The curve labeled HYPAN(Na$^+$)..[PEI.XG], represents the uptake of PTSA by the PEI.XG gel according to Eq. (2) as well as that of protons by the –CO$_2^-$Na$^+$ in the sorbent in accordance with Eq. (3).

$$\overline{>\text{NH}} + \text{H}^+\text{A}^- \leftrightarrow \overline{>\text{NH}_2^+\text{A}^-} \tag{2}$$

$$P\text{–CO}_2^-\text{Na}^+ + \text{H}^+\text{A}^- \leftrightarrow P\text{–CO}_2\text{H} + \text{Na}^+\text{A}^- \tag{3}$$

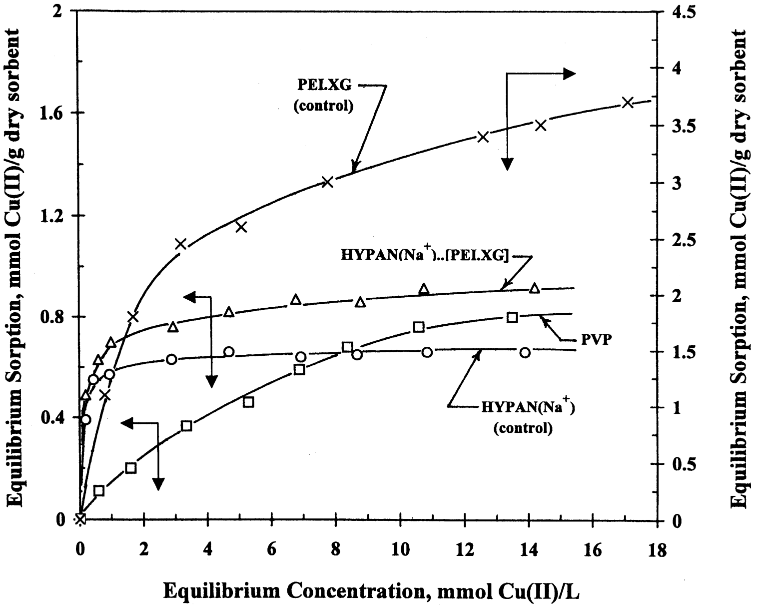

Figure 6. Copper (II) sorption isotherms on different sorbents. Sorbent loading 4.0 g(wet)/L; pH 4.8–5.0; temperature 25°C. Note that the HYPAN(Na$^+$)..[PEI.XG] and PEI.XG curves represent sorption values for the gel-coated granular sorbent and gel-coat control resin, respectively, and the HYPAN(Na$^+$) and PVP curves represent those for partially hydrolyzed polyacrylonitrile (control) and poly(4-vinylpyridine), respectively.

where the overbar has been used to represent the gel-coat phase. Thus, in Eq. (2), >NH represents the free imine groups in the gel coat. These groups alone contribute to the uptake of toluenesulfonate ions by HYPAN(Na$^+$)..[PEI.XG].

Correcting for the proton removal by reaction (Eq. 3) in accordance with the control curve HYPAN(Na$^+$), we computed the PTSA uptake by the PEI.XG gel coat from knowledge of the gel-coat content of HYPAN(Na$^+$)..[PEI.XG]. Such calculated values agree reasonably well with the measured uptake of PTSA by the control resin PEI.XG plotted in Fig. 5.

Figure 6 shows that the Cu(II) sorption, as expected, is higher on the gel-coated sorbent HYPAN(Na$^+$)..[PEI.XG] than on the HYPAN(Na$^+$) control. However, the difference in sorption magnitudes is lower than in the case of PTSA and protons discussed above. The sorbed Cu(II) are shared by both –CO$_2^-$Na$^+$ and >NH sorption sites. Thus, among the 3 reactions (Eqs. 4–6) contributing to Cu(II) uptake, reaction (Eq. 6) corresponds to Cu(II) sharing between –CO$_2^-$Na$^+$ and >NH, and the hence loss of sorption capacity.

$$P\text{–}CO_2^-Na^+ + (1/2)Cu^{2+} \leftrightarrow P\text{–}CO_2^-\left(\frac{1}{2}Cu^{2+}\right) + Na^+ \tag{4}$$

$$\overline{>NH} + (1/2)Cu^{2+} \leftrightarrow \overline{>NH \rightarrow \left(\frac{1}{2}Cu^{2+}\right)} \tag{5}$$

$$P - CO_2^-Na^+\overline{NH<} + \frac{1}{2}Cu^{2+} \leftrightarrow P - CO_2^-\frac{1}{2}Cu^{2+} \leftarrow \overline{NH<} \tag{6}$$

To verify the above scheme, the Cu(II) sorption was also measured on the control resin PEI.XG. These values, plotted in Fig. 6 as the curve labeled PEI.XG, are as expected significantly higher than the Cu(II) capacity of the gel-coated resin that would be computed from the measured sorption on HYPAN(Na^+)..[PEI.XG].

All the equilibrium sorption data for PTSA and Cu(II) fitted well to the Langmuir isotherm equation. Defining the parameters A_s and K_b as the saturation sorption capacity (mmol sorbate/g dry sorbent) and the sorption binding constant (L/mol), respectively, the Langmuir isotherm is written as

$$x^* = \frac{(10^{-3}\,K_b)A_sC^*}{1 + (10^{-3}\,K_b)C^*} \tag{7}$$

where x^* is the equilibrium sorption (mmol sorbate/g dry sorbent) and C^* is the equilibrium sorbate concentration (mmol/L).

The values of A_s and K_b, determined by least squares fit of the sorption data in Figs. 5 and 6, are presented in Table 3. The binding of both PTSA and Cu(II) at the carboxylate site is much stronger than the binding at the amine sites. Thus the K_b values for sorption on HYPAN(Na^+)..[PEI.XG], which involves sorption at

Table 3. Langmuir Isotherm Parameters for Sorption of PTSA and Cu(II) on Different Sorbents

	Langmuir Isotherm Eq. (7)		
Sorbate/Sorbent	A_s mmol/g Dry Sorbent	K_b L/mol	Correlation Coefficient
PTSA/HYPAN(Na^+)[a]	1.46	2813	0.999
PTSA/HYPAN(Na^+)..[PEI.XG)	2.50	1175	0.998
PTSA/PEI.XG[a]	8.42	466	0.993
PTSA/PVP	5.07	206	0.995
Cu(II)/HYPAN(Na^+)[a]	0.66	7256	0.999
Cu(II)/HYPAN(Na^+)..[PEI.XG]	0.93	2708	0.998
Cu(II)/PEI.XG[a]	4.16	387	0.995
Cu(II)/PVP	1.40	111	0.971

[a] Control.

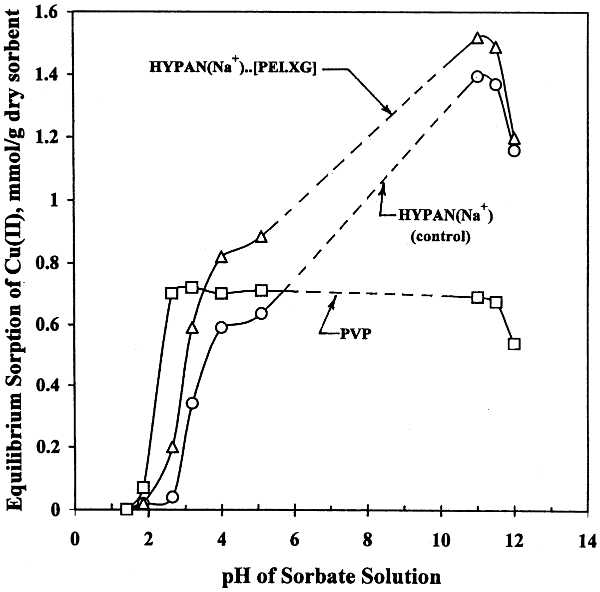

Figure 7. Effect of pH on equilibrium sorption of Cu(II) on HYPAN(Na^+).[PEI.XG], HYPAN(Na^+) control, and PVP at 25°C.

both carboxylate and amine sites, are significantly higher than those on PEI.XG and PVP, but are smaller than those on HYPAN(Na^+). The A_s value for Cu(II) sorption on PEI.XG is nearly one-half of the A_s value for PTSA sorption on the same resin, implying that on average 2 amine sites are used for each Cu(II) and that all sites are accessible for Cu(II) sorption. On the contrary, a comparison of the corresponding A_s values on PVP reveals that only approximately 50% of the sites in it are available for Cu(II) sorption. This highlights the greater accessibility of sorption sites produced by gel coating.

Effect of pH

The effect of pH, which was measured only for Cu(II) sorption on HYPAN(Na^+), HYPAN(Na^+)..[PEI.XG], and PVP resins, is shown graphically in Fig. 7. While the Cu(II) sorption on all the sorbents falls sharply at $pH < 2.0$, above this pH PVP is seen to have much greater tolerance to pH variation than do the other 2 resins, and the sorption decreases only at $pH > 11$ in ammoniacal medium. The Cu(II) sorption on both HYPAN(Na^+) and HYPAN(Na^+)..[PEI.XG] in ammoniacal medium increased markedly, indicating that $Cu(NH_3)_4^{2+}$ has much greater affinity than $Cu(H_2O)_4^{2+}$ on the carboxylate anionic sites. While

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the sorption on HYPAN(Na^+) in the presence of ammonia takes place by the ion-exchange reaction

$$P\text{–}CO_2^-Na^+ + \frac{1}{2}Cu(NH_3)_4^{2+} \leftrightarrow P\text{–}CO_2^-\left[\frac{1}{2}Cu(NH_3)_4^{2+}\right] + Na^+ \tag{8}$$

The sorption on HYPAN(Na^+)..[PEI.XG] takes place both by this reaction and by the amine coordination to the cuprammonium complex ion:

$$\overline{>NH} + Cu(NH_3)_4^{2+} \leftrightarrow \overline{>NH \rightarrow Cu(NH_3)_3^{2+}} + NH_3\ (H_2O) \tag{9}$$

The greater basicity of $>NH$ ($pK_b = 3.2$) compared to NH_3 ($pK_b = 4.7$) facilitates this reaction and the sorption decreases only slightly at $pH > 11$.

Effect of Common Ions

The equilibrium sorptions of Cu(II) on HYPAN(Na^+), HYPAN(Na^+)..[PEI.XG], and PVP in the presence of varying concentrations of Na_2SO_4 and NaCl are plotted in Figs. 8 and 9, respectively. The sorption preference in these plots has been defined by

$$\text{Preference (\%)} = \frac{\text{Sorption in presence of salt}}{\text{Sorption in absence of salt}} \times 100 \tag{10}$$

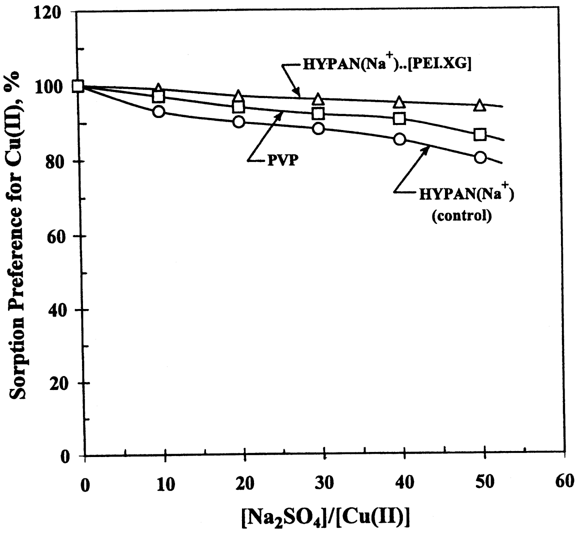

Figure 8. Plot of sorption preference for Cu(II) versus mol ratio of Na_2SO_4/Cu(II) in the substrate solution at temperature 25°C.

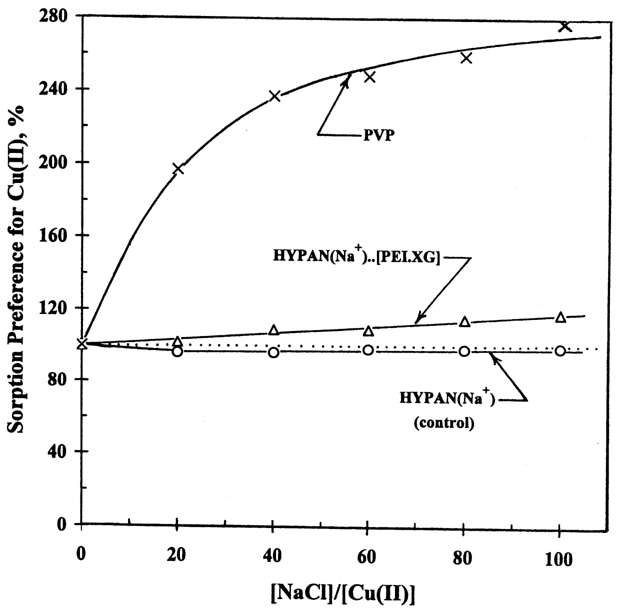

Figure 9. Plot of sorption preference for Cu(II) versus mol ratio of NaCl/Cu(II) in the substrate solution at 25°C.

The sorption data in Fig. 8 show that Na_2SO_4 has very little stripping effect on PVP and HYPAN(Na^+)..[PEI.XG], which is explained by the sorption being wholly or largely by a complexing mechanism; however, the effect is relatively large for HYPAN(Na^+) on which the sorption occurs solely by cation exchange at the carboxylic site.

Due to the complexing nature of the Cl^- ion, NaCl can produce markedly different effects on ionic and chelating sorbents. Though HYPAN(Na^+) is a cation exchanger, the sorption is little affected even by high concentration of NaCl in the substrate solution due to very strong binding of Cu^{2+} to the carboxylate ion, as shown by the markedly high value of K_b (Table 3). The effect of Cl^- on the Cu(II) sorption by PVP is particularly noteworthy for its enhancing effect. For example, in a 10 mmol/L $CuSO_4$ solution the Cu(II) sorption on PVP increases by nearly 200% in the presence of 1 mol/L NaCl. Because in a variety of complex anions, such as $(CuCl_3)^-$ and $(CuCl_4)^{2-}$, are formed in the presence of Cu^-, the copper chloride can be regarded as the complex copper salts (12), such as $Cu[CuCl_3]_2$ and $Cu[CuCl_4]$, the sorption on PVP can be represented by

$$\overline{>N} + Cu[CuCl_3]_2 \quad \leftrightarrow \quad \overline{>N \rightarrow Cu[CuCl_3]_2} \tag{11}$$

$$\overline{>N} + Cu[CuCl_4] \quad \leftrightarrow \quad \overline{>N \rightarrow Cu[CuCl_4]} \tag{12}$$

to account for the significantly enhanced Cu(II) uptake. The distinct green color of PVP(Cu^{2+}) in the presence of a high concentration of Cl^- confirms the presence of $(CuCl_4)^{2-}$, which is a green anion. However, the Cu(II) sorption on HYPAN(Na^+)..[PEI.XG] under similar conditions increases by only about 20% (Fig. 9). This smaller effect is at least partly due to the significant amount of sorption caused by ion exchange at the carboxylate active site.

Sorption Rate Behavior

For rate measurements, the 2 sorbents HYPAN(Na^+)..[PEI.XG] and PVP, used for comparative study, were wet sieved to obtain the same narrow range of particle size 0.50–0.90 mm. The fractional attainment of equilibrium sorption was measured as a function of time under identical conditions through a rotational speed (200–300 rpm) of the sorbent basket well above the experimentally determined minimum for elimination of film diffusional resistance. The rates of sorption, compared in Figs. 10 and 11 for PTSA and Cu(II), respectively, reveal sig-

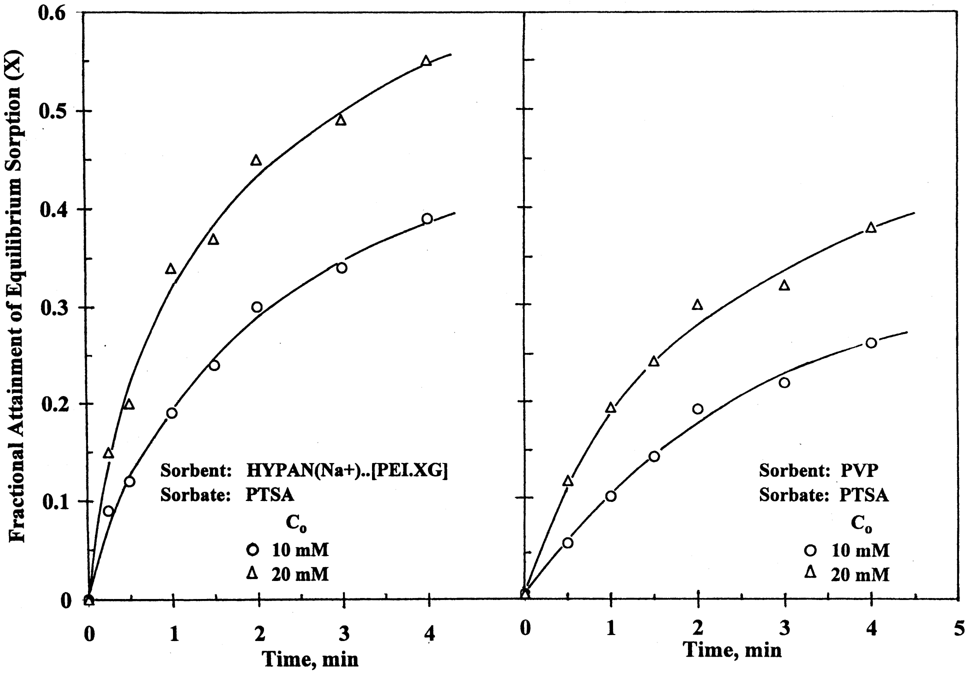

Figure 10. Comparison of rates of sorption on HYPAN(Na^+)..[PEI.XG] and PVP, both of particle size 0.5–0.9 mm, in PTSA solutions of different concentrations C_o. Sorbent loading 4.0 g(wet)/L; pH 2.0; temperature 25°C; vigorous agitation.

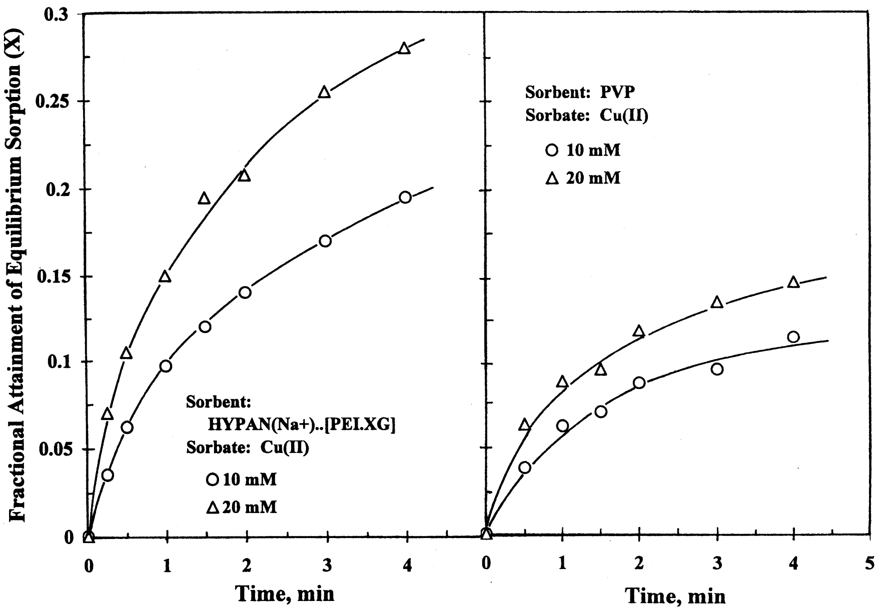

Figure 11. Comparison of rates of sorption on HYPAN(Na$^+$)..[PEI.XG] and PVP, both of particle size 0.5–0.9 mm in $CuSO_4$ solutions of different concentrations, C_o. Sorbent loading 4.0 g(wet)/L; pH 4.8; temperature 25°C; vigorous agitation.

nificantly faster kinetics on the macroporous gel-coated sorbent; the initial rate of sorption on this sorbent was nearly twice that on the commercial resin PVP. However, both sorbents remove the strong acid PTSA much faster than does Cu(II) from the solution, which would be attributed to significantly faster diffusion of protons compared to Cu(II) ions.

The basket reactor employed for the sorption rate study was especially suitable for the "interruption test," which has been described as the best technique for distinguishing between particle and film diffusion control (13). For the test performed separately for PTSA and Cu(II) sorbates, the sorbent basket was removed from the sorbate solution for a brief period (5 minutes) and then reimmersed. A change in the momentary sorption rate following the interruption indicated particle diffusion control (pdc) of the sorption rate under the experimental conditions employed.

The effect of external solution concentration on the sorption rate was measured because knowing it might help one find the controlling mechanism. The experiments were performed with relatively high concentration of sorbate in the external solution to reduce the effect of sorption reversibility. The data presented in Figs. 10 and 11 show that the external solution concentration in the relatively high range used in the present case has a significant effect on the rate of sorption. Such a concentration effect is not consistent with the predictions of the ordinary pdc model, but is in accord with the progressive shell-core or ash-layer model.

Sorption can be assumed to follow a shell-core scheme only if the reaction is irreversible and is fast compared to diffusion. However, several studies reported in the literature (14,15) have shown that when sorption occurs from dilute acid solutions on relatively weak base resins, a significant reversibility is observed in the sorption isotherm. Even in those cases where the feed solutions have relatively high concentrations of acids, regions in the vicinity may consist of advancing concentration fronts where the acid concentrations are low. Here the conventional shell-core model may fail to explain the sorption.

Bhandari, Juvekar, and Patwardhan (16) modified the shell-core model by incorporating the effect of sorption reversibility. However, the modified shell-core model retains the form of the conventional model and is described for the finite-bath experiment by the equation

$$\frac{6\bar{D}_{\mathrm{e}}}{\bar{C}_{\mathrm{e}}\bar{r}_0^2}\int_0^t C\,dt = X_{\mathrm{e}}\left[1 - 3\left(1 - \frac{X}{X_{\mathrm{e}}}\right)^{2/3} + 2\left(1 - \frac{X}{X_{\mathrm{e}}}\right)\right] \tag{13}$$

where $\bar{D}_{\mathrm{e}}$ is the effective shell diffusivity for sorption (assumed constant); C_{e} is the equilibrium concentration of the sorbed species in the resin (mmol/L); r_0 is the radius of the resin bead (cm); C is the concentration of the sorbate species in the solution at time t (seconds); X is the fractional attainment of equilibrium sorption at time t; and X_{e} is fractional conversion of resin at equilibrium, given by $x_{\mathrm{e}}/x_{\mathrm{s}}$, where x_{e} is the equilibrium sorption (mmol/g wet sorbent) corresponding to the sorbate concentration C and x_{s} is the saturation sorption capacity (mmol/g wet sorbent) determined from the sorption isotherm. Both X and X_{e} are functions of time.

The conventional shell-core model is based on the assumption that saturation of the shell ($X_e = 1$), which is in contrast compared to partial filling as described by the modified shell-core model. Thus for the same quantity of sorbed acid, the conventional model predicts a thinner shell and hence a shorter diffusion path than the modified shell-core model. The conventional model would therefore yield a smaller value of diffusivity, compared to the modified model, for the same rate of sorption.

In the present study, the sorption isotherms of both PTSA acid and Cu(II) clearly indicate that the sorptions tend to attain saturation levels at substrate concentrations greater than 10 mmol/L. Thus, at feed concentrations $C_{\mathrm{o}} \gg 10$ mmol/L one can assume that $X_e \approx 1$, especially in the initial period of sorption, so that the conventional form of the shell-core model can be expressed as follows:

$$\frac{6\bar{D}_{\mathrm{e}}}{\bar{C}_{\mathrm{e}}\bar{r}_0^2}\int_0^t C\,dt = [1 - 3(1 - X)^{2/3} + 2(1 - X)] \tag{14}$$

which also results on substituting $X_e = 1$ in Eq. 10.

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In terms of the "equivalent ratio," *w,* defined as the ratio of the total sorption capacity of the resin to the total sorbate content of the external solution, finite-solution volume experiments can be used to approximate "infinite solution volume (ISV)" conditions (17) for $w \ll 1$ mEq$_r$/mEq. For an ISV case, Eq. (14) can be simplified to

$$\left[\frac{6\bar{D}_e C}{\bar{C}_e \bar{r}_0^2}\right] t = [1 - 3(1 - X)^{2/3} + 2(1 - X)] \tag{15}$$

for fitting data in the low-conversion range.

The rate data of Fig. 10 for PTSA sorption that correspond to a relatively high feed concentration (20 mmol/L) were fitted to Eq. (14) by plotting the right hand side versus $\int_0^t Cdt$ for the 2 sorbents HYPAN(Na$^+$)..[PEI.XG] and PVP being compared. As can be seen from Fig. 12, a good linear fit was obtained for both the sorbents. The slopes of the linear plots were used to evaluate the effective diffusivities $\bar{D}_e$ for PTSA in the 2 sorbents. Because the gel-coated sorbent used for rate measurements was a mixture of different shaped particles, though belonging to a narrow size range, the radius of an equivalent sphere (18) having volume equal to the average volume of particles in the size fraction was used for the calculation

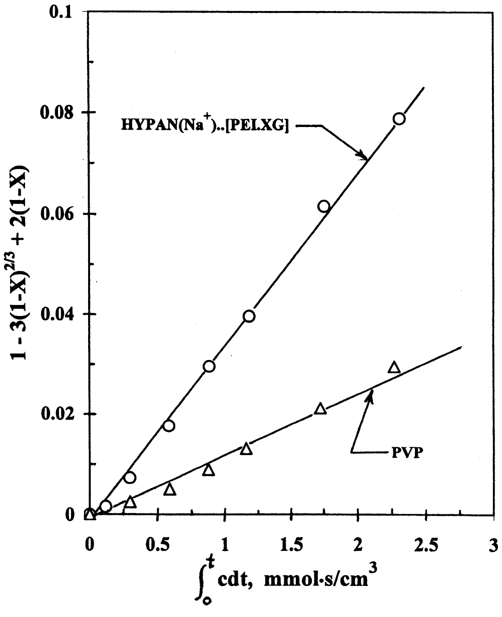

Figure 12. Test of Eq. (14) for the rate data in 20 mmol/L PTSA solution (Fig. 10).

Table 4. Effective Diffusion Coefficient in the Particle Phase at 25°C

	$\overline{D}_e$ for Sorbate, cm^2/s	
Sorbent	PTSA	Cu(II)
HYPAN(Na+)..[PEI.XG]	5.7×10^{-6}	0.5×10^{-6}
PVP	2.9×10^{-6}	0.18×10^{-6}

PVP used is Reillex 425.

of $\overline{D}_e$. The values recorded in Table 4 show that the gel-coated sorbent had about twice the diffusivity of the conventional bead-form PVP resin.

Because the kinetic data of Fig. 11 were obtained with experimental conditions such that $w \ll 1$, ISV conditions would be reasonably well approximated, especially in related low-conversion ranges. The data of Fig. 11 were therefore fitted to Eq. (15). As can be seen from Fig. 13, a good linear fit was obtained for the initial stages (up to 30%) of conversion. The slopes of the linear plots were used to evaluate the initial effective diffusivities of Cu(II) in the 2 sorbents. The values recorded in Table 4 show that, as would be expected, the Cu(II) diffusivities are much less than the proton diffusivities in the respective sorbents, and for both pro-

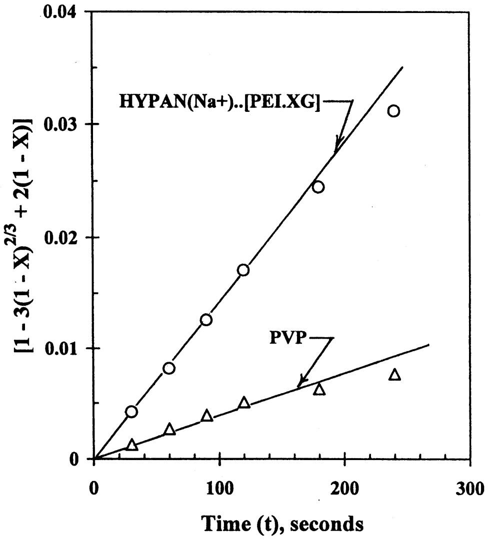

Figure 13. Test of Eq. (15) for the rate data in 20 mmol/L $CuSO_4$ solution (Fig. 11).

ton and Cu(II) the gel-coated sorbent HYPAN(Na^+)..[PEI.XG] had significantly higher diffusivities than did the bead-form PVP resin.

CONCLUSIONS

A method is described for the preparation of a gel-coated sorbent, HYPAN(Na^+)..[PEI.XG], for which PEI resin is gel coated on the particulate substrate HYPAN(Na^+) by a Cu(II)-mediated process, named CR process of gel-coating, cross-linked with glutaraldehyde and rendered macroporous by decomposition of predeposited $CaCO_3$, the substrate HYPAN(Na^+) being derived a priori from macroporous PAN by limited hydrolysis with NaOH-H_2O_2. The performance of this gel-coated sorbent, containing about 15% (wt/wt) of PEI.XG as a macroporous resin coating, is compared, in respect of sorption capacity and sorption rate, with a conventional bead-form PVP resin, Reillex 425, through the use of PTSA and Cu(II) as test sorbates. Even though the sorption is largely confined to the surface layer of PEI.XG resin of the gel-coated sorbent, while that in conventional PVP resin beads occurs globally, the sorption capacity of the gel-coated sorbent is significantly higher than that of PVP beads for both PTSA and Cu(II) in the range of low (<2 mmol/L) substrate concentrations. The difference is more marked between the PEI.XG gel-coat layer and the PVP resin beads, the former having more than 3 times higher sorption of PTSA and more than 10 times higher sorption of Cu(II) in sorbate solutions of relatively low concentration (<2 mmol/L).

The effect of pH on Cu(II) sorption is highly significant for both the gel-coated sorbent HYPAN(Na^+)..[PEI.XG] and the control sorbent HYPAN(Na^+); the sorption fell sharply in an acidic media at $pH < 3$, but increased by about 100% in a strongly ammoniacal medium (pH 11). This is attributed to the strong binding of $Cu(NH_3)_4^{2+}$ to the carboxylate sites in both the gel-coated sorbent and the control. However, sorption on PVP is not affected by pH in acidic media down to $pH \approx 2.5$ and in ammoniacal media until $pH \approx 11.5$.

A comparison of the sorption rate behavior of HYPAN(Na^+)..[PEI.XG] and PVP reveals that under similar conditions the initial rate of attainment of equilibrium sorption on the former is nearly twice that on the latter in both PTSA and $CuSO_4$ solutions. Application of the conventional shell-core model equation to the initial sorption rate data yields for the gel-coated particles diffusivity values that are 2 to 3 times higher than those obtained for PVP resin beads.

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