

A Thermally Regenerable Composite Sorbent of Crosslinked Poly(acrylic acid) and Ethoxylated Polyethyleneimine for Water Desalination by Sirotherm Process

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ABSTRACT: Crosslinked poly(acrylic acid) (XPAA) made by copolymerization of acrylic acid and ethylene glycol dimethacrylate in bulk was further reacted with 80% ethoxylated polyethyleneimine, and the latter insolubilized by treatment with glutaraldehyde. The resulting composite sorbent, XPAA(EPELXG), containing carboxylic acid groups and weakly basic tertiary amine groups in close proximity in the same resin bead exhibited thermally regenerable desalination property, simulating the well-known Sirotherm™ resins. For NaCl and MgCl₂, the sorbent has saturation capacities of 0.796 and 0.839 meq/g (dry) sorbent, respectively, at 30°C but less than 0.1 meq/g (dry) sorbent at 80–90°C. The equilibrium sorption data at 30°C fit well to both Langmuir and Freundlich isotherms for single-component sorption and to Butler-Ock-

rent and Jain-Snoeyink models for bicomponent sorption. Although the sorption of NaCl exhibits a plateau in the pH range of 4–5, that of MgCl₂ increases sharply above pH 4 because of additional sorption by cation exchange at the ionic sites formed at higher pH. The sorption rate data show characteristics of particle-diffusion controlled ion-exchange process, yielding diffusivity values of 1.0–1.3 × 10⁻⁶ cm²/s for NaCl and 3.0–3.5 × 10⁻⁷ cm²/s for MgCl₂, in the initial period at 30°C, with the diffusivity falling abruptly in both cases at higher conversions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2741–2750, 2009

Key words: desalination; ion-exchange resin; polyacrylic acid; polyethyleneimine; sirotherm resin; composite sorbent; sorption

INTRODUCTION

Salinity is one of the most widespread kinds of water pollution found in the world. The importance of the method of removing, at low cost, even small amounts of salinity from waters of marginal quality, such as brackish surface water, cannot be overemphasized. Desalting of brackish water can be achieved by several methods. These can be broadly classified into two groups. Methods in the first group remove water from the salt solution; these include reverse osmosis, distillation, and freezing processes. Methods in the second group remove salt from the salt solution, such as the electro dialysis and ion-exchange processes. Conventional ion-exchange processes have not been widely used for desalination of brackish water for the main reasons of unfavorable economics and problems of effluent disposal, because for every equivalent of salt removed from the solution, at least one equivalent

of regenerant must be used, and most likely discarded to the environment. To overcome these problems, attention has been directed by many researchers to thermally regenerated ion-exchange resins and regenerant recycle systems. The use of heat rather than costly chemicals has the obvious advantage of lower operating costs, possibility of using solar energy for the process, and no addition to the chemicals load of the effluent. Such a process, designated the “Sirotherm” process,¹ was developed at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Melbourne, Australia. The Sirotherm process uses a physical mixture of weakly basic and weakly acidic ion-exchange resins, or resins containing both weak acid and weak base resin components within one bead, for the removal of salts from an aqueous solution by varying the temperature to produce sorption at the ambient temperature and desorption at a higher temperature. The following equilibrium may be written for such a system:



where R_AH is a weakly acidic resin and R_B is a weakly basic resin. The forward reaction is favored at a lower temperature and the reverse reaction is

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avored when the mixed bed is heated to a higher temperature, thus allowing salt adsorption and resin regeneration in a thermally variable manner. This is the basis of the Sirotherm process, in which the regenerant is only the feed water at a higher temperature rather than acids or alkalis.

The conventional mixed-bed system, in marked contrast to the Sirotherm system, uses resins of the strong electrolyte type:



where R_AH is a strongly acidic resin and R_BOH is a strongly basic resin. As the water produced by the exchange reaction is feebly ionized and the equilibrium in eq. (2) is shifted almost fully to the right, a nearly complete removal of NaCl (deionization) by ion exchange is feasible. In (1), however, an appreciable concentration of Na^+ and Cl^- ions are maintained in the solution by the hydrolysis of the weak resin salts R_ANa and R_BHCl . Consequently, a high quality deionized water cannot be produced with a mixed bed of weak resins. The Sirotherm process is thus suitable only for partial removal of salts from water of moderate salinity. In many applications, however, a high quality of water is not necessary so that the resin system of eq. (1) with thermally reversible exchange properties become an advantage. The operating capacity of the Sirotherm resins restricts the economic upper range of salinities to be treated to between 2000 and 3000 mg/L, which conforms to the treatment needs of effluent from cooling water, the largest volume industrial effluent.

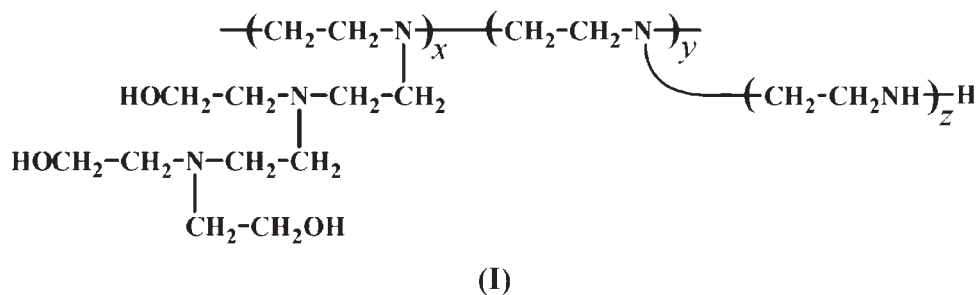
The capacity of a mixture of weak-acid and weak-base resins to remove salt in a Sirotherm demineralization process depends on many factors. These include the polymeric structure of the resins, the acidity and basicity of functional groups, the ratio of acid to basic groups, and the resin affinities for counter ions, besides pH, ionic strength, and temperature of the substrate solution. Methods of predicting the behavior of any pair of acidic and basic resins to select the optimum type and resin ratio have been described.² Weak-base amine resins and weak-acid carboxylic resins suitable for the Siro-

therm process can be identified by comparing their titration curves at the ambient temperature and at higher temperatures. Amine resins become weaker when heated. Most suitable amine resins are those which possess flat or plateau-shaped titration curves that displace to lower pH values with increasing temperature. Similarly, for carboxylic resins, those showing flatter titration curves and a bigger reduction in acidity with heating are preferred for the Sirotherm process. An overlap of the titration curves of the basic resin and the acid resin is essential for the Sirotherm process. Flatter or plateau-shaped titration curves, which mean large change in resin ionization corresponding to a small change in solution pH, enhance the overlap and promote the Sirotherm process. On the contrary, steeper titration curves lead to smaller overlap and hence weaker Sirotherm effect.

Studies at CSIRO identified³ polyvinylbenzyl-diethylamine (PVBDEA) as the most promising weak-base resin, showing plateau-shaped curves at 20° and 80°C with a difference of 1.2 of a pH at half neutralization. Later polyallylamines were found² to have even higher capacities than PVBDEA. Composite resin beads have been produced by binding together both the acidic and basic microion exchangers within a permeable matrix.² The capacity of the composite beads is slightly greater than that of the original mixed-bed systems (1–1.4 meq/g). Though this capacity is lower than that of the conventional chemically regenerated systems, the former does refer to the simultaneous removal of cations and anions.

In earlier articles,^{4,5} we presented titration curves of the commercially available ethoxylated polyethyleneimine (EPEI), which is a water-soluble weak-base resin (I) with a large number of tertiary amine functionalities, in addition to primary and secondary amine functionalities. The titration curves of EPEI were determined at different temperatures in saline solutions of different concentrations, together with those for the weak-acid resin, poly(acrylic acid) (PAA), to measure the extent of overlap as indicator of the salt sorption capacity.

The amine-type resin I (Scheme 1) was then gelled on partially hydrolyzed polyacrylonitrile



Scheme 1 Typical formula of ethoxylated polyethyleneimine.

(PAN) woven fabric. This sorbent, designated PAN(CO₂H)(EPEI.XG), was found to be effective for removal of NaCl from water.⁵ A sorbent made similarly by gelcoating polyethyleneimine (PEI), instead of EPEI, on partially hydrolyzed PAN fabric was, however, found to be inefficient in this respect. This was explained by the presence of significantly larger number of tertiary amine groups in EPEI as compared to PEI. It is known¹ that the tertiary amine exhibits higher salt sorption capacity than primary and secondary amines in combination with carboxylic acid.

Though the aforementioned cloth-type sorbent, PAN(CO₂H)(EPEI.XG), based on partially hydrolyzed PAN cloth, afforded very fast kinetics in desalination by the Sirotherm process, the sorbent had certain drawbacks, namely, (1) water solubility of the hydrolyzed PAN cloth, which allowed only low degrees of conversion of —CN groups of PAN to —COOH groups for retaining the water insolubility of the woven PAN fabric; (2) relatively low value of NaCl sorption equilibrium constant (Langmuir equilibrium constant, $K_b = 9 \times 10^{-4}$ L/mmol at 30°C) and hence low salt uptake in dilute solutions of NaCl (e.g., 0.065 mmol NaCl/g in 0.1M NaCl solution at 30°C); and (3) unsuitability of the cloth-type sorbent for column operation. In the present work, therefore, a granular composite sorbent consisting of XPAA and crosslinked (EPEI.XG) was prepared and used for the Sirotherm desalination process.

According to Bolto and Jackson,⁶ “thermally regenerable ion-exchange resins must be composed of discrete acidic and basic domains grouped together in a porous particle of the conventional size for ion-exchange resins of 0.3–1.2 mm”. Depending on the method of manufacture, two extreme types of structure for such composite resins may be envisaged. A so-called “mosaic structure” consisting of a mosaic of acidic and basic domains of 0.01–5- μ m size would be expected to result from the polymerization of a mixture of monomers.⁷ In such a structure, a larger amount of internal salt formation (—CO₂⁻...⁺NH—) between the carboxylate and protonated amino groups, which is detrimental to the Sirotherm process, would be expected.⁶

The extent of such internal neutralization would, however, be less in the structure of resin prepared by encapsulation of microparticles of one polymer by a matrix of the polymer of the opposite type. Hatch,⁸ for example, prepared Sirotherm resins of this type by encapsulation of poly(acrylic acid) microparticles in a poly(vinylbenzylchloride) matrix, and then reacting the benzyl chloride groups with dimethylamine. Bolto and Jackson⁶ similarly used crosslinked polyallylamine microparticles rather than the amine monomer in the preparation of Siro-

therm resin by encapsulation in XPAA matrix, the latter being prepared by copolymerization of acrylic acid and divinyl benzene. By this method, the polyamine would “not be in such intimate contact with the acrylic acid monomer as the acrylic monomer would be with an amine monomer because of the expected incomplete penetration of the acrylic acid monomer into the polyamine microparticles”.⁶ Resins made in this way by encapsulating polypropyldiallylamine in polyacrylic acid exhibited thermally regenerable ion-exchange capacity of 0.12–0.44 meq/g, which is rather low indicating that a high degree of internal neutralization still took place.⁶

In the present work, we therefore adopted an approach of using both amine and acid components of the sorbent in the form of polymers, one in the crosslinked, i.e., insoluble, state (as particles) and the other initially in a soluble form, to be insolubilized later by crosslinking it on the other crosslinked polymer. Thus, granular XPAA was first made by crosslinking copolymerization of acrylic acid and ethylene glycol dimethacrylate; the XPAA was then coated with 80% EPEI in methanolic suspension, and the coated EPEI was insolubilized by crosslinking with glutaraldehyde. The Sirotherm behavior of this acidbase composite sorbent was studied using NaCl and MgCl₂ in aqueous solutions as substrates.

EXPERIMENTAL

Materials

The amine resin used for making the composite sorbent was 80% EPEI of equivalent weight 78 g, obtained as 37 wt % aqueous solution from Sigma-Aldrich Chemical (Bangalore, India; Cat. No. 306185-250G). The monomer acrylic acid (AA) (Cat. No. 14,723-0), crosslinking agent ethylene glycol dimethacrylate (EGDMA) (Cat. No. 33,568-1), and initiator 2,2'-azobisisobutyronitrile (Cat. No. 44,109-0), used for making crosslinked polyacrylic acid (XPAA), were also from Sigma-Aldrich. Glutaraldehyde (25 wt % aqueous solution, Laboratory Reagent) was obtained from S. D. Fine Chemicals (Mumbai, India).

Sorbent

The procedure for preparation of the composite sorbent, designated as XPAA(EPEI.XG), is shown schematically in Figure 1. A monomer mixture of 76 wt % AA and 24 wt % EGDMA containing 0.4 wt % AIBN was bulk polymerized in a number of 50-mL glass ampoules (filled to half the capacity and purged with nitrogen) by heating in water bath at 70°C for 2 h. The ampoules were broken and kept immersed in deionized water for 2 days to facilitate

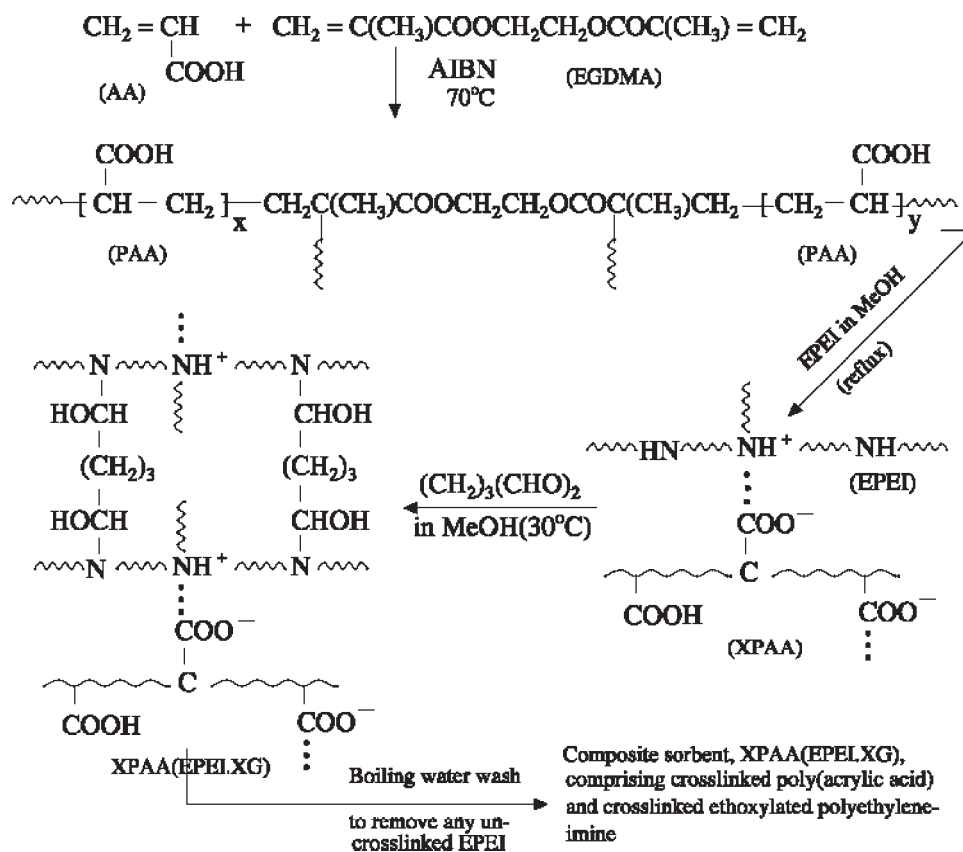


Figure 1 Schematic of the method of preparation of XPAA(EPEI.XG) by copolymerization of acrylic acid (AA) and ethylene glycol dimethacrylate (EGDMA), followed by reaction with 80% ethoxylated polyethylenimine (EPEI) and insolubilization of the latter by treatment with glutaraldehyde.

the solid polymer detaching from the glass. The polymer (XPAA), therefore obtained, was wet ground to less than 1.2-mm size powder. XPAA (100 g) was heated in 500 mL methanolic solution of 10 wt % EPEI under reflux with constant stirring for 6 h. The resulting EPEI-coated polymer, XPAA(EPEI), was subsequently crosslinked by stirring in excess of 10% (w/w) glutaraldehyde solution in methanol at room temperature for 3 h. The resulting brown colored product, XPAA(EPEI.XG), was kept in boiling water for 1 h to remove any free EPEI, washed repeatedly with deionized water, superficially dried to remove free water, and stored as wet solid (38% moisture).

The proton capacity of XPAA(EPEI.XG), measured in 0.10N HCl, is 1.84 meq/g (dry), whereas the carboxylate content of the sorbent, estimated by measuring the uptake of NaOH in 0.10N NaOH solution, is 9.0 meq/g (dry). The carboxylate/amine ratio of 4.9 indicates insignificant penetration of EPEI chain segments into the XPAA matrix, as would be desired.

The elemental composition (Table I) of the sorbent XPAA(EPEI.XG), as compared with that of the precursor resin XPAA, shows an increase in N content because of the addition of glutaraldehyde-cross-

linked polyamine (EPEI.XG) to XPAA, whereas the FTIR spectra, shown in Figure 2, confirms the presence of amine groups in XPAA(EPEI.XG). The measured properties of the composite sorbent XPAA(EPEI.XG) are recorded in Table II.

Analysis

The concentration of sodium chloride was determined by measuring the Cl^- concentration, because $[\text{Na}^+] = [\text{Cl}^-]$, when no other salt is present in the solution. The well-known Volhard's method⁹ was used for Cl^- estimation. The concentration of Mg^{2+} in MgCl_2 solution in the absence of other salts was measured by the volumetric EDTA method.⁹ The concentrations of both Na^+ and Mg^{2+} in bicomponent solutions were measured by atomic absorption spectrometry.

Ion experiments

Sorptions of NaCl and MgCl_2 on XPAA(EPEI.XG) were measured both in single component and binary solutions. In addition, the sorption of MgCl_2 was measured on XPAA from single-component solutions, for comparison with that on XPAA(EPEI.XG),

TABLE I
Comparison of Elemental Compositions of XPAA and XPAA(EPEI.XG)

Sample	Elemental composition, % (w/w)			
	C	H	N	O
XPAA	52.2	5.7	–	41.3
XPAA(EPEI.XG)	51.4	6.9	2.6	38.2

to see the effect of amine addition to the polyacid. This was, however, not possible for NaCl, because there is practically no sorption of NaCl on poly (acrylic acid). For equilibrium sorption measurements a small scale dynamic contact between the granular sorbent and the sorbate solution of specified composition was effected in tightly stoppered flasks at 30°C on a mechanical shaker for 10 h. The extent of sorption was calculated from the residual concentration of the sorbate in the equilibrated solution. A range of concentrations of the sorbates, NaCl and MgCl₂, both in single-component and bi-component solutions were employed. The sorptions of NaCl and MgCl₂ in single component solutions were also measured at different pH values of the substrate.

For the determination of sorption kinetics, a rectangular basket made of polypropylene screen (0.50-mm opening) was used to hold the sorbents. The basket was fitted to the shaft of a variable-speed motor and rotated, whereas the sorbate solution was brought into contact for a specified period. In this way, the sorbent could be separated instantly from the sorbate solution at any desired time.

Sorption rates were always measured at stirring speeds much above the minimum speed above

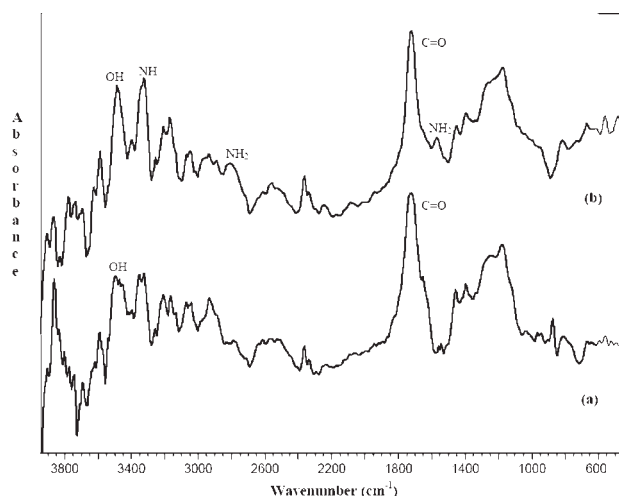


Figure 2 Comparison of FTIR spectra of (a) crosslinked poly(acrylic acid) (XPAA) and (b) composite sorbent XPAA(EPEI.XG).

TABLE II
Properties of Composite Sorbent XPAA(EPEI.XG) Used for Desalination Study

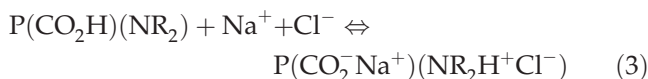
Water content (w/w)	38%
Particle diameter (mm)	
Wet	0.3–1.2
Dry	0.28–1.0
BET surface area (m ² /g) dry	0.670
Carboxylic content (meq/g) dry	9.0
Amine content (meq/g) dry	1.84

which the kinetic values are not influenced by the degree of agitation, as determined by experimental measurement of sorption rates at different stirring speeds using a relatively low solution concentration (0.10M) of the sorbate.

RESULTS AND DISCUSSION

Single-component sorption isotherms

With amine and carboxylate functionalities present in close proximity in the composite sorbent particle, the sorption of NaCl on XPAA(EPEI.XG) can be represented by reaction (3)



where P represents sorbent particle. Because the sorbent XPAA(EPEI.XG) contains excess COOH groups (see Table II), the sorption of MgCl₂ can occur by both reactions (4) and (5), namely,

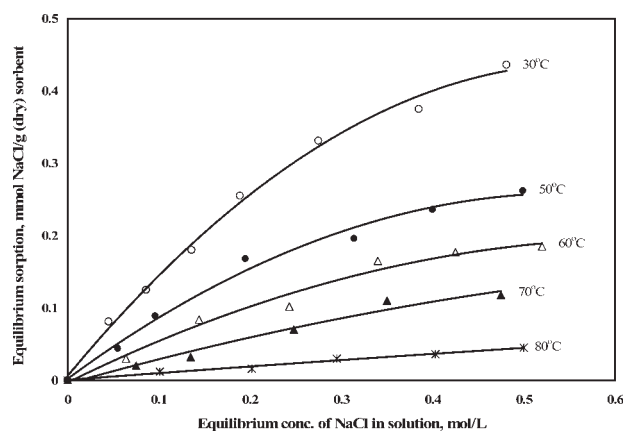
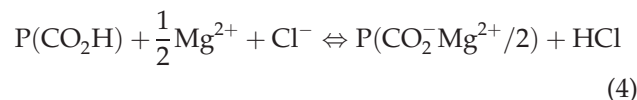


Figure 3 Equilibrium sorption isotherms for NaCl on composite sorbent XPAA(EPEI.XG) at different temperatures in the range 30–80°C. Sorbent loading: 80 g (wet)/L; feed solution pH 6.0.

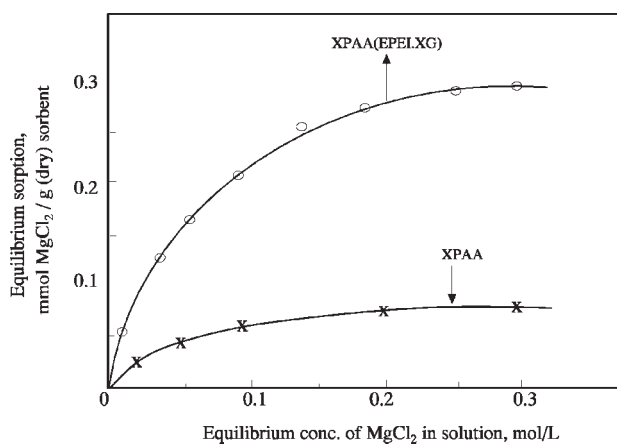
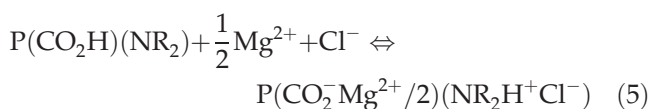


Figure 4 Comparison of equilibrium sorptions of MgCl_2 on crosslinked poly(acrylic acid) (XPAA) and on composite sorbent XPAA(EPEI.XG) at 30°C . Sorbent loading 80 g (wet)/L; feed solution pH 6.0.



The equilibrium data of the single-component sorption of NaCl on XPAA(EPEI.XG) from aqueous solutions are plotted in Figure 3. In view of reactions (4) and (5), the sorption of MgCl_2 was measured both on XPAA and XPAA(EPEI.XG). These data are plotted in Figures 4 and 5, respectively. The significantly larger sorption on XPAA(EPEI.XG), as compared with that on XPAA, can be attributed to the Sirotherm type effect. A comparison of sorption data in Figures 3 and 5, moreover, shows that although the sorption capacity for both NaCl and MgCl_2 decreases with the increase of temperature, this effect is greater in the case of NaCl , indicating relatively weaker binding of NaCl on the sorbent.

All the equilibrium sorption data of NaCl and MgCl_2 on XPAA(EPEI.XG) fitted well to both Langmuir and Freundlich isotherms, though the former gave a somewhat better fit. Defining the parameters A_s and K_b as the saturating sorption capacity

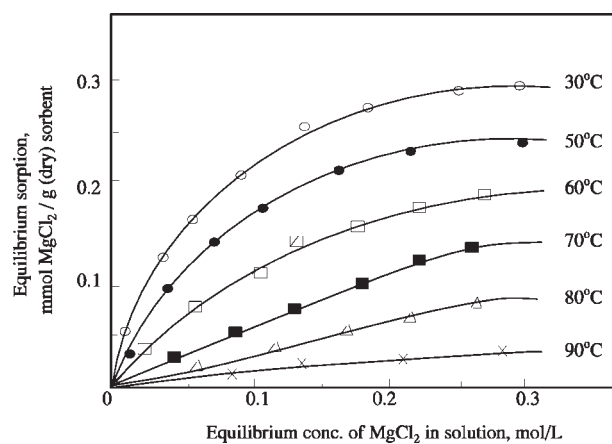


Figure 5 Equilibrium sorption isotherms for MgCl_2 on composite sorbent XPAA(EPEI.XG) at different temperatures in the range $30\text{--}90^\circ\text{C}$. Sorbent loading: 80 g (wet)/L; feed solution pH 6.0.

(meq/g dry sorbent) and sorption binding constant (L/meq), respectively, the Langmuir isotherm is written as

$$x^* = \frac{K_b A_s C^*}{1 + K_b C^*} \quad (6)$$

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

The Freundlich isotherm is written as

$$x^* = p(C^*)^q \quad (7)$$

where p and q are Freundlich parameters, and x^* and C^* are as defined earlier.

The values of A_s , K_b , p , and q , determined by least squares fit of the sorption data in Figures 3 and 5 are presented in Table III. A comparison of the values reveal that the saturation capacities of the sorbent for NaCl and MgCl_2 are similar, which indicate that possibly same sites are involved in the sorption process. However, MgCl_2 has a much higher binding constant (K_b) as also a lower value of the Freundlich

TABLE III
Langmuir and Freundlich Isotherm Parameters for Sorption of NaCl and MgCl_2 on XPAA(EPEI.XG)

Sorbate	Langmuir isotherm, eq. (6)		
	A_s , meq/g dry sorbent	k_b , L/meq	Corr. coeff.
NaCl	0.796	2.3×10^{-3}	0.999
MgCl_2	0.839	6.7×10^{-3}	0.999
	Freundlich isotherm, eq. (7)		
	p	q	Corr. coeff.
NaCl	6.0×10^{-3}	0.701	0.994
MgCl_2	31.7×10^{-3}	0.480	0.990

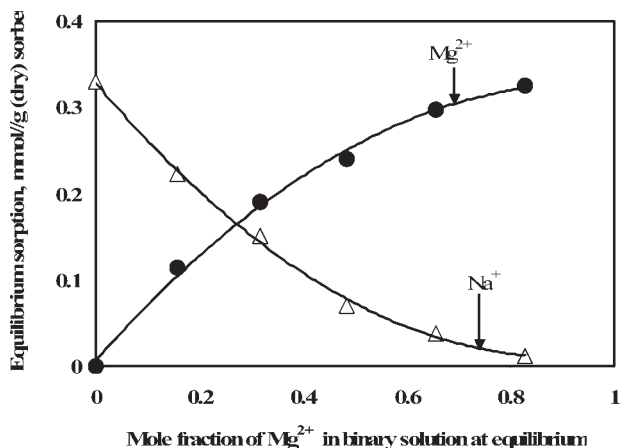


Figure 6 Equilibrium sorption isotherms for NaCl and MgCl₂ in bicomponent solutions on composite sorbent XPAA(EPEI.XG) at 30°C. Sorbent loading: 80 g (wet)/L; total concentration of Na⁺ and Mg²⁺ in solution initially: 0.30 mol/L; feed solution pH 6.0.

parameter *q*, indicating that MgCl₂ has a stronger binding than NaCl on the composite sorbent.

As the equilibrium sorption decreases for both NaCl and MgCl₂ at higher temperatures, implying that sorption and desorption can take place reversibly in successive cold and hot cycles, the feed solution itself can be used as a regenerant by heating it to a higher temperature, which is the basis of the Sirotherm process. In this case, the difference in sorption capacities at room temperature and a suitable higher temperature represents the “effective capacity” of the sorbent.

Binary sorption isotherm

The equilibrium sorption data for XPAA(EPEI.XG) in binary adsorbate systems of NaCl and MgCl₂ at 30°C are presented in Figure 6. A comparison of the data shows that the divalent ions are preferred to monovalent ions for sorption on the composite sorbent. Thus at 0.50 equivalent fraction of MgCl₂, the equilibrium sorptions of NaCl and MgCl₂ are, respectively, 0.145 mmol/g dry and 0.390 meq/g dry.

There are several models for prediction of binary sorption using single-component sorption parameters. Thus the single-component Langmuir isotherm [eq. (6)] was extended to binary sorption by Butler and Ockrent¹⁰ yielding

$$x_i^* = \frac{A_{S,i}K_{b,i}C_i}{1 + K_{b,1}C_1 + K_{b,2}C_2} \quad (i = 1 \text{ or } 2) \quad (8)$$

This equation is thermodynamically consistent only where the sorption capacities for the two species are equal.¹¹ For the case where the two capacities are not equal, Jain and Snoeyink¹² modified the Butler-Ockrent model based on the assumption that sorption without competition occurs on some sites

and that the number of sites for noncompetitive sorption is proportional to the difference between the maximum loadings of the two species. For $A_{S,2} > A_{S,1}$, as in the present case, the binary component equations of Jain and Snoeyink take the form

$$x_1^* = \frac{A_{S,1}K_{b,1}C_1^*}{1 + K_{b,1}C_1^* + K_{b,2}C_2^*} \quad (9)$$

$$x_2^* = \frac{(A_{S,2} - A_{S,1})K_{b,2}C_2^*}{1 + K_{b,2}C_2^*} + \frac{A_{S,1}K_{b,2}C_2^*}{1 + K_{b,1}C_1^* + K_{b,2}C_2^*} \quad (10)$$

The first term on the right side of eq. (10) is the Langmuir-like expression for the amount of component two that sorbs without competition, whereas the second term, based on the Langmuir-like model for competitive sorption, represents the amount of component two sorbed on the surface in competition with component one.

By using the single-component parameter values as given in Table III, the sorptions of NaCl and MgCl₂ from binary mixtures were computed by using the binary Langmuir isotherms, represented by eqs. (8)–(10). These are plotted in Figure 7, for comparison with experimentally observed values. Both the Butler-Ockrent and Jain-Snoeyink models are seen to predict binary sorption of NaCl and MgCl₂ reasonably well. This would be expected because the single-component sorption capacities of NaCl and MgCl₂ on the sorbent are quite similar.

Effect of pH

The effect of pH on the sorption of NaCl and MgCl₂ at 30°C is shown in Figure 8. Because the sorbent

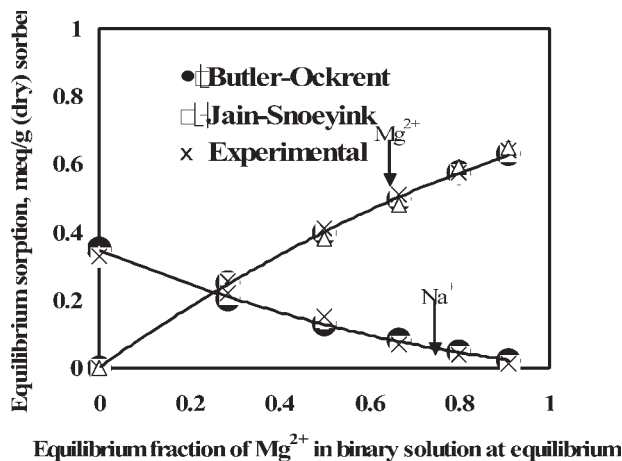


Figure 7 Comparison of experimental sorption values of NaCl and MgCl₂ at 30°C with those calculated from Butler-Ockrent and Jain-Snoeyink bicomponent sorption models for different compositions of the bicomponent solution. Sorbent loading: 80 g (wet)/L; total concentration of Na⁺ and Mg²⁺ in solution initially: 0.30 mol/L; feed solution pH 6.0; temperature 30°C.

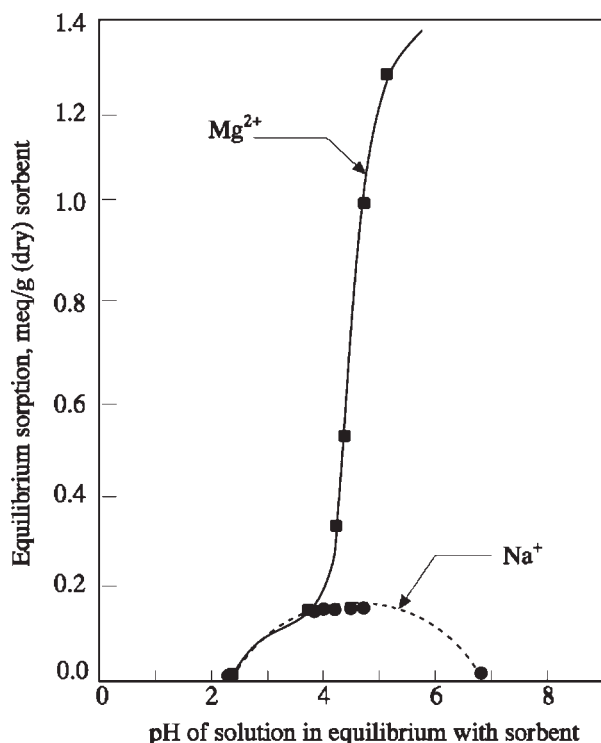


Figure 8 Effect of pH on sorption of NaCl and MgCl₂ on composite sorbent XPAA(EPELXG) at 30°C. Other conditions are similar to those given in Figures 3 and 5, respectively.

XPAA(EPELXG) contains both carboxylic and amine functionalities, with carboxylic to amine ratio equal to 4.9, the sorbent is capable of neutralizing some amount of acids and bases to act as buffer over a fairly wide range of substrate pH. Thus, experimentally, in the presence of 5 wt % sorbent, the pH of the equilibrated solution was found to be in the nar-

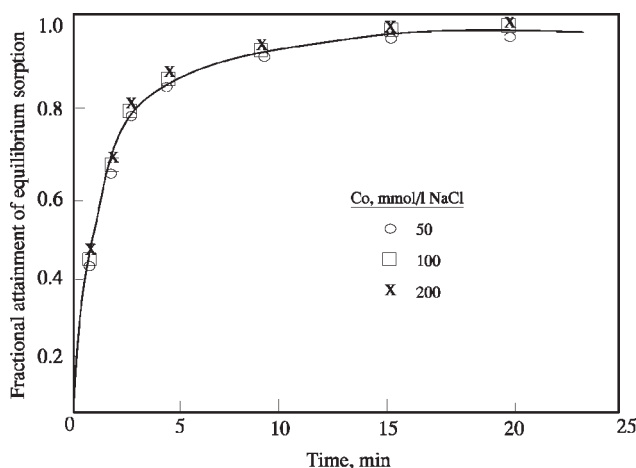
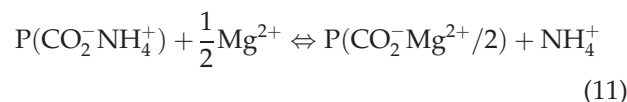


Figure 9 Rate of sorption of NaCl on sieved XPAA(EPELXG) of particle size 0.5–1.0 mm in NaCl solutions of different concentrations, C_o . Sorbent loading: 80 g (wet)/L; feed solution pH: 6.0; temperature 30°C; vigorous agitation.

row range of 4–5 irrespective of the feed solution pH in the range 3–8. The sorption of NaCl was fairly constant over this range but reduced sharply at both lower and higher pH values (Fig. 8).

The effect of pH on the sorption of Mg²⁺ (Fig. 8) is very different from that on Na⁺ sorption, especially in the equilibrated solution pH range 4–6, where the sorption of Mg²⁺ is found to increase sharply, instead of decreasing. This can be attributed to significant contribution to Mg²⁺ sorption by cation exchange, as shown by eq. (11), at the ionic sites formed at higher pH (by addition of NH₄OH):



Sorption kinetics

The information of greatest practical interest that kinetic studies can give is the rate, i.e., fractional attainment of equilibrium as a function of time, $\alpha(t)$. Such kinetic data (Figs. 9 and 10) for the sorption of NaCl and MgCl₂ from single-component solutions at 30°C were obtained using a rotational speed (200–300 rpm) of the sorbent basket, which was much above the experimentally determined minimum required for elimination of film diffusional resistance. It is seen that NaCl has much higher rate of sorption, with 83% of equilibrium being attained in 3 min, as compared to 49% in 3 min for MgCl₂.

For particle-diffusion controlled ion-exchange processes, $\alpha(t)$ is a function^{13,14} of Dt/r_0^2 , where D is

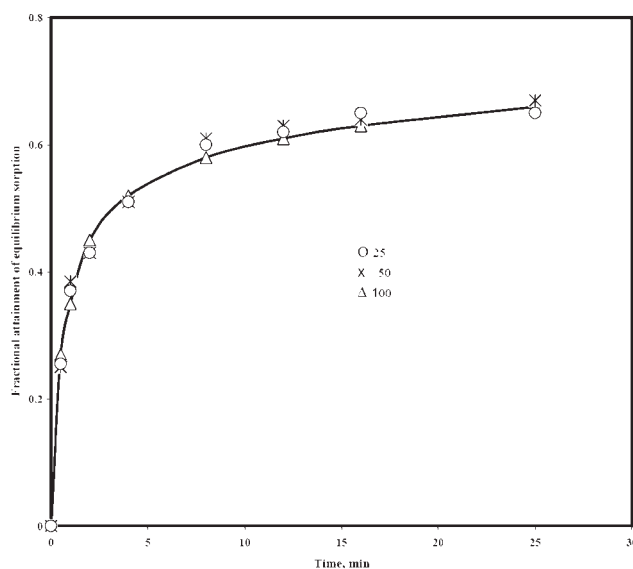


Figure 10 Rate of sorption of MgCl₂ on sieved XPAA(EPELXG) of particle size 0.5–1.0 mm in MgCl₂ solutions of different concentrations, C_o . Sorbent loading: 80 g (wet)/L; feed solution pH: 6.0; temperature 30°C; vigorous agitation.

the diffusion coefficient of the counter ions in the resin, t is the time and r_0 is the particle radius. Therefore, the time required to attain any given conversion should be inversely proportional to the square of the radius, and it should be independent of other variable, such as concentration. From the results presented in Figures 9 and 10 it is seen that the rate of attainment of equilibrium sorption is practically independent of the sorbate concentration in the external solution. This may then be interpreted as indicating that particle diffusion and not film diffusion was rate controlling in the sorption process under the conditions employed.

In a simple semiempirical approach, one can postulate rate equations involving reaction rate or mass transfer coefficients and estimate these coefficients by fitting the equations to experimental results. Based on this approach, many different equations have been postulated and used to describe ion-exchange kinetics. In using a semiempirical approach it is, however, more realistic to apply the linear driving force concept,^{15,16} often used by engineers in heat and mass transfer calculations. Its underlying premise is that rate is proportional to the system's distance from equilibrium. Thus, for particle-diffusion control, as in the present case, we can write

$$d\bar{C}_S/dt = k_p(\bar{C}_S^* - \bar{C}_S) \tag{12}$$

Here \bar{C}_S and \bar{C}_S^* represent the concentrations of resin-bound salt species at time t and at equilibrium, respectively; k_p is the rate coefficient for particle-diffusion control. (Quantities with overbars refer to the resin phase and an asterisk represents equilibrium condition.). \bar{C}_S^* is given by

$$\bar{C}_S^* = w \cdot x_S^* \tag{13}$$

where w is the resin loading (g/L) and x_S^* is the equilibrium sorption capacity of the resin (mmol or meq/g dry resin). \bar{C}_S is given by

$$\bar{C}_S = \alpha \cdot w \cdot x_S^* \tag{14}$$

where α is the fractional attainment of equilibrium sorption at any time t .

Differentiating eq. (14),

$$d\bar{C}_S/dt = wx_p^*(d\alpha/dt) \tag{15}$$

Substituting eqs. (13)–(15) into eq. (12), we obtain

$$d\alpha/dt = k_p(1 - \alpha) \tag{16}$$

Because $\alpha = 0$ at $t = 0$, eq. (16) yields on integration

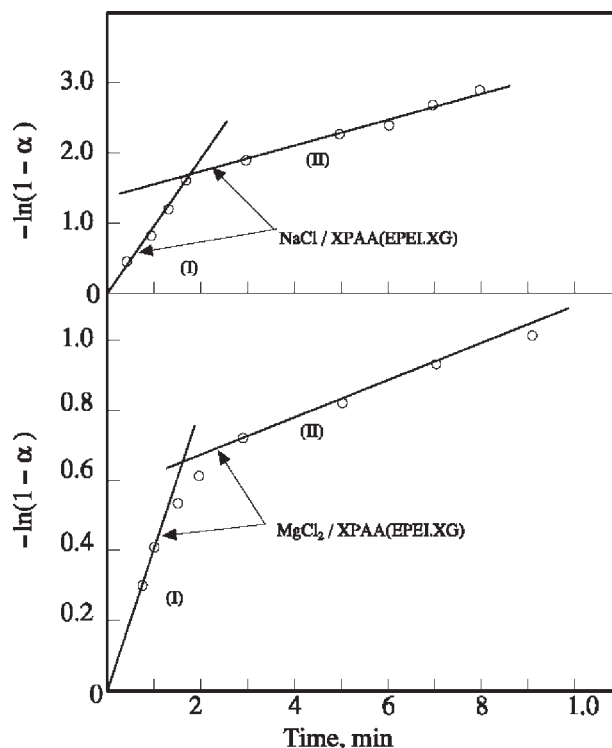


Figure 11 Test of eq. (17) with data of Figures 9 and 10 for sorption of NaCl and MgCl₂ on XPAA(EPELXG) at 30°C.

$$-\ln(1 - \alpha) = k_p t \tag{17}$$

Equation (17) provides a convenient means of testing the applicability of eq. (12) to kinetic data in the form of fractional attainment of equilibrium sorption, α . Equation (17) is, however, applicable only if k_p , and hence diffusivity of the solute in the resin, is independent of the extent of sorption. The kinetic data of Figures 9 and 10 were tested by plotting $-\ln(1 - \alpha)$ versus t . It is evident from Figure 11 a good fit is obtained only in the initial period (phase I) with α up to 0.75 for NaCl and up to 0.40 for MgCl₂. The values of k_p obtained by least squares fitting of the experimental α versus t data in phase I are 0.75 min⁻¹ and 0.25 min⁻¹ for NaCl and MgCl₂, respectively. Because for particle-diffusion control the rate coefficient k_p is proportional to the diffusivity of the solute in the resin,¹⁷ the relative diffusivities of the two salts can be calculated from the ratios of k_p values. The relative diffusivities of NaCl and MgCl₂ into the resin can thus be taken as 3 : 1. The deviation from linearity at higher values of α (Fig. 11) may be attributed to a decrease of intraparticle diffusivity because of sorption of the salt species.

The k_p values obtained above can be used for predicting salt uptake by the sorbent or change in salt concentration in the aqueous solution, C_{sr} , as a function of time in the initial period. Thus, because C_s is given by

$$C_s = C_{s0} - \alpha w x_p^* \quad (18)$$

where C_{s0} is the initial salt concentration in solution, substitution of α from eq. (17) gives

$$C_s = C_{s0} - [1 - \exp(-k_p t)] w x_s^* \quad (19)$$

The value of x_s^* for a given resin loading, w , and initial salt concentration, C_{s0} , can be obtained by an iterative procedure from eq. (7), rewritten as

$$x_s^* = p(C_{s0} - w x_s^*)^q \quad (20)$$

where the Freundlich isotherm parameters p and q , are known from Table III.

With particle diffusion rate controlling, the fractional attainment of equilibrium α as a function of time t can also be described by Barrer's integration¹⁵ of Fick's flux equation in an "infinite solution volume (ISV)" case:

$$\alpha(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} n^{-2} \exp\left(-\frac{\pi^2 n^2 \bar{D} t}{\bar{r}_0^2}\right) \quad (21)$$

where the terms \bar{r}_0 , \bar{D} , and n represent the average radius of resin bead, resin diffusivity, and integer numbers, respectively.

In terms of the 'equivalent ratio' (ϵ), 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 employed to approximate ISV conditions¹⁸ for $\epsilon \ll 1$ meqr/meq. Because the kinetic data of Figures 9 and 10 were obtained with experimental conditions such that $\epsilon < 0.6$, ISV conditions would be reasonably well approximated, especially in relation to low conversion ranges.

To a good approximation, eq. (21) can be simplified to

$$\alpha(t) \cong \left[1 - \exp\left(-\frac{\pi^2 \bar{D} t}{\bar{r}_0^2}\right)\right]^{1/2} \quad (22)$$

from which the particle diffusion coefficient \bar{D} is approximately obtained as

$$\bar{D} = -0.233 \cdot \bar{r}_0^2 \cdot t^{-1} \log[1 - X^2] \quad (23)$$

Using the data of Figures 9 and 10 in the initial period yielded values of $1.0\text{--}1.3 \times 10^{-6}$ cm²/s for NaCl and $3.0\text{--}3.5 \times 10^{-7}$ cm²/s for MgCl₂ in the composite sorbent, in conformity with the estimate of diffusivity ratio 3 : 1 obtained earlier from the semiempirical approach.

CONCLUSIONS

A granular sorbent, XPAA(EPELXG), composed of XPAA and 80% EPEL, immobilized by treating with glutaraldehyde, is found to be effective for removal of NaCl and MgCl₂ from water by a thermally reversible (Sirotherm) process by operating between ambient temperature (30°C) for sorption and a higher temperature (80–90°C) for desorption (sorbent regeneration). The single-component sorption data at 30°C for NaCl and MgCl₂ fit well to both Langmuir and Freundlich isotherms, whereas the Butler-Ockrent and Jain-Snoeyink binary sorption models give good fit to the binary sorption data for the two solutes at 30°C. Although the sorption of NaCl is nearly independent of pH in mildly acidic media, that of MgCl₂ increases rapidly with pH both in mildly acidic and alkaline media, which can be attributed to additional sorption of MgCl₂ by cation exchange at higher pH. The sorption rates at 30°C for both NaCl and MgCl₂ under high degree of agitation are explained well by particle-diffusion controlled models, yielding initial diffusivity values of $1.0\text{--}1.3 \times 10^{-6}$ cm²/s and $3.0\text{--}3.5 \times 10^{-7}$ cm²/s for NaCl and MgCl₂, respectively.

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