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Ammonium Removal from Aqueous Solutions Using Sulfonated Polystyrene Grafted Silica Gel Sorbent

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Abstract: A novel non-swelling sulfonated polystyrene grafted silica gel sorbent was synthesized for use in ammonium removal from aqueous solutions. The ammonium sorption equilibrium isotherm was determined at 298 K by batch experiments, and the effects of flow rate and initial solution pH on the sorption were measured by breakthrough experiments in a laboratory scale fixed bed column. The equilibrium data were fitted to the Langmuir, Freundlich, Langmuir-Freundlich, and Toth isotherm models. The breakthrough data were fitted to a dynamic isothermal mathematical model with an axial dispersion term to obtain the effective diffusion coefficient. The sorption rate of the sulfonated polystyrene grafted silica gel is higher than that of ion-exchange resins, which enables shorter cycle times in column processes for the grafted silica gel.

Keywords: Ammonium removal, sulfonated polystyrene grafted silica gel

INTRODUCTION

Ammonia removal from industrial wastewaters is necessary in the fertilizer, metallurgical, oil, and food industries as well as in production of inorganic and organic chemicals (1, 2). Ammonia occurs in aqueous solutions as pure

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ammonia (NH_3) or ionized ammonia, namely, ammonium (NH_4^+). If the pH is lower than 7, then most of ammonia occurs in ammonium form (2).

Sorption, such as ion-exchange and adsorption, is used for ammonium removal from aqueous solutions at concentrations below $500\,\mathrm{mg\,dm^{-3}}$. For solutions stronger than $500\,\mathrm{mg\,dm^{-3}}$, these techniques are used as a secondary method (1). In fertilizer plants, for example, ammonium nitrate has been removed using a continuous countercurrent Chem-Seps process that requires two parallel Higgins contactors for the separation of cations and anions. Both ion-exchange and regeneration are carried out simultaneously in the Higgins contactor. If the cation-exchanger is regenerated by 24% nitric acid and the anion-exchanger by 7% ammonia, the process produces concentrated ammonia nitrate (12–24)% for use as a raw material in fertilizer production (3–6).

The Chem-Seps and other ammonium removal processes employ gel-type ion-exchange resins, *i.e.* sulfonated polystyrene-divinylbenzene resins (PS-DVB), in acidic form as a cation-exchanger, although they have lower ammonium selectivity than zeolites, such as clinoptilolite (3–10). In contrast to municipal wastewaters, there are industrial wastewaters that contain only traces of other cations, and thus the low selectivity of ion-exchange resins does not complicate the separation (3). Unlike the zeolites, the acidic ion-exchange resins can be regenerated by strong mineral acids, *e.g.*, HNO_3 and H_2SO_4. This is an important advantage, since the acid regeneration enables ammonia recovery in the useful salt form more often than in using zeolites. The drawback of ion-exchange resins is related to the polymer matrix. Although the matrix of sulfonated PS–DVB is chemically stable in the presence of strong mineral acids, the matrix swells considerably and then affects the behavior of the resin beds in the ion-exchange columns. More precisely, the swelling and shrinking during service-rinse-regeneration cycles cause channeling and irregular flow in the resin bed. This distorts the concentration front, leading to a wide elution curve as well as a low eluted ion concentration (9).

The present work introduces the synthesis and characterization of a novel sulfonated polystyrene grafted silica gel sorbent. The acid capacity, ammonium capacity, amount of polymer, and prevailing chemical groups at the surface are determined for the synthesized sorbent. In order to characterize the sorption performance of the grafted silica gel, the ammonium sorption equilibria, kinetics, and regenerability are studied. Chemical stability and the retaining activity are ensured in the presence of strong mineral acids.

SYNTHESIS OF THE SORBENT

Grafting is a well-known technique in the preparation of chromatographic stationary phases (sorbents) for analytical use, but its potential in the manufacturing of technical sorbents has not been recognized. The grafting in the present study is based on the same technique and similar chemicals as used in the manufacture of fiberglass reinforced composites (11). Thus, the grafted silica gel sorbents are not expected to be much more expensive than commercial ion-exchange resins. The binding of the polymer with the silica gel surface takes place by the use of silane coupling agents. These organofunctional silanes create covalent chemical bonds between the silanol groups at the surface and the polymer. In the present work, the synthesis is principally the same as in the papers of Revillon and Carlier (12, 13) and in our previous paper (14), where the synthesis was employed to prepare acid catalysts. Here, the sulfonated polystyrene grafted silica gel is, however, synthesized using a slightly modified receipt than in our previous work, and thus the synthesis is briefly shown in Fig. 1 and in the following steps.

1. *Polymerization*. Functionalized polystyrene was prepared by polymerizing 225 g of styrene (Fluka $>99\%$) with 8.2 g of a chain transfer agent, 3-mercaptopropyltrimethoxysilane (Fluka, $>97\%$), and 0.85 g of an initiator, AIBN (Fluka, $>98\%$), in 980 g of toluene at 80°C. The silane solution was added during 5 h. After an additional 1 h, the radical polymerization was stopped by hydroquinone (Fluka, $>99\%$). The functionalized polymer was recovered by evaporating the toluene.
2. *Grafting*. 40.5 g of the functionalized polystyrene was grafted onto 20.0 g of silica gel (Fluka Silica gel 100, $d_p = 0.2–0.5$ mm) in 860 g of toluene at 110°C for 24 h. The grafted silica gel was purified by Soxhlet extraction in toluene for 24 h.
3. *Sulfonation*. 26.3 g of polystyrene grafted silica was sulfonated by 85 cm^3 of chlorosulfonic acid (Merck, $>97\%$) in 380 g of chloroform (Fluka, $>99\%$) at 50°C for 2.5 h. A product was washed with methanol and water, and it was finally dried at 70°C under vacuum.

All three steps were carried out in a 1.5-dm^3 jacketed glass reactor that was equipped with a reflux condenser. Temperature was controlled using a Lauda U3 thermostat coupled with a R400 controller. The polymerization and grafting steps was conducted under argon (AGA, $>99.9\%$). Toluene (technical grade) was dried with a 3A molecular sieve.

EXPERIMENTAL

The acid capacity of the sulfonated polystyrene grafted silica gel was determined in the same way as Unger (14) has reported for chromatographic silica. When determining the ammonium capacity, Unger's procedure for the acid capacity was employed as modified:

1. Sorbent was loaded to the ammonium form by a 2M NH_4Cl solution,
2. Washed with de-salted water, and

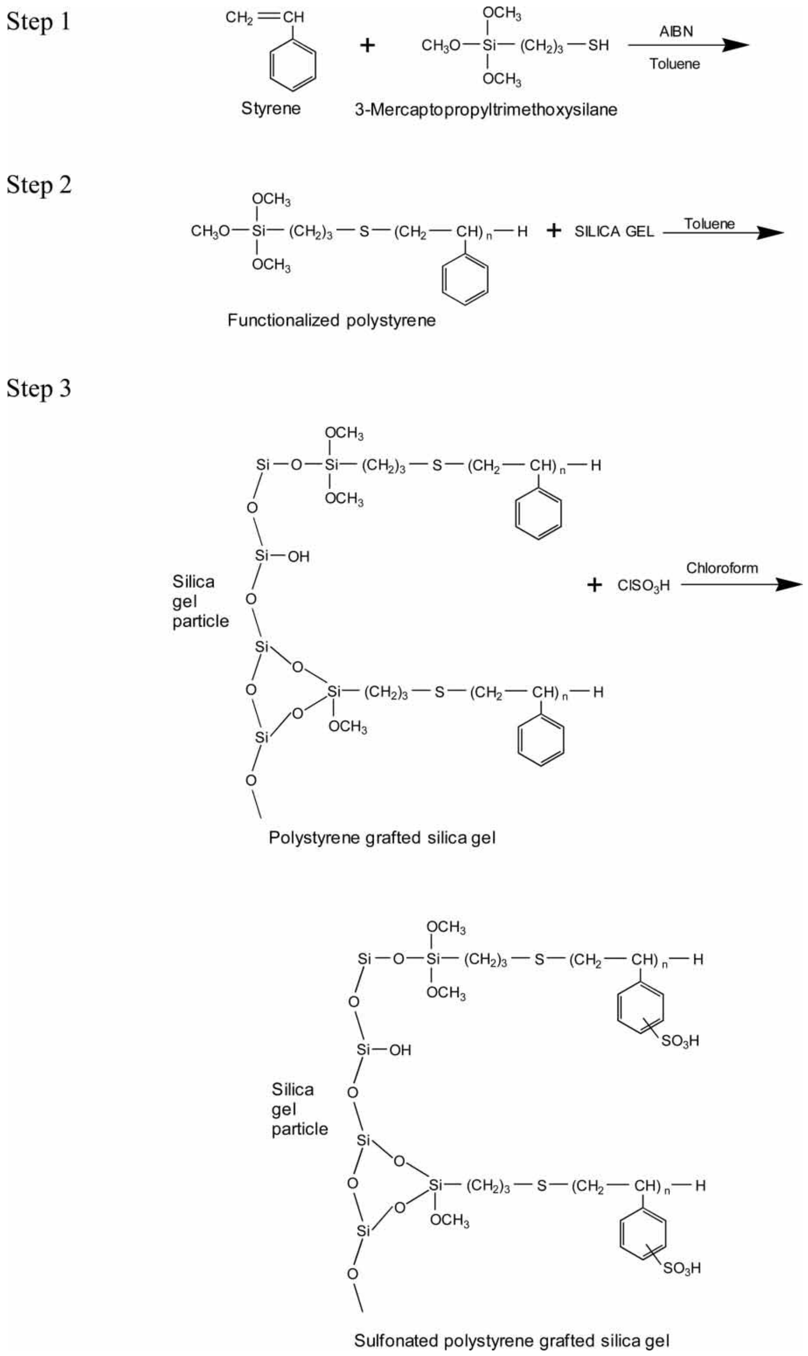

Figure 1. (1) Polymerization, (2) grafting, and (3) sulfonation steps in the synthesis of sulfonated polystyrene grafted silica gel sorbent.

3. Eluted with a 2M NaCl solution to convert the sorbent completely into the Na^+ form. The eluate was collected, and an aliquot was analyzed by an ammonia selective electrode.

Thermogravimetric analysis (TGA) was carried out for the sulfonated polystyrene grafted silica gel with Netzsch STA 409 apparatus at a heat rate of $5^\circ C\,min^{-1}$ from room temperature up to about 700°C using synthetic air (AGA, >99.99%) as a reactive gas and nitrogen (AGA, >99.999%) as a protective gas. For Fourier transform infrared spectroscopic (FTIR) analysis, the grafted silica gel was powdered, diluted with dry KBr (95% KBr), and pressed to a pellet. FTIR absorbance spectra were measured using a Perkin–Elmer FTIR 2000 spectrometer over the range $4500–450\,cm^{-1}$ at $2\,cm^{-1}$ resolution and $0.5\,cm^{-1}$ spectral intervals as the average of ten scans.

The degree of swelling of the sulfonated polystyrene grafted silica gel sorbent was determined by measuring the diameter and/or area of sorbent particles first swollen in water and finally when dry. In order to be sure that a real swelling maximum has been achieved, the sorbent particles were equilibrated in solution for several days. Measurement of the diameter and/or area was carried out using apparatus consisting of an optical microscope connected to an image analyzer with image analysis software (SigmaScan Pro 4.0).

The ammonium sorption isotherm at 298 K for the concentration range of $0.4–140\,mg\,dm^{-3}$ was determined by batch experiments in a 1-dm^3 jacketed glass reactor stirred with a pitched four-blade turbine at $700\,min^{-1}$. A Lauda B water thermostat was used for temperature control. The breakthrough and regeneration experiments were measured at 298 K in a laboratory-scale fixed bed glass column. The velocities and dimensions are shown in Table 1. In all the experiments, the ammonium solutions were prepared by NH_4Cl and distilled water. After each sorption experiment, the sorbent was regenerated by 2 M HCl solution.

The ammonium concentrations were determined using an Orion 95-12 ammonia selective electrode and a Schott CG 841 measuring device. For the analyses, the pH of the solutions was raised to 11 by 1M NaOH solution. The determination method is presented in the APHA standard (16).

Table 1. Experimental values required for the dynamic calculation

Variable	
Feed concentration	$140\,mg\ NH_4^+\,dm^{-3}$
Particle diameter	0.35 mm
Bed porosity	0.45
Bed i.d.	28 mm
Bed length	14 mm
Bed density	$580\,kg\,m^{-3}$
Fluid density	$998.054\,kg\,m^{-3}$
Fluid viscosity	$0.9808 \times 10^{-3}\,kg\,m^{-1}\,s^{-1}$

In this study, all ammonia present was regarded as being in the ammonium form, because the pH was always kept ≤ 7.

EQUILIBRIUM MODELS

Sorption equilibrium data were fitted to the Langmuir, Freundlich, Langmuir–Freundlich, and Toth isotherm models. The well-known and widely accepted Langmuir model is written in the textbook of Ruthven (17) as

$$q^* = \frac{q_s bc}{1 + bc} \tag{1}$$

where q^* is the sorbate concentration in equilibrium, q_s is the saturation sorbate concentration, b is the adsorption equilibrium constant, and c is the bulk concentration.

The Freundlich model is commonly used for liquid phase sorption data, although its thermodynamical basis is not indisputable (17, 18):

$$q^* = Kc^n \tag{2}$$

where K is the Freundlich constant and n is an empirical exponent.

The Langmuir–Freundlich model is commonly regarded as an empirical model, but it has been observed to model a wide variety of sorption data (17, 18):

$$q^* = \frac{q_s bc^n}{1 + bc^n} \tag{3}$$

The Toth model is used as an equilibrium correlation in the adsorption data handbook of Valenzuela and Myers (19). Although the thermodynamical basis of the Toth model has been considered questionable, Toth himself (20) has proved the thermodynamic consistency of the model:

$$q^* = \frac{q_s c}{(b + c^n)^{1/n}} \tag{4}$$

The Langmuir and Toth models follows the Henry law at low sorbate concentrations, that is the linear dependence of sorbate concentration and bulk concentration. The dependence is nonlinear for the Freundlich and Langmuir–Freundlich models, and thus they do not fulfil the Henry law requirement of thermodynamical consistency.

DYNAMIC MODEL

The dynamic single-bed sorption column model is based on the following assumptions:

1. One sorbing component (NH_4^+) with a non-sorbing carrier (water);
2. Low-concentration feed, constant fluid velocity in the column;

3. An isothermal column;
4. Spherical adsorbent pellets of identical size;
5. The pressure drop is neglected; and
6. Radial velocity and concentration gradients inside the bed are negligible.

Applying these assumptions to the mass balance of the aqueous phase through a packed bed, the following equation is obtained (17, 18):

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial t} = D_L\frac{\partial^2 c}{\partial z^2} \tag{5}$$

where t is time, v is the fluid velocity, z is the length coordinate of the column, ε is the bed porosity, and D_L is the axial dispersion coefficient.

The sorption rate of the sorbent particle is assumed to follow the linear driving force (LDF) approximation (17, 18):

$$\frac{\partial q}{\partial t} = \frac{10D_e}{d_p}(q_i - q) \tag{6}$$

where q is the sorbate concentration, D_e is the effective diffusion coefficient, and d_p is the diameter of sorbent particle.

The boundary conditions are for the Eq. (5):

$$c(0, z) = 0$$
$$c(t, 0) = c_{feed}$$
$$\frac{\partial c}{\partial z}(t, L) = 0$$

The Langmuir-Freundlich and Toth isotherms were chosen for the ammonium sorption equilibria in the dynamic model. The fluid phase mass-transfer coefficient was calculated from the correlation of Wilson and Geankoplis given by Ruthven (17). The fluid diffusion coefficient was obtained by the Wilke-Chang equation (21). Table 1 shows the experimental values required for the dynamic calculation.

NUMERICAL TECHNIQUES

Partial differential equations (PDEs) representing mass balance were solved by numerical method of lines (NUMOL): the PDEs were converted to the system of ordinary differential equations (ODEs) by discretization of the spatial derivatives with finite differences (22). The convection term was discretized by a five-point centered approximation formula for first-order derivatives (DSS024). The dispersion term was discretized by a five-point centered approximation formula for second-order derivatives (DSS044). The ODEs were integrated by backward difference method implemented in the LSODES software. The number of axial grid nodes used was at least 50.

The parameters of the dynamic model and the isotherm models were estimated by minimizing the weighted sum of residual squares, *i.e.*, the differences between the experimental and estimated concentrations (23). The objective function (Q) to be minimized was expressed as follows:

$$Q = \sum w(y - y)^2$$

Equally weighted concentrations ($w = 1$) gave the best fit. For the dynamic model and the isotherm models, the y's were solution concentrations and solid concentrations, respectively. The objective function of the isotherm models was minimized by the Levenberg-Marquardt algorithm. A simplex algorithm was used for the dynamic model. The solution of the dynamic model and the parameter estimation was carried out using MODEST software (23).

RESULTS AND DISCUSSION

The titrated dry acid capacity of the synthesized sorbent is 0.92 mmol g^{-1}. Thus, the wet capacity of the sorbent is 0.53 mol H$^+$ dm^{-3}, which is 25–30% of the typical values for gel-type ion-exchange resins. The ammonium capacity of the grafted silica gel is 24.5 mg g^{-1} (1.36 in mmols). Evidently, since the ammonium capacity is higher than the acid capacity, ammonium is sorbed by both an ion-exchange mechanism and physical bonds. Ammonium physisorption along with ion-exchange has also been observed for the ion-exchange resins (24). TGA analysis (Fig. 2) reveals the following facts:

1. Oxidation and degradation of sulfonic acid groups occur above 80°C in air;
2. Decomposition of polystyrene occurs above 250°C; and

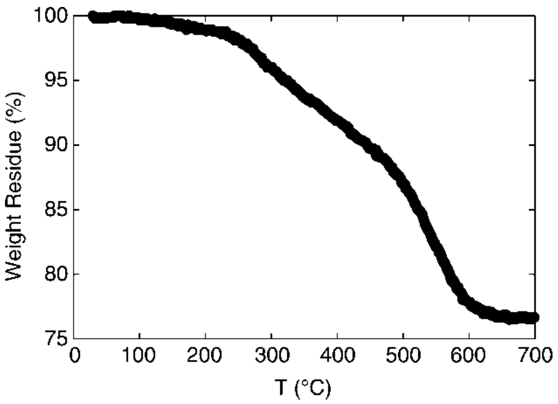

Figure 2. Thermogravimetric analysis of sulfonated polystyrene grafted silica gel sorbent.

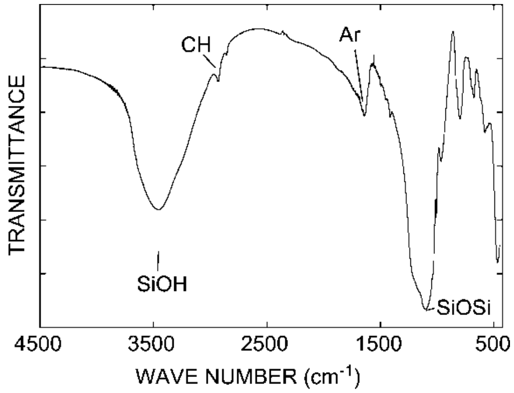

Figure 3. FTIR spectrum of sulfonated polystyrene grafted silica gel sorbent.

3. The amount of chemically bound sulfonated polystyrene in the grafted silica is approximately 22 w-%.

The reaction of silanols to siloxane gives 1.5 w-% weight loss. Fig. 3 shows the FTIR spectrum of the grafted silica gel. The peaks of the silanol group at 3450 cm^{-1} and siloxane group at 1100 cm^{-1} are the easiest to identify. Since the amount of silica gel in the sample is high and the absorbance of silanol and siloxane groups is very strong, the peaks of other groups, such as sulfonic acid groups, are partly covered. The peaks at 600–700 cm^{-1} comes from the sulfonic acid groups. The polystyrene gives the aromatic peak at 1640 cm^{-1} and CH peak at 2930 cm^{-1}, and its presence in the sample is clear. Due to the strong absorbance of silanol and siloxane groups, the spectrum does not reveal the presence of the Si–O–C bonds that bind the polymer with the silica gel surface. The swelling experiments revealed that the sulfonated polystyrene grafted silica gel does not swell at all in water. This result was expected, since water should have no effect on the matrix of the silica gel and on the non-cross-linked grafted polystyrene chains.

To compare the accuracy of different isotherm models and the reliability of the parameter estimates, the ammonium equilibrium data obtained from the batch experiments were fitted to the Langmuir, Freundlich, Langmuir-Freundlich, and Toth models. Table 2 shows the regression results, including the statistics for the goodness of fit, the parameter estimates, and the confidence intervals of the parameter estimates. The two-parameter Langmuir model depicts unsatisfactorily the ammonium equilibrium data. The coefficient of determination (R^2) is 94.69%, the residual sum of squares (RSS) is 5.78, and standard error of estimate is 0.761, which all represent a poor fit. The Freundlich model provides a slightly better fit. Its R^2 value is 97.66%, RSS value is 2.55, and standard error of estimate is 0.505. Evidently, more than two parameters are required to obtain a satisfactory

Table 2. Parameter estimation for the isotherm models

Isotherm model	Henry law region	Parameter estimation	
Freundlich	Nonlinear	$R^2 = 97.66\%$ $K = 2.79 \pm 0.21\,\mathrm{mg\ NH_4^+\ g^{-1}\ (mg\ NH_4^+\ dm^{-3})^{-n}}$ $n = 0.261 \pm 0.020$	Total SS 109 RSS 2.55 Std. Err. of Estimate 0.505
Langmuir	Linear	$R^2 = 94.69\%$ $q_s = 8.87 \pm 0.45\,\mathrm{mg\ NH_4^+\ g^{-1}}$ $b = 0.213 \pm 0.054\ \mathrm{(mg\ NH_4^+\ dm^{-3})^{-1}}$	Total SS 109 RSS 5.78 Std. Err. of Estimate 0.761
Langmuir–Freundlich	Nonlinear	$R^2 = 98.88\%$ $q_s = 13.3 \pm 2.4\,\mathrm{mg\ NH_4^+\ g^{-1}}$ $b = 0.225 \pm 0.043\ \mathrm{(mg\ NH_4^+\ dm^{-3})^{-n}}$ $n = 0.486 \pm 0.078$	Total SS 109 RSS 1.22 Std. Err. of Estimate 0.368
Toth	Linear	$R^2 = 98.90\%$ $q_s = 17.5 \pm 6.33\,\mathrm{mg\ NH_4^+\ g^{-1}}$ $b = 0.729 \pm 0.185\ \mathrm{(mg\ NH_4^+\ dm^{-3})^{n}}$ $n = 0.278 \pm 0.095$	Total SS 109 RSS 1.20 Std. Err. of Estimate 0.365

fit. The three-parameter Langmuir–Freundlich and Toth models give, in practice, equally accurate fits. For example, Toth model provides R^2 value 98.90%, RSS value 1.20, and standard error of estimate 0.365.

The accuracy of the isotherm model is essential for interpolation, but the reliability of the parameter estimates is also necessary to predict the ammonia sorbate concentration outside the experimental data range. The Freundlich model has the smallest confidence intervals of the parameter estimates. For both the parameters, the confidence intervals are smaller than 8%. Although the thermodynamical basis of the Langmuir model is the most firm of the models in this work, only the parameter q_s is reliable. The confidence interval of parameter b is 25%. The thermodynamical assumptions of the Langmuir model are simply not valid for a sorbent with a heterogeneous surface. The confidence intervals of Langmuir–Freundlich model are smaller (16–19%) than those of the Toth model (15–36%). However, it is to be emphasized that none of the models can be used for reliable extrapolation, and the usability of each model must be ascertained by experiments.

Fig. 4 shows the fits of the Freundlich, Langmuir, Langmuir–Freundlich, and Toth models to the ammonium equilibrium data. As can be seen, the Langmuir and Freundlich models provide poor fits, but the fits of the Langmuir–Freundlich and Toth models are good. The isotherm form of

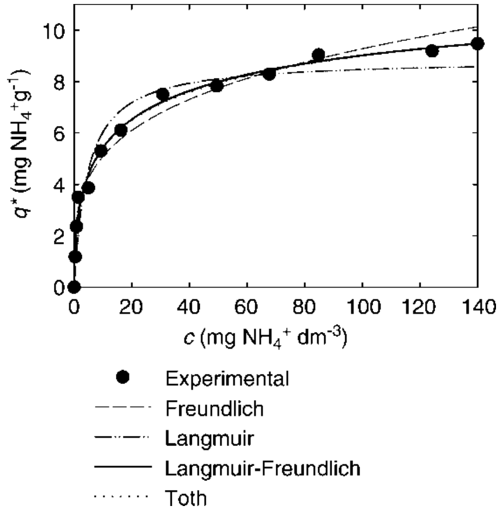

Figure 4. Ammonium sorption equilibria and isotherm models on a sulfonated polystyrene grafted silica gel.

the grafted silica gel is highly favorable for ammonium sorption, since the form is convex. Experimental ammonia sorption equilibria and pH values at equilibrium can be seen in Table 3. Measured pH values corresponded well the theoretical values calculated on the basis of eluted H^+ ions.

At first, it was intended to determine the sorption rate, namely kinetics, of the sulfonated polystyrene grafted silica gel using batch experiments in a mechanically agitated vessel, in which film diffusion could be easily

Table 3. Ammonia sorption equilibria and pH values at equilibrium. Initial pH was 6.00 in the batch sorption experiments

c (mg NH_4^+ dm^{-3})	q^* (mg NH_4^+ g^{-1})	pH_{eq} (−)
0.39	1.18	3.59
0.83	2.36	3.29
1.40	3.50	3.12
4.92	3.86	3.08
9.33	5.30	2.94
16.2	6.11	2.88
30.7	7.51	2.79
49.5	7.83	2.77
67.7	8.29	2.75
84.8	9.04	2.71
124.2	9.19	2.70
140.0	9.53	2.69

be excluded. The experimental arrangement was planned on the basis of published data for the ion-exchange resin, where sampling every 2.5 min is sufficient. For example, Lin and Wu (7) have reported that the commercial ion-exchange resin reaches equilibrium in 20–30 min in a batch ammonium sorption experiment. Surprisingly, the kinetics of the grafted silica gel was so rapid that equilibrium was reached before 2.5 min. Therefore, we were compelled to determine the kinetics by breakthrough experiments in a column.

The effects of flow rate on the sorption were measured by breakthrough experiments. These data were used to determine sorption kinetics for the sulfonated polystyrene grafted silica gel. The experimental data were fitted to a dynamic isothermal mathematical model in order to obtain the effective diffusion and axial dispersion coefficients. The effective diffusion coefficient is the rate-determining parameter in the LDF equation. Table 4 shows the parameter estimation results of dynamic modeling. In the dynamic model, the effect of the isotherm equation on the accuracy of fit was also compared. The Toth isotherm model that follows the Henry law at low concentrations give a slightly better fit than the Langmuir–Freundlich model. The R^2 values of the Toth and Langmuir–Freundlich models are 99.46 and 99.42%, respectively. Although the Toth and Langmuir–Freundlich models are not statistically equal, the parameter estimates of the effective diffusion coefficient ($0.0206 \times 10^{-9}\,m^2\,s^{-1}$) and axial dispersion coefficient ($1.53 \times 10^{-6}\,m^2\,s^{-1}$) are equal for both the isotherm models. The confidence intervals of the parameter estimates are small. The fits of the dynamic model with the two isotherm models can be seen in Fig. 5. On the basis of Fig. 5, it is impossible to distinguish the fits of the two models. In general, the dynamic model provides an excellent fit on the breakthrough data showing that all parts of model, including the LDF equation for the kinetics and the isotherm models for the equilibria, are accurate and valid.

The effect of initial solution acidity on the sorption was studied by breakthrough experiments with pH of 1, 4, and 7 (Fig. 6). The amount of sorbed ammonium decreased as the pH decreased, *e.g.*, at pH 1.00 the amount of sorbed ammonium was negligible. Low pH decreases the ammonium removal efficiency, since NH_4^+/H^+ selectivity is low. To obtain the greatest

Table 4. Parameter estimation for the dynamic model with two different isotherm equation

Langmuir–Freundlich	Toth
$R^2 = 99.42\%$	$R^2 = 99.46\%$
$D_e = (0.0206 \pm 0.0043) \times 10^{-9}\,m^2\,s^{-1}$	$D_e = (0.0206 \pm 0.0067) \times 10^{-9}\,m^2\,s^{-1}$
$D_L = (1.53 \pm 0.05) \times 10^{-6}\,m^2\,s^{-1}$	$D_L = (1.53 \pm 0.05) \times 10^{-6}\,m^2\,s^{-1}$
Total SS 33150	Total SS 33150
RSS 192	RSS 179
Std. Err. of Estimate 4.93	Std. Err. of Estimate 4.73

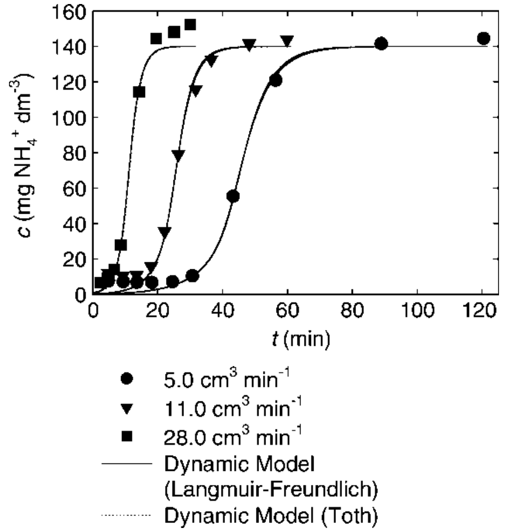

Figure 5. Breakthrough curves showing effect of flow rate on the sorption of ammonium (5.0 cm^3 min^{-1}: $\mathrm{pH}_{\mathrm{initial}} = 7.00$, $\mathrm{pH}_{\mathrm{eq,measured}} = 2.49$, and $\mathrm{pH}_{\mathrm{eq,theoretical}} = 2.43$; 11.0 cm^3 min^{-1}: $\mathrm{pH}_{\mathrm{initial}} = 7.02$, $\mathrm{pH}_{\mathrm{eq,measured}} = 2.47$, and $\mathrm{pH}_{\mathrm{eq,theoretical}} = 2.46$; 28.0 cm^3 min^{-1}: $\mathrm{pH}_{\mathrm{initial}} = 7.00$, $\mathrm{pH}_{\mathrm{eq,measured}} = 2.50$, and $\mathrm{pH}_{\mathrm{eq,theoretical}} = 2.49$).

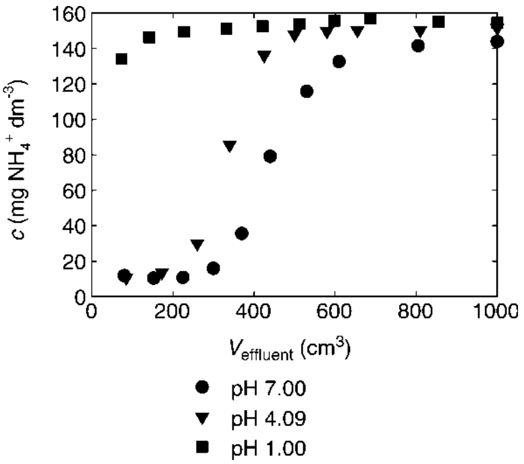

Figure 6. Breakthrough curves showing effect of pH on the sorption of ammonium ($\mathrm{pH}_{\mathrm{initial}} = 7.00$: $\mathrm{pH}_{\mathrm{eq,measured}} = 2.47$ and $\mathrm{pH}_{\mathrm{eq,theoretical}} = 2.46$; $\mathrm{pH}_{\mathrm{initial}} = 4.09$, $\mathrm{pH}_{\mathrm{eq,measured}} = 2.30$ and $\mathrm{pH}_{\mathrm{eq,theoretical}} = 2.57$; $\mathrm{pH}_{\mathrm{initial}} = 1.00$: $\mathrm{pH}_{\mathrm{eq,measured}} = 1.00$, and $\mathrm{pH}_{\mathrm{eq,theoretical}} = 1.00$).

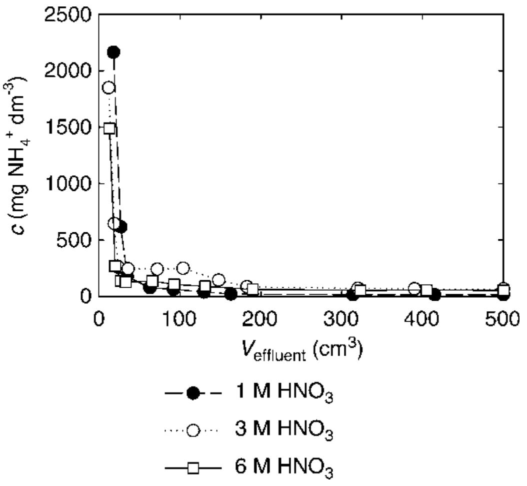

Figure 7. Regeneration curves in the eluation of ammonium.

ammonia removal efficiency the pH should be kept just below 7. However, it should be borne in mind that low NH_4^+/H^+ selectivity is beneficial for regeneration.

Figure 7 shows the regeneration experiments that were carried out using 1, 3, and 6 M HNO_3. The rapid kinetics of the grafted silica gel hindered the obtaining of exact elution curves. The regeneration experiments revealed that ammonium can be eluted rapidly using a strong mineral acid. In addition, highly concentrated ammonium solution can be obtained. The maximum ammonium concentration of elution peak is over 2000 mg dm^{-3}. Practically all ammonium was eluted already with 100 cm^3. The stability of the grafted silica gel was elucidated in connection with the regeneration experiments. It appeared that the acid and ammonium capacities of the sorbent after the sorption and regeneration experiments were the same as that of the fresh sorbent. Thus, the synthesized sorbent is stable in the presence of a strong mineral acid as well as in acidic aqueous solutions.

CONCLUSIONS

Sulfonated polystyrene grafted silica gel sorbent is synthesized in three steps, including polymerization, grafting, and sulfonation steps. The synthesized sorbent contains 22 w-% covalently-bound polymer supported over silica gel, and it provides an acid capacity of 0.92 mmol g^{-1} and ammonum capacity of 1.36 mmol g^{-1}. The higher ammonium capacity compared to the acid capacity reveals that ammonium is sorbed by both physisorption and chemisorption on the synthesized sorbent. Ammonium is strongly sorbed on the sulfonated polystyrene grafted silica gel, which can be seen in the favorable form of the ammonium isotherm. Equilibrium data obtained from batch experiments were fitted to four isotherm models: the Toth and Langmuir-Freundlich isotherm models provided the best fit. The breakthrough data from the column experiments were fitted to a dynamic model. It was found that the linear driving force approximation depicts accurately the kinetics and that the dynamic model with the Langmuir-Freundlich isotherm equation gives as good fits as with the Toth equation. A fitted effective diffusion coefficient shows that the sorption rate onto the sulfonated polystyrene grafted silica gel is higher than the literature values for ion-exchange resins. Breakthrough experiments were also carried out using different initial pH of ammonium solutions. Low pH decreases the sorption efficiency, since NH_4^+/H^+ selectivity is low. The fast kinetics of the sorbent also occurred in regeneration experiments, and ammonium elutes rapidly in regeneration by HNO_3. The ammonium capacity did not deteriorate during several successive sorption-regeneration cycles.

Although the sorption capacity of the sulfonated polystyrene grafted silica gel is lower than that of the ion-exchange resins, the rapid kinetics and non-swelling, as well as the rigid structure, improve the ammonium sorption process performance. In the sorption columns, higher velocities and shorter cycle times can be used than in the processes with ion-exchange resins so higher sorption capacities can be obtained. By supporting the sulfonated non-crosslinked polystyrene onto silica gel via chemically resistant bonds, the good properties of polymeric and inorganic sorbents can be combined.

NOMENCLATURE

b	adsorption equilibrium constant
c	concentration
D_e	effective diffusion coefficient
D_L	axial dispersion coefficient
d_p	particle diameter
K	Freundlich constant
L	bed length
n	exponent
Q	object function
q	sorbate concentration
q^*	sorbate concentration at equilibrium
q_i	sorbate concentration at the surface of sorbent
q_s	saturation sorbate concentration
t	time
v	fluid velocity
y	variable in the object function
z	distance measured from column inlet
ε	bed porosity

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REFERENCES

1. Patterson, J.W. (1985) *Industrial Wastewater Treatment Technology*; Butterworth: Boston, 235–255.
2. Jääskeläinen, E. and Paatero, E. (1999) Properties of the ammonium form of versatic 10 in a liquid–liquid extraction system. *Hydrometallurgy*, 51: 47–71.
3. Higgins, I.R., Chopra, R.C., and Roland, L.D. (1978) Continuous ion exchange achieves unique solutions in pollution control. *Institution of Chemical Engineers Symposium*, 54: 105–110.
4. Bolto, B.A. and Pawlowski, L. (1987) *Wastewater Treatment by Ion-Exchange*; E. & F. N. SPON: London, 180–182.
5. Van Moorsel, W.H. (1975) Ion exchange for nitrogen removal. *Ammonia Plant Safety and Related Facilities*, 17: 87–92.
6. Brennan, J.F. (1976) The Chem-Seps nitrogen recovery process: a pollution solution that works. *Environmental Symp. Proc.*, 16: 217–249.
7. Lin, S.H. and Wu, C.L. (1996) Ammonia removal from aqueous solution by ion exchange. *Ind. Eng. Chem. Res.*, 35 (2): 553–558.
8. Cooney, E.L., Booker, N.A., Shallcross, D.C., and Stevens, G.W. (1999) Ammonia removal from wastewaters using natural Australian zeolite II. Pilot-scale study using continuous packed column process. *Sep. Sci. Technol.*, 34 (14): 2741–2760.
9. Buday, M. (1994) Reutilization of ammonia from wastewater using cation exchange resins. *Wat. Sci. Tech.*, 30 (9): 111–119.
10. Haralambous, A., Maliou, E., and Malamis, M. (1992) The use of zeolite for ammonium uptake. *Wat. Sci. Tech.*, 25 (1): 139–145.
11. Plueddemann, E.P. (1982) *Silane Coupling Agents*. Plenum: New York.
12. Revillon, A. and Leroux, D. (1995) Functional silica supported polymer. *V. 'Onto' Versus 'From' grafting processes. React. Funct. Polym.*, 26: 105–118.
13. Revillon, A. and Leroux, D. (1997) Acidic properties of functionalized silica-supported polymers: relation between reactivity and morphology. *J. Appl. Polym. Sci.*, 65: 2557–2565.
14. Helminen, J. and Paatero, E.. Inorganic solid supported polymer acid catalyst – sulfonated polystyrene grafted silica gel in liquid phase esterification Submitted.
15. Unger, K.K. (1979) *Porous Silica—Its Properties and Use as Support in Column Liquid Chromatography*. Elsevier: Amsterdam.
16. APHA. In *The Standard Methods for Water and Wastewater Examination*. American Public Health Association: Washington, 1992.
17. Ruthven, D.M. (1984) *Principles of Adsorption and Adsorption Processes*; Wiley: New York.
18. Tien, C. (1994) *Adsorption Calculations and Modeling*; Butterworth: New York.
19. Valenzuela, D.P. and Myers, A.L. (1989) *Adsorption Equilibrium Data Handbook*; Prentice Hall: New Jersey.
20. Toth, J. (1997) Some consequences of the application of incorrect gas/solid adsorption isotherm equations. *J. Colloid. Interface. Sci.*, 185: 228–235.

21. Reid, R.C., Prausnitz, J.M., and Poling, B.E. (1987) *The Properties of Gases & Liquids*; McGraw-Hill: New York.
22. Schiesser, W.E. (1991) *The Numerical Method of Lines: Integration of Partial Differential Equations*; Academic Press: San Diego.
23. Haario, H. (1994) *MODEST Users Manual*; ProfMath Oy: Helsinki, Finland.
24. Sitharamayya, S. and Garg, S.K. (1978) Ammonia sorption by cation-exchange resins. *Indian J. Technol.*, 16 (March): 112–114.