

Performance of sulphonic cation exchangers in the recovery of ammonium from basic and slight acidic solutions

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Abstract

Two sulphonated polystyrene-divinylbenzene cation exchangers (gel type Purolite SGC 100 × 10 MBH and macroporous Purolite C160 MBH) have been investigated for NH₄⁺ ions uptake from the ammonium-rich simulated solutions, corresponding to the caustic condensate of the nitrogen fertilizers production. One component (NH₃ or NH₄NO₃) solutions and the mixtures with varying molar ratio of these compounds have been used at the total concentration 0.214 mol/L. Batch and column experiments have been conducted to establish the influence of the matrix structure on the performance of the cation exchangers investigated during the sorption and the desorption. Batch sorption isotherms and breakthrough curves have shown the similar behaviour of the cation exchangers in the removal of NH₄⁺ and NH₃. On decreasing the influent pH from 11.4 to 5.74 a decrease in breakthrough capacity (BC) from 2.57 to 1.93 mol/L was observed. The distribution coefficients (K_d), calculated from the batch sorption isotherms, are higher for the basic feed solution than for slightly acidic one. Both the degree of the cation exchanger regeneration (N/N_0) and the efficiency of the NH₄⁺ ions recovery (N_R), obtained using 0.7 bed volume (BV) of eluent (20% nitric acid) are lower for Purolite C 160 MBH than those for Purolite SGC 100 × 10 MBH. Using 5 BV of eluent the efficiency of the ammonium recovery amounted to 100% for both cation exchangers investigated. With respect to the efficiency of NH₄⁺ ions sorption and regeneration cation exchangers investigated are applicable for the recovery of ammonium ions from caustic condensate in the nitrogen fertilizers production.

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Keywords: Ammonium; Cation exchangers; Sorption; Regeneration; Recovery

1. Introduction

The removal of ammonia and ammonium ions from industrial effluents is a problem of environmental and economic concern. The major sources of these contaminants include: nitrogen fertilizers production, chemical fiber plants, aquaculture industry, agricultural run-off and others. Ammonium concentration depends on the source of the contamination. It can vary from less than 1 mg/L in aquaculture industry [1] to 10-fold higher in the wastewaters of chemical industry. Complete removal of ammonia is required because of its toxicity to fish species. The exposure of the seabass juvenile to stable ammonia concentrations from 0.24 to 0.90 mg/L for 63 days has shown the loss of weight, the growth stagnation and even mortality [2]. Ammonia, present in the aquatic environment, is toxic to all the verte-

brates causing convulsions, coma and death, probably, because elevated NH₄⁺ displaces K⁺ and depolarises neurons causing cell death in the central nervous system [3]. Although recovery of valuable materials from the wastewater and their return to production is also of great importance, especially when great volumes of the caustic condensate (co-product of the nitrogen fertilizers production) is concerned. Many techniques have been proposed for the removal of ammonium. A number of them, such as biological treatment [4], air stripping, chlorination, lead to the destruction of the ammonium species and the recovery becomes impossible. Electromembrane techniques were proposed to treat the ammonium nitrate containing wastewaters, produced in the nuclear fuel cycle [5]. The ammonia containing wastewater, generated from the NH₄Cl manufacturing, was recycled into the upstream manufacturing process using an ion exchange technique and electrodialysis [6]. From a practical standpoint, ion exchange is one of the most promising techniques. A large number of reports have been published investigating the properties of various ion exchangers towards ammonium ions. The

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Nomenclature

C_0	ammonium concentration in influent (mol/L)
C	ammonium concentration in the fractionated effluent (mol/L)
C_e	ammonium concentration in the eluate (mol/L)
C_t	total ammonium concentration in the treated solution (mol/L)
V	volume of the treated solution (L)
V_e	volume of eluate (L)
K_d	distribution coefficient ($\text{cm}^3 \text{g}^{-1}$)
K_b	base dissociation constant (mol/L)
K_a	acid dissociation constant (mol/L)
EC	static exchange capacity (mmol g^{-1})
BC	breakthrough capacity (mmol/mL)
m_s	mass of solute (g)
m_r	mass of the dry resin (g)
RV	resin volume (mL)
BV	bed volume—the ratio of volume of treated solution to volume of resin, dimensionless
N/N_0	regeneration degree of the cation exchanger—the ratio of the capacity of cation exchanger after regeneration to the capacity at breakthrough, dimensionless
N_R	recovery efficiency—the percentage of ions in the eluate compared to the total amount in the solution before treatment

removal of ammonium by natural zeolites was widely investigated [7–9]. The zeolites occur in relatively large minerable sedimentary deposits in many parts of the world and, as a cheap material, is an alternative to synthetic resins [10]. The batch mode and fixed-bed column experiments have been conducted with a strong acid cation exchanger Amberjet 1200 in Na form aiming at the determination of the effects of pH, humic acid and competitive ions, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} [11]. In the presence of organic contaminants ammonium ion uptake on polymeric macronet exchanger Purolite MN 500 in the Na form was examined [1]. Ammonium–hydrogen exchange on two carboxylate resins Wofatit CA-20 and Amberlite IRC-50 was also investigated [12].

The scale of worldwide production of ammonia and ammonium nitrate is of 100 and 11 millions tonnes of nitrogen a year, respectively [13]. The quantity of fertilizers manufactured by Achema AB (Lithuania) is over 1 million tonnes a year. Emissions of NH_4NO_3 and NH_3 from nitrogen fertilizers production to water can be up to 6 and 3 kg/tonnes, respectively. The lowest possible damage to the environment is achievable with best available techniques (BAT) [13].

Despite the large number of different investigations concerning the ammonium removal from water solutions every special case requires individual examination. The behaviour of ion exchangers towards ammonium ions is dependent on various factors, such as ammonium speciation in the solution, the range of concentration of all the species, the medium of the solu-

tion, the content of side materials. The aim of the present work was to determine the effect of the basicity of solutions corresponding to condensate from nitrogen fertilizers production on the ammonium sorption by sulphonic acid cation exchangers (macroporous Purolite C160 MBH and gel type Purolite SGC 100 \times 10 MBH); to evaluate the influence of polymeric matrix on the ion exchange capacity and the regeneration efficiency under the established experimental conditions with respect to ammonium recovery.

2. Materials and methods

2.1. Cation exchangers

Commercially available ion exchange resins Purolite C160 MBH and Purolite SGC 100 \times 10 MBH (Purolite International Ltd., UK), containing sulphonic acid groups bonded to polystyrene-divinylbenzene network were used. Purolite C160 MBH is a macroporous highly crosslinked ion exchanger and Purolite SGC 100 \times 10 MBH is a gel type one. They have been obtained in Na form. Conversion into H form was carried out by treating the resins with 5 BV of 5% HCl at flow rate of 4 mL/min.

$$\text{BV} = \frac{\text{volume of treated solution}}{\text{volume of resin}}$$

After rinsing with distilled water for the excess acidity elution the resin samples were sieved in the range of 0.315–1 mm. For the determination of their water content, resin aliquots were weighted, dried in an oven at 105 °C to reach a constant weight and weighted again. The results were 43.4% of water for Purolite C160 MBH and 44.3% for Purolite SGC 100 \times 10 MBH. The weight of the dry resin was calculated by correcting the weighed amounts of resins used in the experiments.

2.2. Reagents and apparatus

Ammonium stock solutions were prepared from analytical reagent grade ammonium nitrate by dissolving required quantity of the salt. Volumetric standard solutions of sodium hydroxide and hydrochloric acid were used to standardize the solutions of nitric acid and ammonia, respectively. Distilled water was used throughout the work. Solutions were analysed for NH_4^+ ions using Nesslerisation technique [14]. Ammonium concentration was determined using spectrophotometer KFK-2 (Zagorskiy OMZ, Russia); pH measured using microprocessor pHmeter pH 211 (Hanna instruments).

The coefficient of variation (CV) for the data of NH_4^+ analysis was 1.7% [15]. All the experiments were performed in triplicate and the average results are presented.

2.3. Batch experiments

Simulated solutions of NH_3 and NH_4NO_3 used for the batch and column sorption experiments correspond to the caustic condensate of the nitrogen fertilizers production (Table 1). Batch experiments were carried out under the following conditions:

Table 1
Composition and characteristics of the test solutions

Test solution no.	Analytical concentration (mol/L)		Equilibrium concentration (mol/L)		[NH ₃]/[NH ₄ ⁺]	pH
	NH ₃	NH ₄ ⁺	NH ₃	NH ₄ ⁺		
1	0.214	0	0.212	2 × 10 ⁻³	106	11.4
2	0.176	0.038	0.203	0.011	18.5	10.53
3	0.118	0.096	0.180	0.034	5.3	9.97
4	0.059	0.155	0.133	0.081	1.6	9.46
5	0.006	0.208	0.023	0.191	0.1	8.32
6	0	0.214	7 × 10 ⁻⁵	0.2139	3 × 10 ⁻⁴	5.74

[NH₃] + [NH₄⁺] = 0.214 mol/L.

weighed amounts of resin (0.5 g by dry weight) were contacted with various volumes of the feed solution having fixed concentration of 0.214 mol/L to maintain the ionic strength constant [16]. Each sample was equilibrated at room temperature (20 °C) with periodic agitation three times a day at stirring intensity 400 rpm. The sorption of NH₄⁺ ions was sufficiently fast and the time, taken to reach half-saturation was about 1 min. It was observed that ammonium concentration in the solution became almost stable in more than 2 h, and the adsorption equilibrium was reached after 5 h. Although in batch experiments an equilibration for 24 h was employed. After the attainment of equilibrium resin was separated by filtration, the final pH of aqueous phase was measured, and the concentration of the NH₄⁺ ions in the filtrate determined. Upon the data of an additional experiment, carried out without cation exchangers, the loss of ammonium during filtration was negligible.

The NH₄⁺ static exchange capacity of the resin (mmol g⁻¹) was calculated using the following expression

$$EC = \frac{(C_0 - C)V}{m_r} \quad (1)$$

where C_0 and C are the ammonium concentration in the aqueous phase (mmol/mL) before and after the ion exchange period, respectively, V the volume of the aqueous phase (mL) and m_r is the mass of the dry resin used (g).

Distribution coefficient values (K_d) for ammonium were calculated in accordance with [17] using the batch sorption data. K_d defines the ratio of ammonium ion concentration in the cation exchanger (mmol g⁻¹) to the respective concentration in the solution (mmol cm⁻³).

2.4. Column experiments

Twenty-five milliliter samples of ion exchange resin were placed in a column with a diameter of 20 mm and 80 mm in length. The feed solution entered the top of the column and flowed downward at flow rate of 1.13 mL/min corresponding to that used under industrial conditions. The effluent was fractionated into 25 mL portions. The breakthrough volume of the resin was checked by monitoring the NH₄⁺ ions concentration and pH in the fractions of effluent. Breakthrough capacity was calculated.

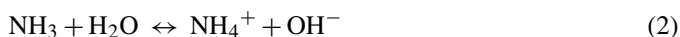
2.5. Desorption experiments

Desorption experiments were performed under dynamic conditions. The retained NH₄⁺ ions were eluted using 20% nitric acid solution at flow rate of 0.4 mL/min. Five-milliliter aliquots of the eluate were collected, and the concentration of eluting agent and released NH₄⁺ ions determined.

3. Results and discussion

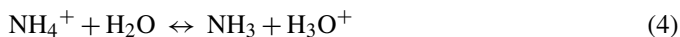
3.1. Batch experiments

Batch sorption isotherm, column breakthrough and desorption studies were conducted to compare two types of strong acid cation exchangers with different structural characteristics. Sulphonic acid ion exchange resins operate mostly through the ion exchange mechanism. Relatively strong acidity of the sulphonic acid group is a reason of ability to ion exchange over a wide pH range [18]. However the pH of the solution is an important factor that controls the sorption of ammonium. Table 1 gives the series of test solutions employed. Varying the ratio of ammonia to ammonium nitrate the total concentration of the ammonium species was maintained constant. The pH of the initial solutions was different resulting from the composition of the solution. NH₃ and NH₄NO₃ dissolved in water give equilibrium concentrations of NH₃ and NH₄⁺. The basicity of the test solution 1 depends on the dissociation constant K_b for ammonia [19]:



$$K_b = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3] = 1.75 \times 10^{-5} \text{ mol L}^{-1} \quad (3)$$

In the solution 6, NH₄⁺ is a weak Brönsted acid which hidrolizes to give an acid solution:



$$K_a = [\text{NH}_3][\text{H}_3\text{O}^+]/[\text{NH}_4^+] = 5.7 \times 10^{-10} \text{ mol L}^{-1} \quad (5)$$

Solutions 2–5 are the mixtures of a weak base (NH₃) and its conjugate acid (NH₄⁺). The pH of the solutions depends on the ratio of the conjugate acid–base pair concentrations:

$$\text{pH} = \text{p}K_a + \log\{[\text{NH}_3]/[\text{NH}_4^+]\} \quad (6)$$

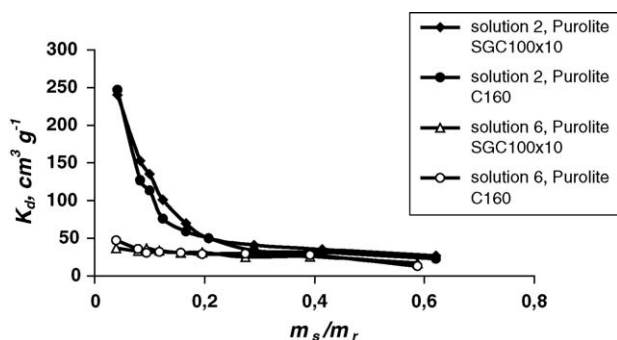
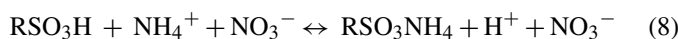


Fig. 1. Dependence of the distribution coefficient K_d on the ratio of the mass of solute (NH_4^+) to the mass of cation exchangers.

When treating the ammonium solutions with hydrogen form of cation exchanger the following reactions take place:



The retention behaviour of the resins towards NH_4^+ ions is promoted by the presence of OH^- ions leading to the neutralization reaction:



In the similar manner the presence of the anion resin in the mixed bed with the cation resin synergized the metal ions uptake [20]. As a parallel, in the mixed resin system H^+ ions generated by the interaction of NaCl with a weak acid resin are sorbed by a weak base resin and govern the salt uptake process [21]. Although the strong acid resins are able to operate over a relatively wide pH range the uptake of ammonium is more favorable at high pH values. In the basic feed solution 2 (see Table 1) the static exchange capacity (EC) with respect to NH_4^+ ions increased, as the ratio of the solute mass to the cation exchanger mass (m_s/m_r) increased, until it reached its maximum values of 5.95 and 5.75 mmol g^{-1} for Purolite SGC 100 \times 10 MBH and Purolite C160 MBH, respectively, however the corresponding values reduced to 4.40 and 4.75 mmol g^{-1} in the slight acidic feed solution 6. In general, the NH_4^+ ions uptake decreases on decreasing the amount of ammonia in the initial solution. The distribution coefficients K_d for NH_4^+ ions calculated from the batch sorption isotherms, refer to the influence of the initial solution pH onto the NH_4^+ sorption. For the basic feed solution K_d values are higher than those for slightly acidic one although an abrupt decrease in K_d for the former is observed on increasing the ratio of the mass of the solute to the mass of the cation exchanger (Fig. 1).

3.2. Column experiments

Column experiments were conducted to obtain the breakthrough curves. The breakthrough capacities as the characteristics of the sorption process have been computed from the breakthrough curves (Fig. 2a and b) accordingly to

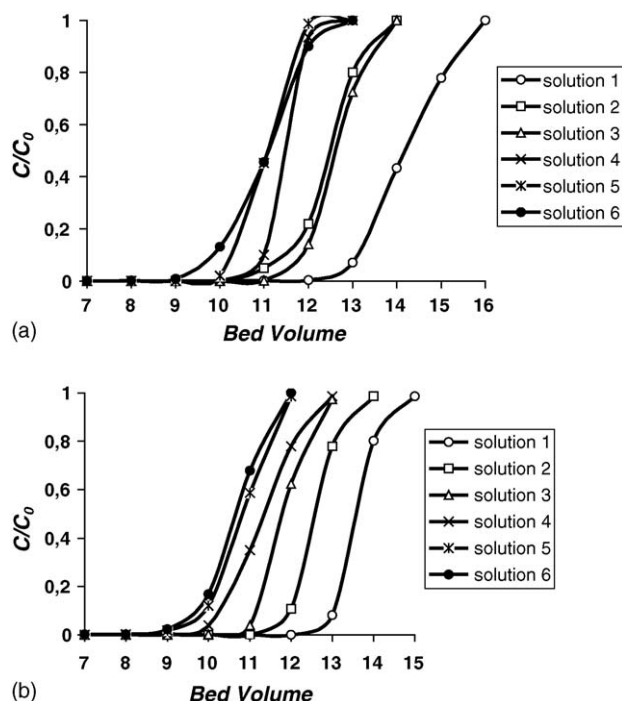


Fig. 2. Breakthrough curves for the sorption of NH_4^+ by Purolite SGC 100 \times 10 MBH (a) and Purolite C160 MBH (b) from NH_3 – NH_4NO_3 solutions. Flow rate 1.13 mL/min.

the equation

$$\text{BC} = \frac{VC_0}{\text{RV}} = \text{BVC}_0 \quad (10)$$

where V is the volume of the solution treated until breakthrough (mL), C_0 the concentration of initial solution (mmol/mL), RV the resin volume (mL), BV the bed volume (the ratio of the volume of treated solution to the volume of resin) and BC is the breakthrough capacity (mmol/mL).

Two concentrations of NH_4^+ ions have been chosen as the breakthrough values: 0.2 g/L corresponding to 5% of the initial concentration and 2 g/L, corresponding to 50% of the initial concentration. It was revealed that the higher the initial solution pH, the higher the ammonium uptake by the two cation exchangers investigated (Table 2). The different pH of the effluents in the series arises from the different solution speciation, and, consequently, different influent pH. When the uptake of NH_4^+ takes place from the ammonia solution (Table 1, solution 1) the effluent pH is near 4. It can be explained as follows: when the solution of weak base NH_3 is brought in contact with strong acid resins, such as Purolite C160 MBH or Purolite SGC100 \times 10 MBH, the neutralization reaction occurs (Eq. (7)). pH of the solutions, leaving the columns, decreases gradually in the series of 1–6 test solutions. The effluent pH of solutions 2–6 ranged from 1.52 to 0.79 because of the excess of H^+ ions liberated from the resin and not involved in the neutralization reaction. After the breakthrough an increase in the effluent pH is observed (Fig. 3a and b), and this indicates that the exhaustion of the resin bed with NH_4^+ is attained.

In the test solution 1 the last portions of the effluent before breakthrough tend to neutral. There is no significant difference

Table 2
Column performance of the cation exchangers for the removal of NH_4^+ from $\text{NH}_3\text{--NH}_4\text{NO}_3$ solutions

Test solution no.	Purolite C 160 MBH			Purolite SGC 100 × 10 MBH		
	Effluent pH at 5% break-through	Breakthrough capacity, mmol/mL of cation exchanger		Effluent pH at 5% break-through	Breakthrough capacity, mmol/mL of cation exchanger	
		5%	50%		5%	50%
1	7.10	2.57	2.98	7.78	2.57	2.79
2	1.52	2.35	2.59	1.73	2.25	2.31
3	1.15	2.35	2.49	1.15	2.35	2.52
4	0.95	2.14	2.31	0.92	2.14	2.17
5	0.79	1.93	2.06	0.83	2.14	2.20
6	0.79	1.93	1.94	0.81	1.93	2.13

Flow rate 1.13 mL/min.

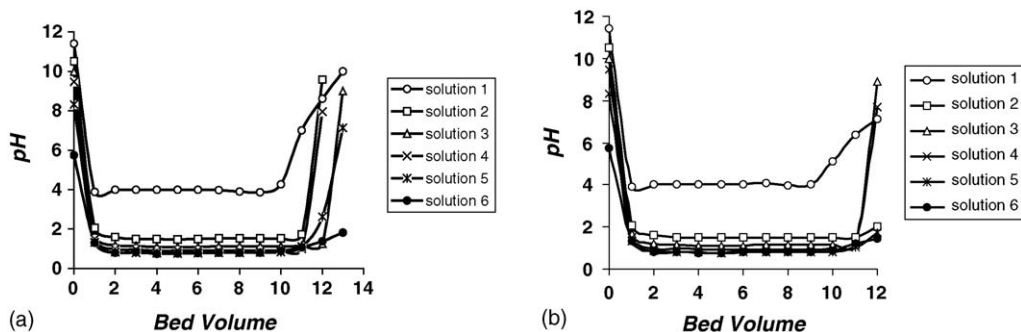


Fig. 3. Effluent pH variation for the NH_4^+ removal by Purolite SGC 100 × 10 MBH (a) and Purolite C160 MBH (b) from $\text{NH}_3\text{--NH}_4\text{NO}_3$ solutions. Flow rate 1.13 mL/min.

between the gel type (Figs. 2a and 3a) and macroporous cation exchanger (Figs. 2b and 3b) operation towards the NH_4^+ ions uptake.

3.3. Desorption experiments

The aim of desorption was the enrichment of the eluate with NH_4^+ ions as high as possible. The retained NH_4^+ ions were eluted using 20% nitric acid solution. The data of Fig. 4 refer to the desorption of NH_4^+ ions from the resins, treated with test solution 2 (see Table 1). The desorption was characterized by

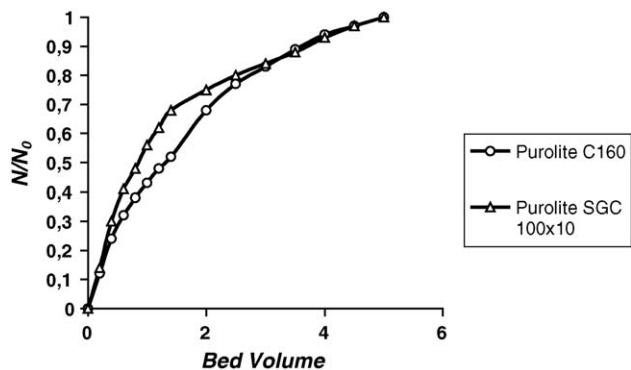


Fig. 4. Dependence of the regeneration degree (N/N_0) on the bed volume of eluent (20% HNO_3) for Purolite C160 MBH and Purolite SGC 100 × 10 MBH, saturated with test solution 2 (Table 1). Flow rate 0.4 mL/min.

the regeneration degree of cation exchanger N/N_0 , i.e. the ratio of the capacity of cation exchanger after the partial regeneration to the capacity at breakthrough.

The initial slopes of the curves reflect different regeneration levels of the two resins, attained with the first portions of regenerant. The comparison of the regeneration behaviour of the resins refers to the faster stripping of NH_4^+ ions from the gel type matrix (Fig. 5a) than that from macroporous one (Fig. 5b).

When the regeneration of the two resins up to 80% with three BV of eluent is achieved, the same evolution of desorption for both cation exchangers proceeds (Fig. 4). To reach the quantitative (complete) recovery of NH_4^+ ions five BV of the eluent are required (Fig. 4). When the saturation is accomplished with the test solutions 2–4, i.e. the mixtures of NH_3 and NH_4NO_3 the regeneration efficiency of the two resins is higher when compared to that obtained after the saturation with one component solutions (Fig. 5a and b). For the macroporous cation exchanger the regeneration curves 1–6 are situated in parallel indicating that the desorption occurs gradually. Fig. 6a and b illustrates the nitric acid and NH_4^+ ions concentrations in the eluate as a function of BV of eluate.

In the eluate the concentration of NH_4^+ ions correlates with the concentration of the acid. The average concentration of ammonium ions in 1–6 eluates from Purolite SGC 100 × 10 MBH cation exchanger is approximately 1.5-fold higher than that from Purolite C160 MBH and vice versa the average concentration of HNO_3 is 1.5-fold higher in the eluates from Purolite C160 MBH. The action of the eluent is more effective for the

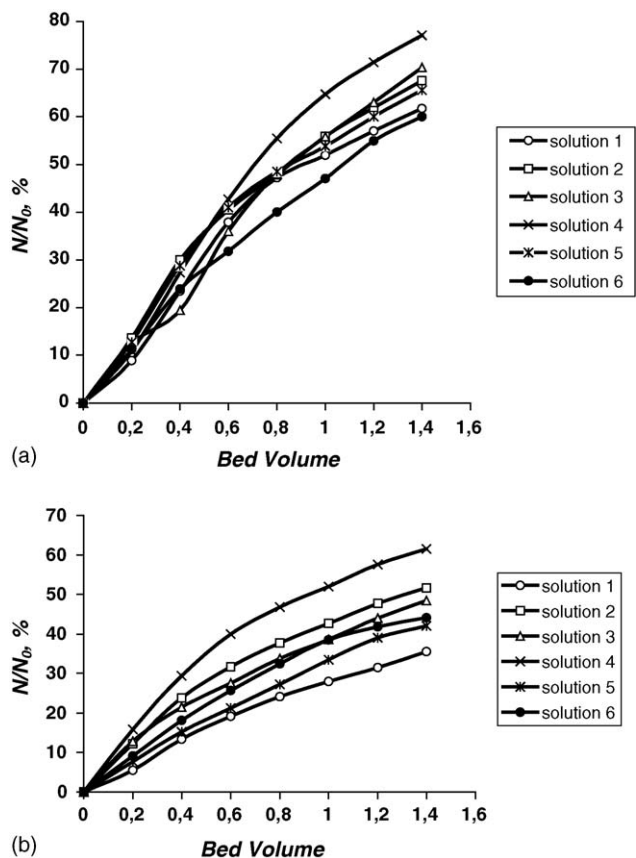
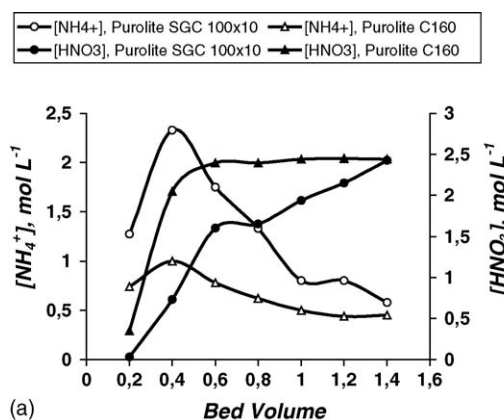


Fig. 5. Dependence of the regeneration degree (N/N_0) on the bed volume of eluent (20% HNO_3) for Purolite SGC 100 \times 10 MBH (a) and Purolite C160 MBH (b). Flow rate 0.4 mL/min.

column, packed with gel type cation exchanger Purolite SGC 100 \times 10 MBH (Table 3). The data of desorption allows to conclude that the latter has a certain superiority against the macroporous Purolite C160 MBH with respect to the regeneration. The inhibiting effect of the macroporous matrix to the desorption process can be attributed to the complicated accessibility of the active sites, situated in the micropores of the polymeric skeleton.



3.4. Efficiency of the NH_4^+ ions recovery

To evaluate the performance of the cation exchangers investigated the ammonium recovery efficiency (N_R) was calculated. Recovery efficiency is defined as a percentage of ammonium ions in the eluate compared to the total amount in the solution before treatment [22]:

$$N_R = \frac{C_e V_e}{C_0 V} \times 100 \quad (11)$$

where C_0 is the ammonium initial concentration in the solution before treatment (mol/L), C_e the total concentration of NH_4^+ ions in the eluate (mol/L), V the volume (L) of the solution treated until $C/C_0 = 0.05$ and V_e is the volume of the eluate (L). Here C (mol/L) is the ammonium concentration in the solution after treatment until breakthrough (mol/L). The efficiency of the NH_4^+ ions recovery using the 0.7 BV of eluent for macroporous cation exchanger Purolite C160 MBH is lower than that for the gel type Purolite SGC 100 \times 10 MBH (Table 4). The two cation exchangers demonstrate high recovery efficiency, obtained with five BV of eluent (Table 4). The content of NH_4^+ ions, passed through the column packed with macroporous ion exchanger, is lower when compared to that for gel type cation exchanger and the total ammonium concentration (C_t) in the solution after treatment (until breakthrough) for Purolite C160 MBH is lower than that for Purolite SGC 100 \times 10 MBH (Table 4). It was determined from the mass balance equation

$$C_t = C_0 - \frac{C_e V_e}{V} \quad (12)$$

where C_0 is the ammonium concentration (mol/L) in influent, C_e the ammonium concentration (mol/L) in eluate, V_e the volume of eluate (L) and V the volume of the treated solution until 5% breakthrough (L).

All over the sorption cycle the concentration of NH_4^+ ions in the fractionated effluent samples from Purolite C160 MBH was lower when compared to that from Purolite SGC 100 \times 10 MBH.

Modern environmental regulations become more stringent and require introducing the most effective methods of

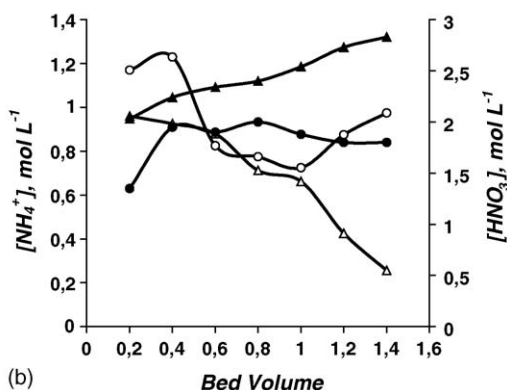


Fig. 6. Concentration of NH_4^+ and HNO_3 in the eluate from the regeneration of Purolite SGC 100 \times 10 MBH and Purolite C160 MBH, saturated with test solution 1 (a) and test solution 6 (b).

Table 3
Concentration of NH_4NO_3 and HNO_3 in the eluate from the regeneration of the cation exchangers, saturated with NH_3 – NH_4NO_3 test solutions, and regeneration degree N/N_0 (%)

Test solution no.	Purolite C 160 MBH			Purolite SGC 100 × 10 MBH		
	NH_4NO_3 (g/L)	HNO_3 (g/L)	N/N_0 (%)	NH_4NO_3 (g/L)	HNO_3 (g/L)	N/N_0 (%)
1	62.74	109.28	24.1	133.53	62.69	47.2
2	99.60	117.05	37.7	113.98	100.80	47.8
3	84.17	112.82	33.7	126.77	78.75	48.0
4	114.34	139.51	46.8	128.20	76.86	55.5
5	57.64	143.26	27.8	126.08	87.57	48.6
6	69.48	141.55	32.4	80.02	106.28	40.0
Average (g/L)						
1–6	81.38	127.25	33.8	118.10	85.49	47.8

Eluent 0.7 BV of 20% HNO_3 . Volume of cation exchanger 25 mL. Flow rate 0.4 mL/min.

wastewater treatment. The selection of the technique for the treatment of wastewater from the nitrogen fertilizers production depends on the concentration of ammonium in waste effluent. The high purification of NH_4NO_3 – NH_3 solutions from ammonium could be reached by means of ion exchange when the influent concentration is close to that used in this work (an order of 0.2 mol/L). Both cation exchangers investigated (macroporous Purolite C160 MBH and gel type Purolite SGC 100 × 10 MBH) demonstrate high ammonium sorption capacity and high recovery efficiency. Experimental results verified the feasibility of the removal of NH_4^+ ions from basic as well as from slight acidic waste streams of nitrogen fertilizers production. From the economic point of view the cation exchange resins can be used repeatedly for sufficiently long time, and nitric acid as a regenerant for the cation exchangers is readily available as a product of the same nitrogen fertilizers plant. Inexpensive alternative ion exchangers, such as natural zeolites, could be introduced into the recovery of ammonium although their selectivity for NH_4^+ ions and the sorption capacity are strongly dependent on the origin of these adsorbents. Usually zeolites have a lower ion exchange capacity when compared to synthetic ion exchange resins [1]. The treatment of NH_4NO_3 – NH_3 solutions by ion exchange can be combined with other methods, such as evaporation or reverse osmosis. The effective method for recovery of ammonium salt from the concentrated solution (10 g/L) is electrodialysis [6].

Table 4
Parameters for the recovery of NH_4^+ from NH_3 – NH_4NO_3 solutions (average for all tested solutions)

Parameter	Purolite C 160 MBH	Purolite SGC 100 × 10 MBH
C_0^a (mol/L)	0.214	0.214
V (L)	0.272	0.271
C_e (mol/L)	1.017	1.476
C_e (g/L)	81.38	118.10
V_e (L)	0.0175	0.0175
C_t (mol/L)	0.0002	0.0003
N_R^b (%)	30.6	44.5
N_R^c (%)	99.93	99.86

^a $C_0 = [\text{NH}_3] + [\text{NH}_4^+]$.

^b N_R , recovery efficiency obtained with 0.7 BV of eluent.

^c N_R , recovery efficiency obtained with 5 BV of eluent.

It is rather difficult to give the economic comparison of various techniques for the removal of ammonium, since such parameters as ammonium concentration in wastewater, influent flow rate, adsorbent particle size, etc., must be taken into account. Nevertheless all the technologies available suggest the possible improvements concerning ammonium removal with the aim to prevent the environmental pollution.

4. Conclusions

- The performance of sulphonic acid cation exchangers (gel type Purolite SGC 100 × 10 MBH and macroporous Purolite C160 MBH) is very close with respect to the ammonium sorption under static as well as under dynamic conditions. In the effluent from the column packed with Purolite C160 MBH the concentration of ammonium ions (until 5% breakthrough) was slightly lower than that in the effluent from the column packed with Purolite SGC 100 × 10 MBH.
- On changing the feed solution from basic to slightly acidic one a decrease in the uptake of ammonium ions was observed. The OH^- ions, resulting from the ionization of NH_3 molecules, act as an acidity buffer for H^+ ions, released from the cation exchanger.
- When the ratio of the solute mass to the cation exchanger mass (m_s/m_r) is <0.1 the distribution coefficients (K_d), obtained by batch experiments, for the basic feed solution are appreciably higher than those for slightly acidic one. On increasing m_s/m_r an abrupt decrease in K_d for the basic feed solution was observed whereas K_d values for the sorption of NH_4^+ ions from the NH_4NO_3 solution remain low and near constant at various m_s/m_r ratios.
- At the regeneration with less than three bed volumes (BV) of 20% HNO_3 the recovery of both NH_4^+ ions and sorptive capacity for the macroporous cation exchanger is lower than that for the gel type one. The lower enrichment of the eluate with NH_4^+ ions was obtained during the initial period of the Purolite C160 MBH regeneration. Inhibiting effect of the Purolite C160 MBH macroporous matrix to the NH_4^+ desorption results in a decrease in the eluate enrichment with NH_4^+ ions for all the compositions, used for the cation exchangers saturation.

- The highest efficiency of the ammonium recovery (near 100%) and complete regeneration of cation exchangers investigated has been achieved with five bed volumes of eluent (20% HNO₃).
- Both cation exchangers investigated (macroporous Purolite C160 MBH and gel type Purolite SGC 100 × 10 MBH) can be used for the removal of ammonium from basic as well as slight acidic waste streams of nitrogen fertilizers production.

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