

## Nitrate Removal from Drinking Water Using Ion Exchange – Comparison of Chloride and Bicarbonate Form of the Resins

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Experiments have been carried out to investigate nitrate removal from aqueous solution using two strong base anion exchange resins (IMAC HP-555 and HP-441 from ROHM&HAAS) in chloride and bicarbonate form. Four theoretical adsorption isotherms were used to describe the experimental results. Influence of initial nitrate concentration, sulphate-nitrate ratio and specific flow rate on the performance of resins was determined. Regeneration curves for various types of regenerants were generated from experimental data and the distribution coefficients for different initial nitrate concentrations and temperatures were estimated.

*Key words:*

Nitrate removal, ion exchange

### Introduction

Increased nitrate concentration in public water supplies presents a potential health hazard due to a reduction to nitrites in gastrointestinal tract. Nitrite causes methemoglobinemia and both nitrate and nitrite have potential to form carcinogenic N-nitroso compounds<sup>1</sup>. Several processes have been described for nitrate removal from potable water among which ion exchange and biological denitrification are the only ones considered feasible and practical for full-scale treatment<sup>2</sup>. For technical and economical reasons ion exchange is more widely used and the main disadvantage of the process is disposal of spent regenerant brine. Possible use of biological process for denitrification of used regenerant in order to achieve multiple use of brine<sup>3,4,5</sup> will probably make the ion exchange the best solution for forthcoming applications.

Use of the ion exchange technology for nitrate removal is based on chloride anion exchange process during which the nitrate ions are being exchanged with chloride ions from the resin. The typical increasing order of selectivity for strong base resins of trimethylamine functional group is bicarbonate, chloride, nitrate and sulphate. As increased selectivity for nitrates over sulphates would lead to increase of the nitrate removal capacity, various resins for nitrate removal have been designed. The main property of the resin, leading to higher nitrate selectivity, is higher number of carbon atoms around ammonium nitrogen in the functional group, which is usually

achieved using ethyl groups instead of methyl. It was stated<sup>6</sup> that higher hydrophobicity of resin matrix and functional groups as well as increased distance between functional groups increase nitrate selectivity. The increased selectivity for nitrates has been attributed to steric strains in the resin due to a higher steric requirement of the ethyl groups and the higher capability of nitrate to reduce these strains<sup>7</sup>.

Effluent from an ion exchange column has increased chloride concentration and reduced alkalinity, which results in an increased potential to selectively dissolve zinc from water fittings. In addition, high total dissolved solids in raw water can cause an increase of chloride concentration in treated water. Although there is no health-based guideline for chloride in drinking water, a concentration of chloride above 250 mgL<sup>-1</sup> is considered to give rise to detectable taste in water<sup>8</sup>. Both problems can be solved by using ion exchange column in bicarbonate form. The purpose of this paper was to compare behaviour of two strong base resins, designed specifically for nitrate removal, in chloride and bicarbonate form.

### Materials and Methods

#### Ion Exchange Resins

HP-441 is a strong base sulphate selective resin of the gel type polystyrene matrix with trimethyl functional group and total exchange capacity of 1.25 mol L<sup>-1</sup> per exchange unit. Resin is designed for nitrate removal from drinking water when sulphate to nitrate ratio does not exceed 1.

HP-555 is a strong base, nitrate selective, macroporous resin with polystyrene matrix and

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triethyl functional group with total exchange capacity of  $0.9 \text{ mol L}^{-1}$  per exchange unit. Resin is designed for nitrate removal from drinking water with high sulphate concentration.

### Ion exchange experiments in column

Experiments were carried out in glass column 1.7 cm in diameter and 15 cm high. Column was filled with 10 mL of settled resin (corresponding mass of dried resin was 3.22 g and 3.27 g for HP-441 and HP-555, respectively). Only new, unused resins were taken for all experiments. The flow rate was controlled by peristaltic pump. To obtain chloride form resins were regenerated downflow with 5 bed volumes of  $w = 10\%$  NaCl solution and washed with distilled water, while  $\text{NaHCO}_3$  was used to convert resins from chloride to bicarbonate form. Flow rate of regenerant solutions was 5 bed volumes/h (BV/h), and of rinse water 10 BV/h.

Feed solution was tap water from Zagreb enriched with  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  for desired nitrate and sulphate concentration. The composition of the feed water is given in Table 1. Flow rates of the feed water were 20, 30 and 40 BV/h. Temperature of feed water was 21–23 °C.

Table 1 – Concentrations of ionic species  $\text{mg L}^{-1}$  in the model solutions used for nitrate removal in column

	$\gamma_{\text{NO}_3^-}$	$\gamma_{\text{SO}_4^{2-}}$	$\gamma_{\text{Cl}^-}$	$\gamma_{\text{HCO}_3^-}$	$\gamma_{\text{Ca}^{2+}}$	$\gamma_{\text{Mg}^{2+}}$	$\gamma_{\text{Na}^+}$
Solution A	102.37	28.13	16.22	206.22	107.34	23.91	16.84
Solution B	197.21	27.67	18.48	209.23	111.69	24.53	17.14
Solution C	294.13	27.11	17.32	214.27	108.53	24.62	17.93
Solution D	100.24	112.8	15.38	203.57	106.61	24.27	18.65
Solution E	104.21	156.7	17.88	199.45	104.60	23.82	17.68

Samples were taken at the end of the column and nitrate breakthrough was considered to be reached when nitrate concentration rose above  $50 \text{ mg L}^{-1}$ , the European maximum contaminant level for nitrate. Operating capacities were estimated at breakthrough point.

### Batch experiments

Resins regenerated in column were dried in an oven at 60 °C for 8 to 10 hours and then stored in a desiccator. Experiments were conducted in closed Erlenmeyer flasks of 500 mL stirred on a heated bath-shaker. Medium was distilled water with added  $\text{NaNO}_3$  for desired nitrate concentration. For each experimental run, 300 mL of prepared model solution was put in the flask together with 0.1 g of dried resin and stirred until equilibrium was reached. Process usually lasted 20 h.

### Chemical analyses

Nitrates were measured by UV detection at 205 nm or together with chlorides and sulphates using ion chromatograph with a 250 mm anion separation column. Bicarbonates were determined by potentiometric titration using pH meter. Calcium and magnesium were measured by complexometric titration with EDTA.

## Results and discussion

### Experiments in column

Chloride concentration in drinking water that gives rise to a detectable taste<sup>8</sup> is set on  $250 \text{ mg L}^{-1}$ . When employing resin in chloride form for nitrate removal of raw water that contains high concentration of ions that are exchanged for chlorides, the concentration of latter shall rise above the proposed value. As shown in Fig. 1 and 2, both resins employed produced water with chloride concentration above  $250 \text{ mg L}^{-1}$  for approximately 50 BV, when inlet water with  $100 \text{ mg L}^{-1}$  of both nitrate and sulphate was used. The basic difference in selectivity of resins can be also seen at the pictures. HP-441 with its trimethyl functional groups and gel structure has nitrate breakthrough before sulphate, while HP-555 with macroporous structure and triethyl functional groups shows higher nitrate selectivity.

Both resins exchanged bicarbonates only partially. HP-441 exchanged bicarbonates only at the beginning of the process when the saturation of functional groups with chlorides was sufficiently high. The effluent concentration of the bicarbo-

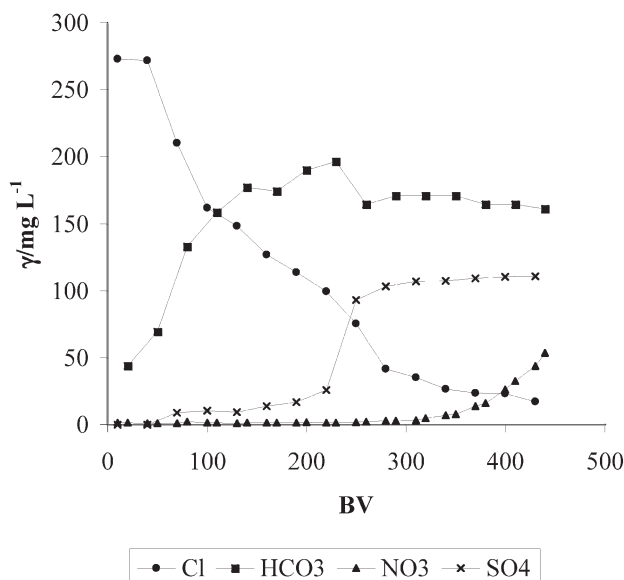


Fig. 1 – Concentrations of ion species in treated water during the nitrate removal of model solution D with HP-555 in chloride form as a function of bed volumes (BV) of treated water

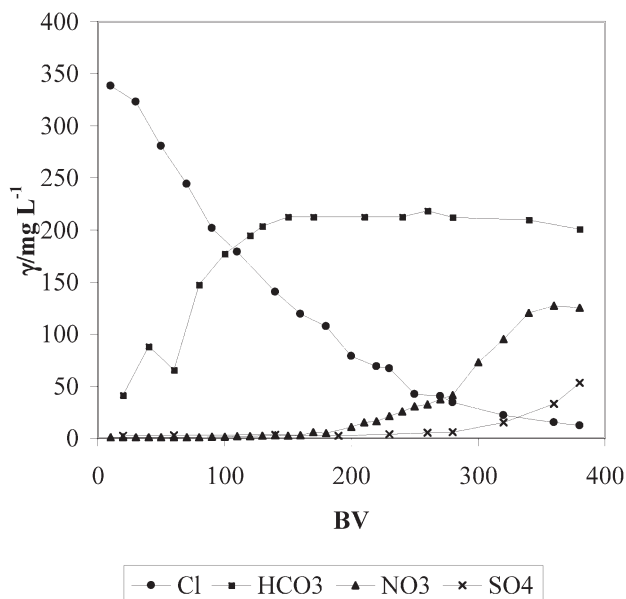


Fig. 2 – Concentrations of ion species in treated water during the nitrate removal of model solution D with HP-441 in chloride form as a function of bed volumes (BV) of treated water

nates for HP-441 reached the value of influent concentration at approximately 150 BV. HP-555 showed somewhat different behaviour towards bicarbonates for it is clearly noticeable from Fig. 1 and 4 that some exchange of bicarbonates occurs in the second part of the process.

During the process, pH value of treated water was rising from 6.8 to 7.4, which meets the requirement for the drinking water.

As an alternative, the bicarbonate form of the resin can also perform the nitrate removal. Resins in bicarbonate form exchange bicarbonates for all other anions in water and therefore no problems with chloride concentration occur. The potential problem when using resin in bicarbonate form is rise of pH of treated water caused by high bicarbonate concentration. In all of the experiments conducted here, the pH value was under 8.5, which meets the standards for drinking water.

However, the regeneration with sodium bicarbonate was quite inefficient as shown at Fig. 3. Especially resin HP-555 was found to be difficult to convert to bicarbonate form directly after nitrate removal. Therefore, nitrate selective resins should be converted to bicarbonate form after exhaustion in two steps: first with NaCl and then  $\text{NaHCO}_3$ .

Regeneration with mixed regenerants ( $w = 10\% \text{ NaCl}$  and  $w = 5\% \text{ NaHCO}_3$ ) was also attempted (Fig. 3) Nitrate removal process that followed regeneration (Fig. 4) showed that the most of the functional groups were saturated with chloride ions rather than bicarbonate, as the process characteristics were similar to nitrate removal in

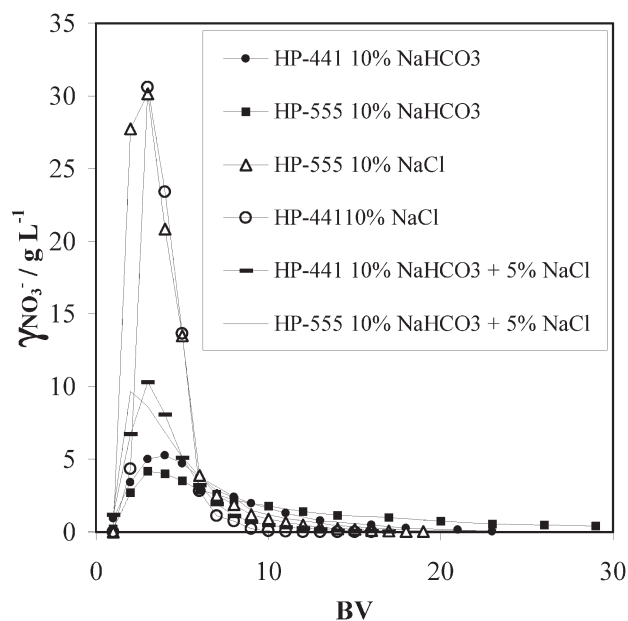


Fig. 3 – Concentrations of nitrates during regenerations with various types of regenerants as a function of bed volumes (BV) of regenerant passed

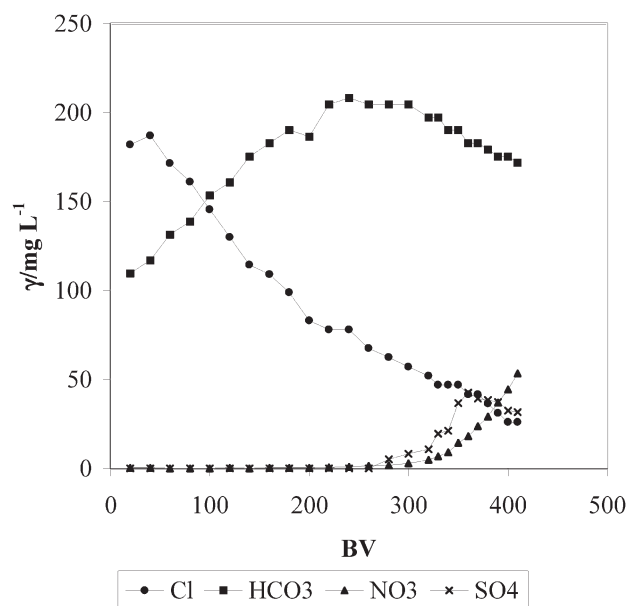


Fig. 4 – Concentrations of ion species in treated water during the nitrate removal of model solution D with HP-555 in mixed chloride and bicarbonate form as a function of bed volumes (BV) of treated water

chloride form (Fig. 1). Anyhow, the regeneration with mixed regenerants is more efficient than with  $\text{NaHCO}_3$  alone and the chloride concentration did not exceed  $250 \text{ mg L}^{-1}$  for the whole duration of the process with resins in mixed form.

The chloride to alkalinity ratio of treated water is shown on the Fig. 5. As waters whose ratio exceeds 0.5 are classified as dezincifying for water

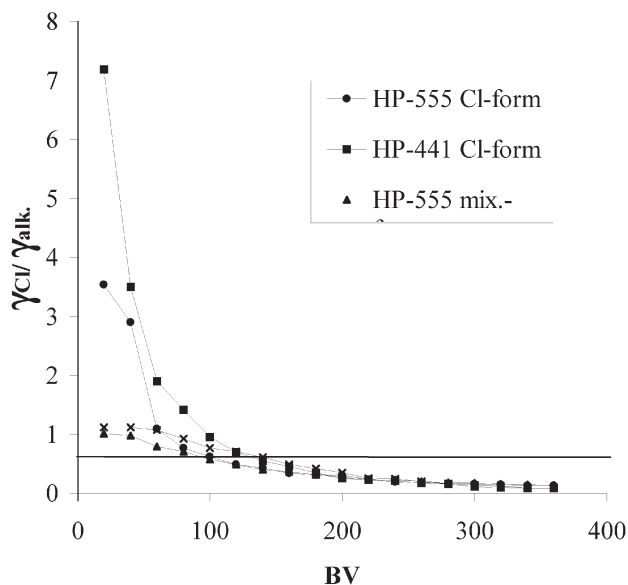


Fig. 5 – Chloride ( $\gamma_{Cl}/\text{mg L}^{-1}$ ) to alkalinity ( $\gamma_{CaCO_3}/\text{mg L}^{-1}$ ) ratio of treated water during nitrate removal with HP-555 and HP-441 in various ionic forms as a function of bed volumes (BV) of treated water

fittings, it is clear that the water in the first phase of the process had rather big potential for zinc dissolution. Effluent from the resins in mixed chloride and bicarbonate form had considerably smaller chloride to alkalinity ratio at the beginning of the process and as soon as the breakthrough of bicarbonate occurred, ratio fell under 0.5. In both forms, sulphate selective resin HP-441 produced water with higher chloride to alkalinity ratio as stated previously<sup>9</sup>.

It can be stated from the estimated breakthrough capacities (Table 2) of the resins in column, that resins in both employed forms showed almost no difference in nitrate removal of solutions with 200 and 300  $\text{mg L}^{-1}$  of nitrate. However, when using lower concentration of nitrate, the behaviour of the resins changed significantly for they had much higher breakthrough capacities in chloride form than in bicarbonate form. It should also be noted that in spite of high nitrate concentrations, the higher total capacity of HP-441 did not cause apparently higher break-

Table 2 – Breakthrough capacities/ $\text{mg mL}^{-1}$  of HP-555 and HP-441 for nitrate removal of solutions A, B and C at flow rate 20 BV/h

$\gamma_{NO_3}/\text{mg L}^{-1}$	HP-441		HP-555	
	Cl-form	HCO <sub>3</sub> -form	Cl-form	HCO <sub>3</sub> -form
102.37 (A)	49.4	38.0	54.2	42.0
197.21 (B)	63.5	64.0	62.5	62.7
294.13 (C)	82.2	75.5	79.0	73.5

through capacity. It is clear that selectivity of the resin towards nitrates contributes more to be breakthrough capacity than the total number of functional groups. This statement is enhanced even more when observing the capacities of resins in nitrate removal experiments using water with various sulphate to nitrate ratio (Table 3). Nitrate breakthrough capacities for HP-441 were strongly influenced by increasing sulphate concentration, while HP-555 showed only minor decrease in capacity values. Values of breakthrough capacities correspond quite well with previous works with the same resins<sup>10</sup> as treated waters were similar in some experiments. As the amount of the used regenerant can greatly alter capacity of the resin<sup>11</sup> the difference between results should be addressed to difference in regeneration procedure.

Table 3 – Breakthrough capacities/ $\text{mg mL}^{-1}$  of HP-555 and HP-441 in chloride form for nitrate removal of model solutions at different flow rates, and sulphate to nitrate ratio (S/N)

	HP-441	HP-555
Solution A, 20 BV/h, S/N = 0.275	49.4	54.2
Solution A, 30 BV/h, S/N = 0.275	41.4	50.8
Solution A, 40 BV/h, S/N = 0.275	36.3	49.5
Solution D, 20 BV/h, S/N = 1.125	32.5	43.1
Solution E, 20 BV/h, S/N = 1.504	23.1	45.5

The influence of flow rate (BV/h) on the nitrate removal capacities was much bigger on the HP-441 than HP-555 (Table 3). This is probably caused by the difference in the matrix structure of the resins, for the diffusion inside macroporous structure of HP-555 seems to be faster, although the selectivity might also have a role.

### Batch Experiments

After experiments in column, batch experiments were conducted. The estimated values for the distribution coefficients are shown in Tables 4 and 5. Distribution coefficients were estimated using equation 1

$$K_d = \frac{c_0 - c_1}{c_1} \cdot \frac{V_1}{m_r}$$

where  $c_0$  is concentration of nitrates in solution at the beginning of the process;  $c_1$  is concentration of nitrates in solution at the end of the process;  $V_1$  is volume of liquid phase and  $m_r$  is mass of dried resin.

As expected, distribution coefficients decreased with increase of initial nitrate concentration. In concordance with selectivity of the

Table 4 – Distribution coefficients/ $\text{mL g}^{-1}$  for HP-441 and HP-555 at 25 °C for different initial nitrate concentrations

Initial nitrate concentration (mmol/L)	HP-555 Cl-form	HP-555 HCO <sub>3</sub> -form	HP-441 Cl-form	HP-441 HCO <sub>3</sub> -form
0.5	28250	37076	19770	19900
0.9	12907	18809	10980	9908
1	7493	7849	6672	5627
1.3	6552	–	6002	–
1.7	3515	3553	5556	3206
2	2969	–	3189	–

Table 5 – Distribution coefficients/ $\text{mL g}^{-1}$  for HP-441 and HP-555 in chloride form at different temperatures for the initial nitrate concentration of 1.3 mmol L<sup>-1</sup>

	25 °C	35 °C	45 °C	55 °C
HP-441 Cl	6002	6717	5362	5800
HP-555 CL	6553	6599	6009	6429

exchangers, HP-555 had much higher coefficients than HP-441 in experiments with low initial concentration of nitrate. When higher concentrations were used, due to a higher total capacity of HP-441, the difference tended to decrease. For every initial nitrate concentration employed, HP-555 in bicarbonate form had bigger coefficients than HP-441 in the same form. At the same time, higher total capacity of HP-441 had more influence on distribution coefficients for the resins in chloride form, when initial nitrate concentration was higher than 1.3 mmol L<sup>-1</sup>.

Behaviour of HP-555 in bicarbonate form is in concordance with the regeneration experiments in which it was not possible to elute the nitrates with NaHCO<sub>3</sub> from HP-555, due to its small affinity for bicarbonates. Based on estimated distribution coefficients, it seems that HP-555 should have better performance in bicarbonate form when used for the nitrate removal in column, but its breakthrough capacities showed no such behaviour. This might be caused by different kinetics for the column experiments.

The temperature effect on equilibrium, presented as distribution coefficients, indicates that temperature around 35 °C is optimal for the chloride to nitrate ion exchange. Increase of the coefficients at 55 °C should be taken cautiously, as nitrate exchange was unstable, failing to reach stable equilibrium (data not shown).

The most commonly used isotherms used to describe the ion exchange<sup>12</sup> are Langmuir (2) and Freundlich (3) isotherms, represented respectively:

$$Q_e = a \cdot b \cdot c_e / (1 + b \cdot c_e) \quad (2)$$

$$Q_e = k \cdot c_e^n \quad (3)$$

where  $Q_e$  and  $c_e$  are, the equilibrium exchange capacity respectively, and equilibrium nitrate concentration, and  $a$ ,  $b$ ,  $n$ ,  $k$ , are isotherm coefficients. Since it was previously suggested<sup>13</sup> that more advanced models better fit the ion exchange process, three-parameter modified Langmuir isotherm (4) and isotherm of Jossens et al.<sup>14</sup> (5) were also tried to model the experimental data for the exchangers in chloride form.

$$Q_e = a_1 \cdot b_1 \cdot c_e^{n_1} / (1 + b_1 \cdot c_e^{n_1}) \quad (4)$$

$$c_e = k_0 \cdot Q_e \cdot e^{n_0 Q_e} \quad (5)$$

where  $a_1$ ,  $b_1$ ,  $n_1$ ,  $k_0$  and  $n_0$  are isotherm coefficients.

As shown on the Fig. 6 and 7, all four models fit the experimental results quite well. Hence, use of more sophisticated isotherm models may not be justified. Observing the values of the isotherm parameters (Table 6) estimated by computer program, using non-linear least square fitting method, could also support this statement. The deviation of parameter  $b_1$  for modified Langmuir isotherm and parameter  $k_0$  of the isotherm of Jossens et al.<sup>14</sup> are rather big compared with Freundlich and standard Langmuir isotherms. It can be concluded that introduction of third parameter in the model is not necessary. It seems that standard isotherms sufficiently represent the nitrate removal by ion exchange.

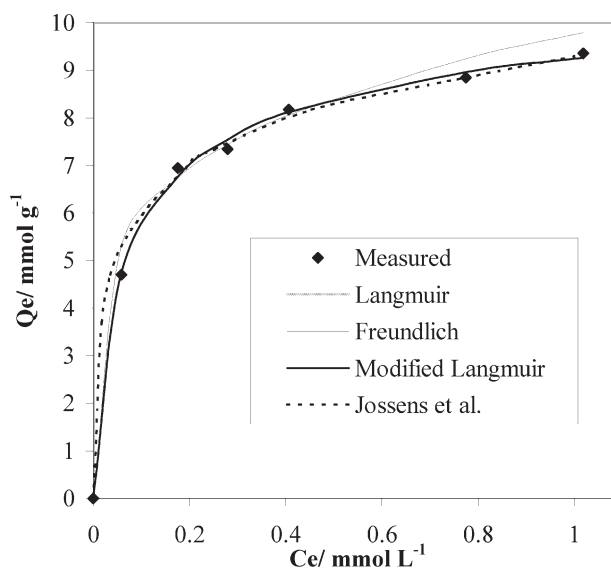


Fig. 6 – Comparison of measured values with theoretical adsorption isotherm models for HP-555 in chloride form

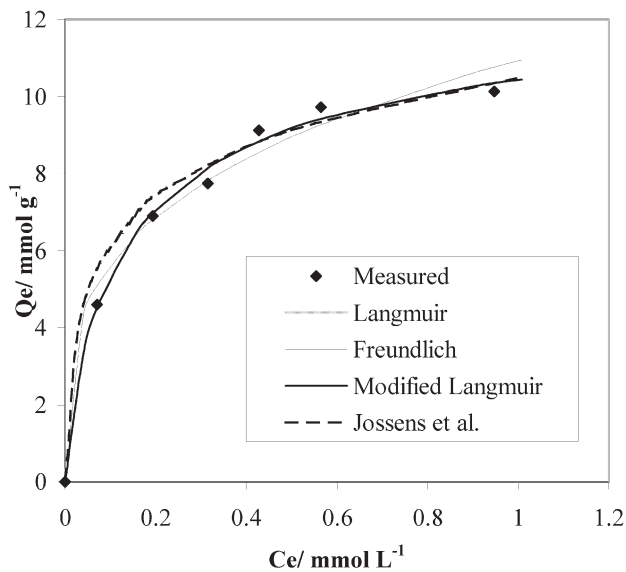


Fig. 7 – Comparison of measured values with theoretical adsorption isotherm models for HP-441 in chloride form

Table 6 – Estimated isotherm coefficients and their deviations for HP-555 and PH-441 in chloride form

Isotherm	Coefficient	HP-555	HP-441
Langmuir	$a$	$9,61 \pm 0,22$	$11,4 \pm 0,41$
	$b$	$15,0 \pm 1,8$	$8,34 \pm 1,2$
Freundlich	$k$	$9,76 \pm 0,281$	$10,93 \pm 0,407$
	$n$	$0,214 \pm 0,0236$	$0,289 \pm 0,0348$
Jossens et al.	$k_o (10^{-6})$	$489 \pm 186$	$1332 \pm 239$
	$n_o$	$0,58 \pm 0,042$	$0,41 \pm 0,106$
Modified Langmuir	$a_1$	$11,13 \pm 0,84$	$12,59 \pm 1,92$
	$b_1$	$4,889 \pm 1,93$	$4,144 \pm 2,69$
	$n_1$	$0,661 \pm 0,11$	$0,773 \pm 0,19$

## Conclusions

Nitrate removal with resins in chloride form showed that chloride concentration, as well as chloride to alkalinity ratio of water product were higher than proposed values<sup>8,9</sup>. Problems can be solved using resins in bicarbonate form with small decrease of useful capacity and significant decrease of efficiency of regeneration. Regeneration of the nitrate selective resin HP-555 was especially inefficient due to a much higher affinity for nitrates than for bicarbonates. For the same reason HP-555 in bicarbonate form also had high distribution coefficients, determined in batch experiments, when initial nitrate concentrations were low. HP-441 was more efficient in experiments

with high nitrate concentrations where total capacity could influence the process more than selectivity. Adsorption isotherms were estimated for chloride form at 25 °C and standard Langmuir and Freundlich isotherms were found sufficient to represent the nitrate to chloride ion exchange.

## List of symbols

- $K_d$  – distribution coefficient  
 $c_0$  – initial concentration  
 $c_1$  – final concentration  
 $V_1$  – volume of liquid phase for the batch experiments  
 $m_r$  – mass of dried resin  
 $Q_e$  – equilibrium exchange capacity  
 $c_e$  – equilibrium nitrate concentration  
 $a, b$  – coefficients for Langmuir isotherm  
 $k, n$  – coefficients for Freundlich isotherm  
 $a_1, b_1, n_1$  – coefficients for modified Langmuir isotherm  
 $k_o, n_o$  – coefficients for isotherm of Jossens et al.

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