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THE INFLUENCE OF RESIN REGENERATION ON NITRATES REMOVAL EFFECTIVITY FROM DRINKING WATER

Summary. The objective of the study was to investigate the capacity of selective resin IONAC SR-7 (Sybron Chemicals Inc., USA) to remove nitrates from drinking water and to optimize the regeneration process, which is based on an estimation of optimum brine concentration and flow rate, which would increase resin regeneration efficiency. Based on the results, 1 dm^3 resin can remove 0.7 eq nitrates. Therefore, the determined value of ion-exchange working capability under particular process conditions (12% NaCl solution and a flow rate of 4 BV/h) is 87.5% of the theoretical ion-exchange capability for the examined resin. It was found that as a result of resin partial regeneration its working sorption capacity decreased to 0.56 meq/ml, which was about 70% of theoretical resin ion-exchange capacity. This represented a 50% reduction of the volume of environmentally harmful waste after regeneration.

Key words: nitrates, ion-exchange, resin ion-exchange

Introduction

Intensification of agricultural production and continuous industrial development have contributed to an increase in nitrate content in drinking water. In some regions of Poland, nitrate content has considerably exceeded the admissible levels of 50 mg per 1 dm^3 (CYPLIK et AL. 2006). This is particularly evident in rural areas, where in private wells the concentration of nitrate nitrogen is often over twenty times above the admissible level. This situation poses a serious threat to the health of people using polluted water. Therefore, it is now necessary to develop a technology which effectively reduces nitrate concentration in drinking water.

A relatively simple and cheap method, which facilitates effective water denitrification, is an ion-exchange process (CLIFFORD and LIU 1993 a, b, 1995). The ion-exchange process has been mainly applied to utilize cooling water in heat and power generating plants, but also may be used to remove microcontaminants from drinking water. In the ion-exchange process, strongly alkaline resins are usually applied, which work in the chloride cycle or the bicarbonate cycle. This process is based on chloride ion exchange, in which these ions are bound by functional groups of resins, to nitrate ions. The strongest competition for nitrate ion sorption in ion-exchange resin comes from sulfate ions. The sulfate ion has a greater charge, wider diameter and, consequently, has a larger hydration rate than a nitrate ion. Therefore, for the denitrification of highly-sulfated water, selective resins are used with the active group put under butylene radicals, which efficiently limit the access of sulfates to active groups of resins. Selective resins, in comparison with non-selective resins, exhibit lower water retention and lower ion-exchange capacity, but at the same time greater selectivity in relation to exchanged anions (CLIFFORD and LIU 1995).

Advantages of the ion-exchange process include low costs, easy process control, a possibility of omitting final water treatment and no need to introduce additional organic compounds to the water. Disadvantages of the process include decreased ion-exchange capability during the process, increased water corrosion and ion concentration change in the water.

The objective of the study was to investigate the capacity of selective resin SR-7 (Sybron Chemicals Inc., USA) to remove nitrates from drinking water and to optimize the regeneration process, which is based on an estimation of optimum brine concentration and flow rate, which would increase resin regeneration efficiency. The effect of multiple regeneration of ion-exchange resin on sorption capacity was also investigated.

Material and methods

Ion-exchange

An ion-exchange resin IONAC SR-7 (Sybron Chemicals Inc., USA) was used in the investigations. This selective resin has a theoretical ion-exchange capacity of 0.8 meq/ml. The testing station consisted of a glass column packed with 30 cm^3 of resin. Water was introduced to the column from the top by a peristaltic pump. The volume of 1 dm^3 of water contained 133 mg NO_3^- (30 mg N-NO_3^-), 100 mg SO_4^2, 40 mg Cl^-, 120 mg HCO_3^- and water pH was 7.4. Resin properties and testing parameters are given in Table 1. Water flow rate in the experiment with 40 ml of resin using the above mentioned apparatus was 30 BV/h. The process was carried out until the column was filled by nitrate ions. For resin regeneration, NaCl solutions at concentrations of 3, 6, 9, 12 and 15% and flow rates of 3, 4, 6, 8 and 10 BV/h were applied.

Analytical methods

Anions contained in the collected samples of drinking water were determined with the assistance of High Performance Liquid Chromatography (HPLC). Measurements were taken using a Merck-Hitachi liquid chromatographer equipped with a UV detector.

Table 1. Physico-chemical properties of resins and operation parameters of ion exchange process
Tabela 1. Fizyczno-chemiczne właściwości żywicy i parametry układu do wymiany jonowej

Parameter	IONAC SR-7
Granulometry (mm)	0.45-0.50
Theoretical capacity of resin (eq/dm^3)	0.8
Limit of temperature (°C)	100
Limit of pH	1-12
High of bed (cm)	20
Diameter of bed (cm)	2
Volume of bed (cm^3)	62
Volume of resin (cm^3)	40

A Polyspher IC AN-1 (Merck) column with a pre-column was used. The applied eluant was a solution made up of 1.5 mM phthalic acid, 1.38 mM Tris and 300 mM boric acid, and pH of 4.0. The column was kept at a temperature of 35°C. Assays were carried out at the 210 nm wavelength and the amounts of anions were calculated on the basis of peak heights (measurements and computer-aided integration). After filtration through a filter with 0.45 µm pores (Milipore), samples were placed on the column in the amount of 20 µl.

Results and discussion

Nitrate sorption on ion-exchange resin

Drinking water was introduced onto the ion-exchange resin. The process was carried out until the column was filled with nitrates and nitrate ions were present at the column outflow. The results of the experiment are presented in Figure 1. On the resin ions were absorbed in the following sequence: bicarbonate ions, sulfate ions and nitrate. The effect of bicarbonate on the ion-exchange process was insignificant. At the beginning of the process, bicarbonate ions were bonded by resin, but at 20 BV their concentration started to increase at the outflow as a result of their elution and release from the column. Finally, the concentration of bicarbonate ions stabilised at the level of 120 mg/dm^3. The conclusion is that in the ion-exchange process bicarbonate ions did not compete with nitrate ions. Undoubtedly, sulfate ions were more strongly bonded by the resin. Initially both bicarbonate ions and sulfates ions were adsorbed on the resin, but did not leave the column before 100 BV. Sulfate concentration increased initially at the outflow to 150 mg/dm^3 and at the end stabilised at the level of 100 mg/dm^3.

The oncoming end of the process was visibly signalled by the chloride ion content, which reduced at the outflow. Throughout the entire ion-exchange process, chloride concentration was reduced from an initial value of 240 mg/dm^3 to 40 mg/dm^3, to its mean value, which was introduced to the column. Finally, the knowledge of chloride concentration in water may be advantageous to the ion-exchange control process.

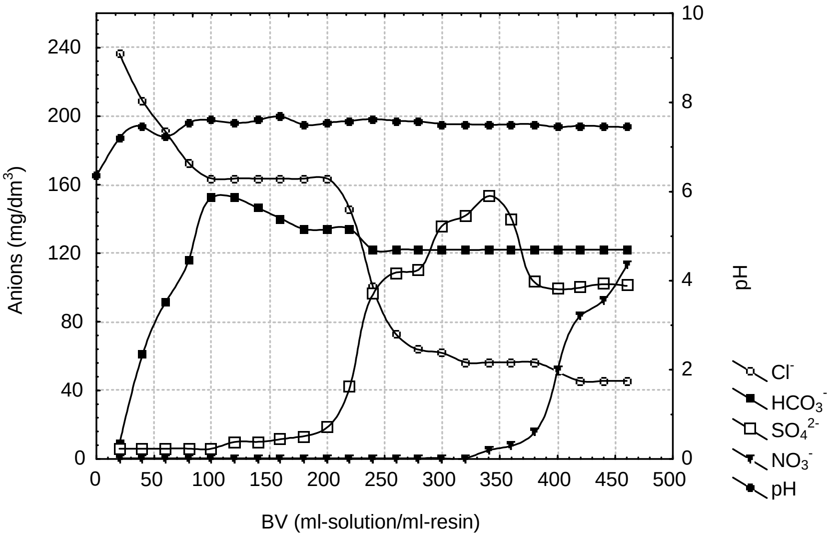

Fig. 1. Changes in anion concentration in drinking water in the process of nitrate removal on ion-exchange resin IONAC SR-7
Rys. 1. Zmiany stężenia anionów w wodzie pitnej w procesie usuwania azotanów na żywicy jonowymiennej IONAC SR-7

Nitrates were most strongly bonded to the resin. This continued until all the unoccupied active centers in the resin were filled. The column was filled by nitrates at 340 BV and then their concentration linearly increased at the outflow. The permissible value, which nitrates exceed, was 400 BV (CLIFFORD and LIU 1993 b, 1995, SAMATYA et AL. 2006, VAARAMAA and LEHTO 2003)]. Moreover, it was found that the affinity of the examined ions to the resin could be arranged in the following sequence: nitrate ions, sulfate ions and bicarbonate ions. In the whole process, pH remained practically unchanged. This was because chloride ions, which were released from the column, did not influence the concentration of hydrogen ions.

Based on the results, 1 l resin can remove 0.7 eq nitrates. Therefore, the determined value of ion-exchange working capability under particular process conditions is 87.5% of the theoretical ion-exchange capability for the examined resin.

The ion-exchange column regeneration

After the ion-exchange process resin was regenerated. This step of the experiment was a very important process and its aim was to regain original ion-exchange properties. The regeneration of resin ion-exchange capability involves filling resin active centers with ions, which are removed from water in the working cycle with ions. The following conditions must be ensured during nitrate removal from drinking water: the concentration of any ions in water cannot exceed the admissible value, ions released from a column cannot be dangerous to the health of livestock or humans and they should not deteriorate the quality of treated water. The annual use of NaCl for nitrate removal from drinking water in functioning installations is 240-360 t. Therefore, optimization of the regeneration process is very important both from the technological and environmental point of view (to prevent an increase in environmentally harmful waste after regeneration).

The effect of flow rate and brine concentration on regeneration efficiency

To determine the flow rate effect on the resin regeneration process, a 6% NaCl solution was used. The regeneration process was carried out at flow rates of 3, 4, 6, 8 and 10 BV/h. To determine the brine concentration effect on the resin regeneration process, NaCl solutions at concentrations of 3, 6, 9, 12 and 15% and a flow rate of 10 BV/h were applied. Figures 2 and 3 illustrate the effect of the flow rate and brine concentration on nitrate and sulfate ion removal in a column. It was found that resin released sulfate ions as first; however, their concentration was much lower than that of nitrate ions at the outflow. It was noticed that with an increase in flow rate and a decrease in brine concentration the concentration of released nitrate and sulfate ions was reduced and peaks on the chromatographic printout were shifted towards each other. Resin was removed from the column for complete regeneration. It involves a removal of nitrate ions from the column. It was found that an increase in brine concentration, which is necessary to complete resin regeneration, reduced brine volume (Fig. 4), whereas an increase in the flow rate caused an increase in brine volume (Fig. 5). An application of a 9% NaCl solution – instead of a 3% solution to regenerate the resin – can reduce brine volume by 70% and a reduction of flow rate from 10 to 4 BV can reduce brine volume by a further 55% (SAMATYA et AL. 2006).

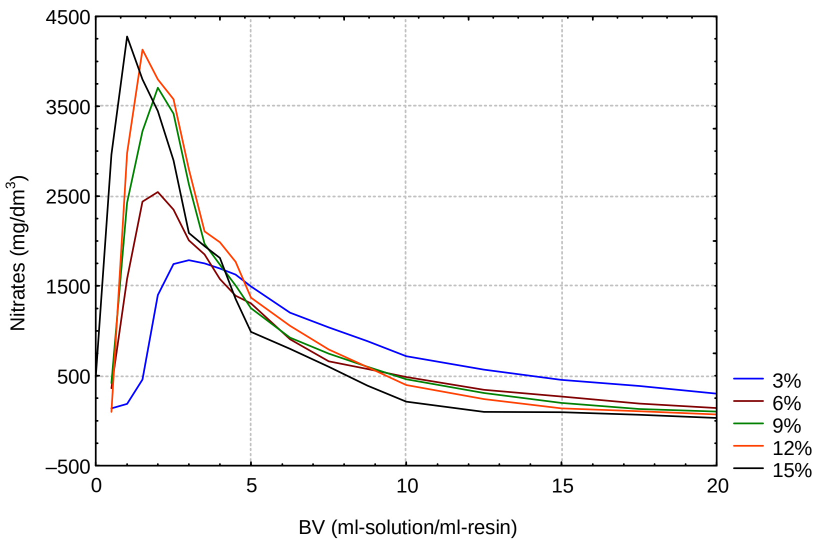

Fig. 2. Desorption of nitrates from resin IONAC SR-7 during regeneration of the column with NaCl solutions at various concentrations
Rys. 2. Desorpcja azotanów z żywicy jonowymiennej w wyniku regeneracji kolumny roztworami NaCl o różnym stężeniu

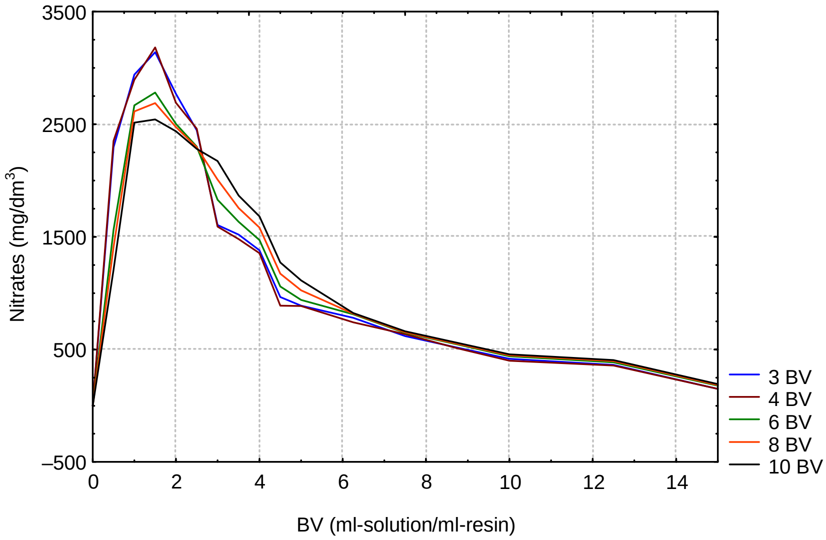

Fig. 3. The effect of flow rate on desorption of nitrates from ion-exchange resin IONAC SR-7
Rys. 3. Wpływ prędkości przepływu na desorpcję azotanów z żywicy jonowymiennej IONAC SR-7

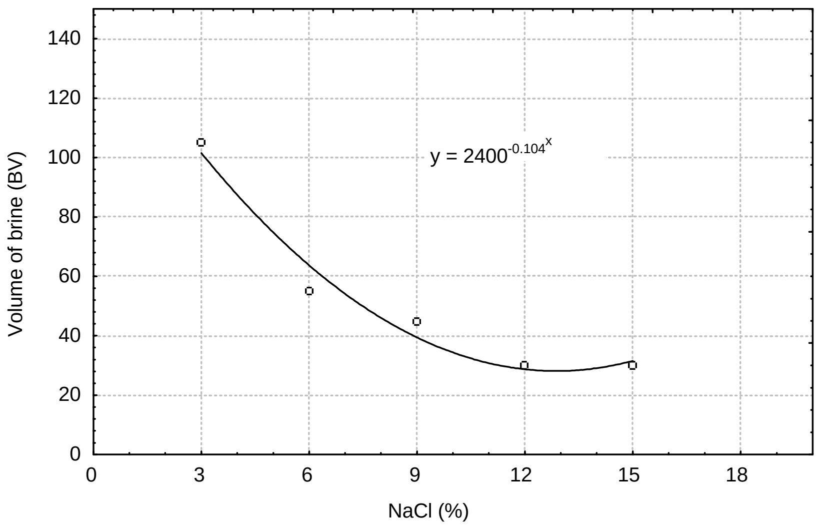

Fig. 4. The effect of NaCl concentration on regenerant volume used in complete regeneration of resin IONAC SR-7
Rys. 4. Wpływ stężenia NaCl na objętość regeneranta użytego do pełnej regeneracji żywicy IONAC SR-7

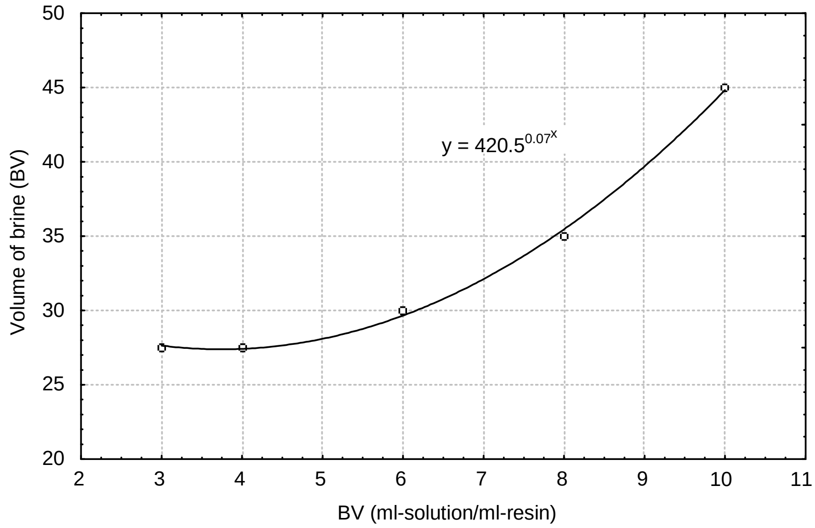

Fig. 5. The effect of flow rate on regenerant volume used in complete regeneration of resin IONAC SR-7
Rys. 5. Wpływ prędkości przepływu na objętość regeneranta użytego do pełnej regeneracji żywicy IONAC SR-7

Changes in sulfate and nitrate release rates from the ion-exchange column

Sulfates are anions exhibiting stronger affinity to ion-exchange resins than nitrates do. Thus, it was necessary to determine not only their binding capacity by resin, but also their desorption rate from the ion-exchange column. Permanent sulfate sorption could have affected significantly a decrease of operating capacity of ion-exchange resin. For analyses 3 and 15% NaCl solutions and regenerant flow rate of 10 BV/h were applied.

It was found that sulfate ions were first to be released from resin, but their concentration in the eluate was markedly lower than that of nitrates. The effect of NaCl concentration in anion desorption from the ion-exchange column, presented in Figure 6, shows that sulfates, although being adsorbed by resin faster, also undergo faster desorption than nitrates (BOUMEDIENE and ACHOUR 2004).

Moreover, it could be seen that the column bounded nitrate ions in bigger amounts than it did in case of sulfate ions. Applying a 3% NaCl solution, sulfates underwent complete desorption when applying 5 BV, while when applying a 15% solution it gave a marked peak, which reached its maximum at 1 BV used regenerant. Next a decrease was observed in the sulfate concentration in the regenerant. The use of a three-fold volume of regenerant per resin volume made possible a complete removal of sulfates from the ion-exchange column.

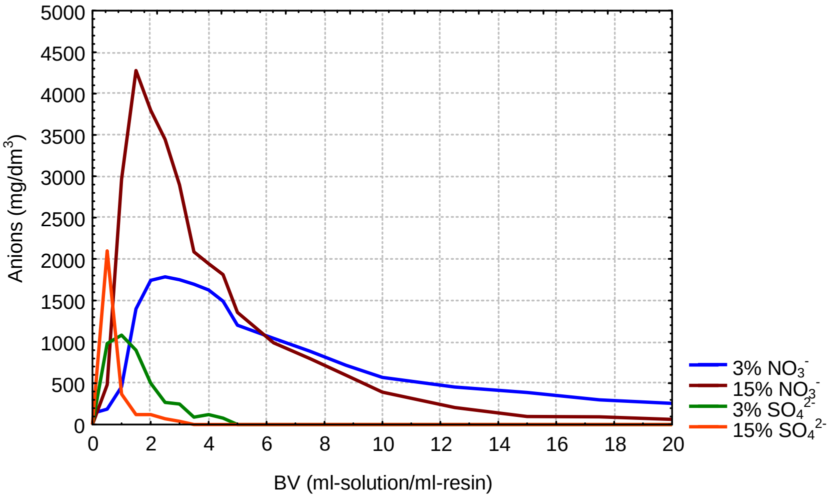

Fig. 6. Changes in anion release rate from ion-exchange resin IONAC SR-7 under the influence of its regeneration with a 6% NaCl solution
Rys. 6. Zmiany szybkości uwalniania anionów z żywicy jonowymiennej IONAC SR-7 podczas jej regeneracji 6-procentowym roztworem NaCl

The effect of multiple resin regeneration on the ion-exchange operating capacity of resin

The effect of multiple resin regeneration on the resin working sorption capacity was investigated at a further stage of the study (Fig. 7). In the study, a flow rate of 4 BV/h was applied and a 12% NaCl solution was used in the regeneration process. It was carried out until complete resin regeneration was achieved. The loading and regeneration of resin was conducted nine times and it was found that resin regeneration did not change the resin working sorption capacity. The penetration of an ion-exchange column by nitrate ions occurred at 320-340 BV.

Resin partial regeneration

Based on the investigations it was decided to conduct partial resin regeneration with the use of a 12% NaCl solution and a flow rate of 4 BV/h. The process was carried out with 10 BV of brine and then an ion-exchange process on the resin. The kinetics of nitrate ion sorption was determined. The results are given in Figure 8. In the case of the first loading, the column was filled at 340 BV, whereas in the second loading carried out after partial resin regeneration at 280 BV, an outflow of nitrate ions was observed.

It was found that as a result of resin partial regeneration its working sorption capacity decreased to 0.56 meq/ml, which was about 70% of theoretical resin ion-exchange capacity. This represented a 50% reduction of the volume of environmentally harmful waste after regeneration. The conclusion is that partial resin regeneration is a more advisable solution. It does not completely regenerate resin sorption capacity, but it efficiently reduces the volume of brine.

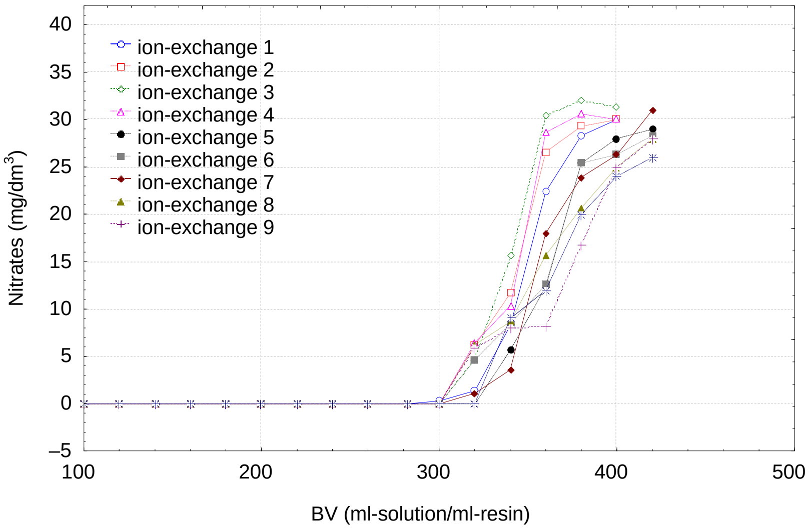

Fig. 7. The effect of the number of regenerations on nitrate sorption on ion--exchange resin IONAC SR-7

Rys. 7. Wpływ liczby regeneracji na sorpcję azotanów na żywicy jonowymiennej IONAC SR-7

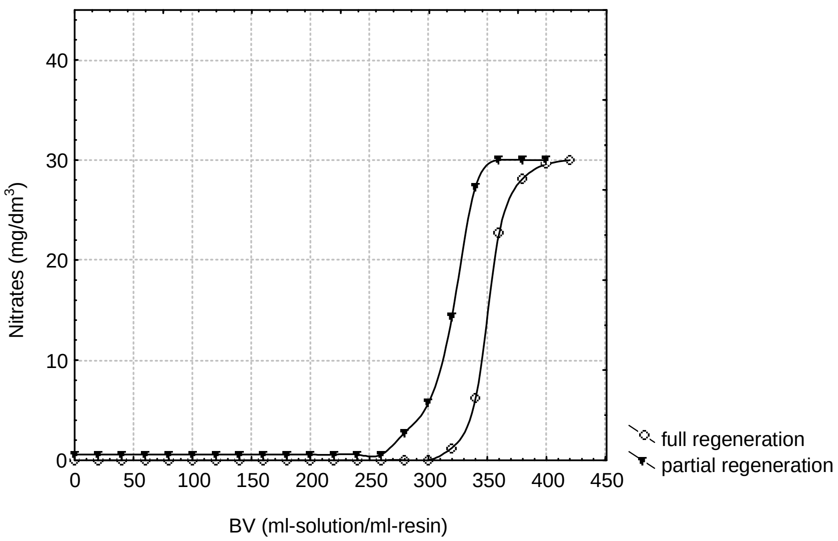

Fig. 8. Nitrate sorption on an ion-exchange column after complete and partial regeneration resin IONAC SR-7

Rys. 8. Sorpcja azotanów na kolumnie jonowymiennej podczas całkowitej i częściowej regeneracji żywicy IONAC SR-7

Results of studies presented to date in literature showed that sulfates undergo desorption from the column more readily than nitrates. Irrespective of the applied regeneration method, its easier elution was caused by the phenomenon of selectivity reversal, occurring in solutions with a strong ionic strength (> 0.25 M). Such selectivity reversal does not occur in case of nitrates, in this way they are more difficult to remove if they are found in the presence of chlorides. Thus, the aim of resin regeneration is the elution of the biggest possible amount of nitrates at a simultaneous minimization of brine consumption. Regeneration of resin bounding nitrates was thoroughly investigated in Glendale (Arizona, USA), where the method of complete and partial regeneration was applied (CLIFFORD and LIU 1995). The adopted concentration of the regeneration solution (NaCl) ranged from 0.25 to 3.0 N (3-18%), which stoichiometrically corresponded to 1-9 eq of chlorides per 1 eq resin.

Conclusions

1. The IONAC SR-7 resin can efficiently remove nitrate ions from drinking water.
2. Chloride brine does not negatively influence the quality of drinking water and it can be used to remove nitrates by the ion-exchange method.
3. Sulfates exhibit lower selectivity towards chlorides than nitrates do.
4. Brine volume can be decreased by increasing brine concentration. It is necessary to complete resin regeneration. However, an increase in the brine flow rate results in the necessity to increase brine volume.
5. The multiple resin regeneration has no effect on the resin operating capacity at the specified parameters of the regeneration process.
6. Partial resin regeneration resulted in a decrease in its working sorption capacity to 70% of theoretical volume; however, it produced half as much effluent following regeneration.

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WPŁYW REGENERACJI ŻYWICY NA EFEKTYWNOŚĆ USUWANIA AZOTANÓW Z WODY PITNEJ

Streszczenie. Celem badań było zbadanie możliwości wykorzystania żywicy selektywnej IONAC SR-7 (Sybron Chemicals Inc., USA) do usuwania azotanów z wody pitnej oraz optymalizacja procesu regeneracji polegająca na określeniu optymalnego stężenia czynnika regeneracyjnego i optymalnej prędkości jego przepływu zapewniających największą skuteczność regeneracji żywicy. 1 dm^3 żywicy umożliwił usunięcie 0.7 eq azotanów. Stwierdzono, że w wyniku częściowej regeneracji (12% NaCl i prędkość przepływu wynosząca 4 BV/h) zmniejszyła się robocza pojemność sorpcyjna żywicy do 0.56 meq/ml, co stanowiło 70% teoretycznej zdolności jonowymiennej żywicy, z równoczesnym zmniejszeniem objętości szkodliwego dla środowiska odpadu poregeneracyjnego o 50%.

Słowa kluczowe: azotany, wymiana jonowa, żywica jonowymienna

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