Environment Protection Engineering

Vol. 35 2009 No. 1

ANDRZEJ M. DZIUBEK*, JOLANTA MAĆKIEWICZ*

REMOVAL OF NITRATES FROM WATER BY SELECTIVE ION EXCHANGE

The applicability of ion exchange on selective anion-exchange resins to the removal of nitrates from groundwater which was to serve for drinking purposes was investigated. The concentration of nitrates in the groundwater treated in the ion-exchange process, in the presence of chloride ions (50 g Cl^-/m^3) and sulfate ions (90 g SO_4^{2-}/m^3), varied from 15 to 30 g N/m^3. The velocity of water flow through the ion-exchange column ranged between 10 and 25 m/h. The exchange capacity of the resin with respect to nitrates determined in the experimental study was 0.5 val/dm^3. The efficiency of the ion-exchange process up to the exhaustion of the ion-exchange capacity of the resin (expressed as the ratio of the treated water volume to the resin volume) was found to vary from 200 to 400.

1. INTRODUCTION

Defined in the Directive of the Health Minister of 29 March 2007, the permissible nitrate concentration in tap water should not exceed 50 g NO_3^-/m^3 (approx. 11.3 g N/m^3). The value is in conformity with the standards that are in force in other countries, including the European Union, and is recommended by the World Health Organization (WHO). Thus, the removal of nitrates from water where their concentrations have been exceeded is a matter of indisputable necessity.

Nitrate removal from water raises troublesome technological problems. Among the available methods technically feasible are biological denitrification and ion exchange. Water subjected to denitrification entails deoxidation as well as the addition of carbon compounds (at least in the form of acetic acid) and phosphorus compunds. In water treatment trains, use is made of heterotrophic denitrification followed by aeration and filtration (and in many instances also sorption) in order to remove the products formed. In technological terms, the mechanism governing the removal of nitrates from water by biological methods is still insufficiently understood. In France,

---

* Institute of Environmental Protection Engineering, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland. E-mail: jolanta.mackiewicz@pwr.wroc.pl, andrzej.dziubek@pwr.wroc.pl

denitrification is conducted on a full technical scale; in Poland this method is still tested. What is more, biological processes being the part of a water treatment train are difficult to automatize. In consequence, the inclusion of denitrification as a unit process will not be cost-effective for low-capacity water treatment plants.

The method of ion exchange on selective anion-exchange resins is much easier to implement in water treatment systems. It is essential to note, however, that resins of this kind require a sanitary safety certificate and that most of the resins being marketed are imports [1], [2].

The other methods used for nitrate removal entail the demineralization of the water being treated. Also in that case relevant research is targeted at the selective removal of nitrates combined with a substantial reduction in the demineralization of the water and at monoselective electrodialysis [3]. Nitrate removal methods of the future involve both technologies based on catalytic reduction [4]–[6] (in the presence of bi- and monometal catalysts) and electrocatalytic technologies. Another promising technology includes heterotrophic denitrification combined with ion exchange [2].

The efficiency of nitrate removal from water by selective ion exchange using the IONAC SR-7 resin (Bayer) has been summarized elsewhere [7].

2. SCOPE AND METHODS

A strong-base ion exchange resin IONAC SR-7 is characterized by a selectivity with respect to nitrates which is three times as high as the selectivity of any of the anion exchangers available on the market. This is what enables the removal of nitrates from sulphate-containing water, without the risk of resin breakthrough. According to the manufacturer of the ion-exchange mass, other nitrate-selective ion-exchange resins pose such risk when their capacity for nitrates has been exhausted, and when sulphate ions displace the nitrate ions from the active sites. When such a phenomenon occurs, the filtrate will contain higher concentrations of nitrates than the raw solution. The resin used in our study (quaternary amine) has an exchangeable chloride ion in the functional group, a grain size varying between 0.3 and 1.20 mm, a water-swollen volume of 1.15, and an operation temperature of up to 80 °C. The recommended bed depth should not be lower than 0.8 m, while filtration velocity should not exceed 30 m/h. The process of removing nitrates from water via ion exchange on this anion-exchange resin is conducted in a selective mode. The presence of sulphates and chlorides does not disturb the course of the process. The mechanism of ion exchange consists in the exchange of nitrate ions for chloride ions when the water being treated does not contain sulphates, and in a two-phase exchange of nitrates when sulphates are present in the water. In the first phase, nitrates and sulphates are exchanged for chlorides, and in the second phase nitrates are exchanged for sulphates and chlorides. In the study on the removal of nitrates using an Imac HP-555 anion-exchange resin, SIEROŃ and ŚWIDERSKA-BRÓŻ have given preference to the two-phase mechanism [1].

The investigations reported on in the present paper were conducted on a laboratory scale, using a model column of a 28-mm diameter and a bed depth of 0.40 m, at a filtration velocity of 10–25 m/h, in four resin cycles. In cycles I and II, the concentration of nitrates in the water being treated amounted to 15 g N/m^3, while that in cycles III and IV was 30 g N/m^3; the velocity of filtration being 10 m/h in cycles I and II, and 25 m/h in cycles III and IV.

3. RESULTS

In addition to an increased content of nitrates, the untreated water contains chlorides (approx. 50 g Cl$^-$/m^3 on average) and sulphates (approx. 90 g SO_4^{2-}/m^3). The plots of figures 1 to 4 show the results obtained during ion exchange, which have been related to the bed volume (the ratio of the volume of filtered water to the volume of ion-exchange mass). Thus, in the course of cycle I and cycle II, total alkalinity of the water ranged between 0.3 and 3.1 val/m^3, while during cycle III and cycle IV alkalinity soon stabilized at the level typical of tap water (figure 1).

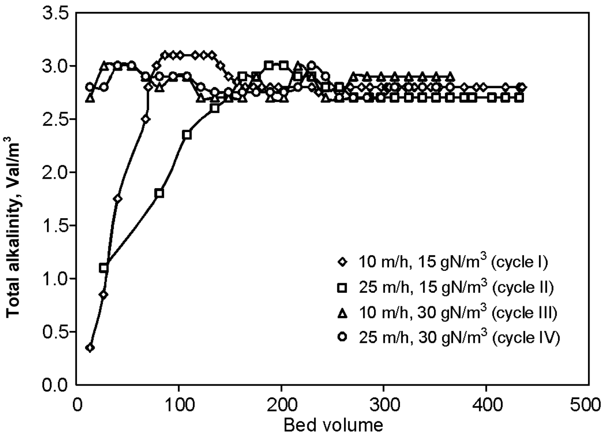

Fig. 1. Variations in total alkalinity of water during ion exchange

These marked differences are attributable to the method with which the ion exchanger was prepared and to the type of the water (distilled or tap water) with which it was rinsed. In the course of the cycles, the concentration of chlorides in the filtered water declined gradually until it reached the value characteristic of tap water (figure 2). In cycles III and IV (rinsing with tap water), the concentrations of chlorides followed the pattern of achieving a typical tap water value which was similar to the pattern observed during cycles I and II (rinsing with distilled water) but this was attained within a shorter time. The comparison of the results obtained in particular cycles made it clear that the efficiency of the ion-exchange process depended largely on the filtration velocity. In each of the cycles, the breakthrough of sulphates occurred sooner as compared to that of nitrates, and the content of sulphates rose to a value which was higher than the initial one. The removal of sulphates from the water being treated continued even after the ion-exchange capacity of the resin for nitrates had been exhausted (figure 3). The effect of sulphates on the removal of nitrates has also been observed by other investigators [8].

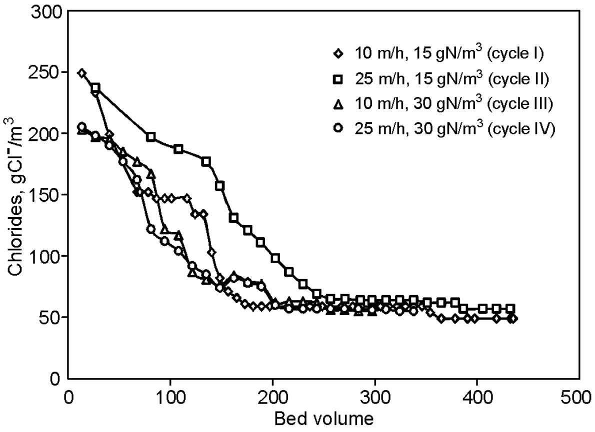

Fig. 2. Variations in chloride content in water during ion exchange

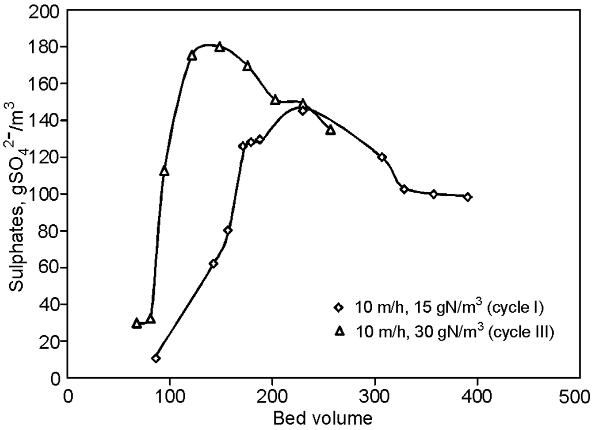

Fig. 3. Variations in sulphate content in water during ion exchange

The efficiencies of nitrate removal determined in particular cycles did not differ essentially; in every instance the reduction in the concentrations of nitrates amounted to at least 99% (figure 4). In cycles III and IV, the point of nitrate breakthrough was observed at bed volumes higher than 200, where the efficiency of nitrate removal approached 70%, and in cycles I and II at the bed volume of approximately 400, where the efficiency of nitrate removal amounted to 40%. It seems, however, essential to emphasize that the lowest concentration of nitrates in the treated water was obtained at the filtration velocity of 10 m/h and the initial content of nitrates amounting to 30 g N/m^3. The longest time of resin operation was recorded at the filtation velocity of 10 m/h and the initial nitrate concentration of 15 g N/m^3.

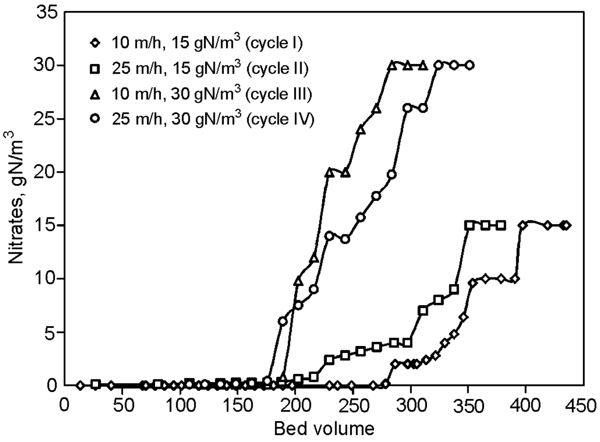

Fig. 4. Variations in nitrate content in water during ion exchange

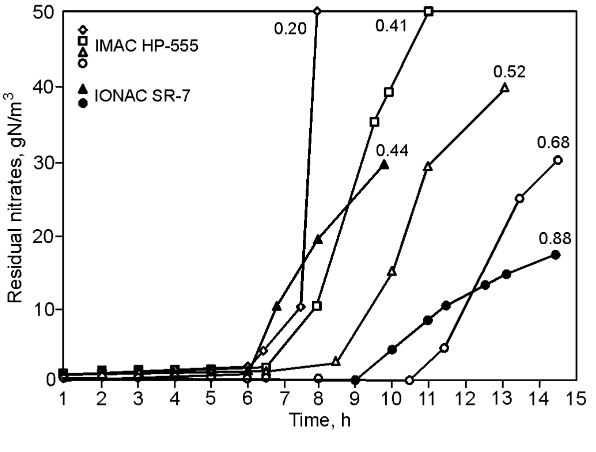

Fig. 5. Effect of filtration velocity on concentration of nitrates related to quotient of molar concentrations of sulphates and nitrates

SIEROŃ and ŚWIDERSKA-BRÓŻ [1] have stressed the contribution of the sulphates-to-nitrates ratio to the removal of nitrates from water by ion exchange using the Imac HP-555 resin. That was why we decided to compare the efficiencies of the resins in order to determine (for the concentrations of nitrates of 15 and 30 g N/m^3) how the ratio mentioned influences the residual concentrations of nitrates (figure 5.). The increase in the value of the molar ratio accounted for the extension of the resin operation time not only to the point in time for filter breakthrough by nitrates, but also to the point in time at which the permissible concentration of nitrates was achieved. This relation conforms with the data obtained for the Imac HP-555 resin [1]. The examination of the effect of the sulphates-to-nitrates molar ratio on the bed volume of the effluent has also revealed that the efficiencies of the IONAC SR-7 and Imac HP-555 anion-exchange resins are comparable (figure 6).

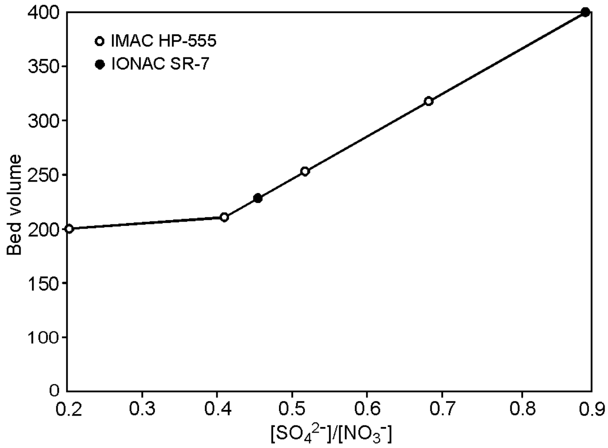

Fig. 6. Effect of quotient of molar concentrations of sulphates and nitrates on bed volume

On the basis of the results obtained the total amount of nitrates retained by the anion exchanger was determined. Then the quantity of the nitrates retained was related to the volume of the ion exchanger mass. The total ion-exchange capacity calculated via the above route varied from 0.36 to 0.49 val/dm^3 (being markedly lower than the relevant value included in the manufacturer's specification: 0.65 val/dm^3) and was found to depend on the initial content of nitrates in the water subjected to treatment by the ion-exchange method.

4. CONCLUSIONS

The study has demonstrated that selective anion-exchange resins can be used with success for the removal of nitrates. The IONAC SR-7 and Imac HP-555 resins were found to be nitrate-selective, so they can be of use in water treatment processes. The exchange capacity of the IONAC SR-7 mass determined in the course of the study was lower than the one specified by the manufacturer. This is to be attributed to the fact that the exchange capacity value obtained in our investigations is valid for nitrates only. In spite of this, the selectivity of the ion exchanger was high; the exhaustion of the nitrate removal capacity occurred at the bed volume ranging from 200 to 280 and was indicated earlier by the appearance of sulphate ions at concentrations which were even higher than those in raw water. During the ion-exchange cycle, upon exhaustion of the ion-exchange capacity of the resin for nitrates, the phenomenon was observed of sulphate removal from the water without nitrate breakthrough. It was found that the presence of sulphates in the water did not disturb the removal of nitrates. The inclusion of the ion-exchange process into the water-treatment train requires equalization of the physicochemical composition of the water being treated in the whole cycle, and this necessitates the application of retention tanks.

REFERENCES

[1] SIEROŃ A., ŚWIDERSKA-BRÓŻ M., *Usuwanie azotanów z wody w procesie wymiany jonowej*, Ochrona Środowiska, 1998, Vol. 20, No. 4, 7–9.

[2] APOLINARSKI M., *Nowe kierunki w technologii usuwania azotanów z wód podziemnych*, Ochrona Środowiska, 2005, Vol. 27, No. 3, 21–26.

[3] WIŚNIEWSKI J., RÓŻAŃSKA A., *Usuwanie azotanów z roztworów wodnych metodą elektrodializy*, Ochrona Środowiska, 2002, Vol. 24, No. 4, 11–15.

[4] CHEN Y.-X., ZHANG Y., CHEN G.-H., *Appropriate conditions or maximizing catalytic reduction efficiency of nitrate into nitrogen gas in groundwater*, Water Research, 2003, Vol. 37, No. 10, 2489–2495.

[5] REDDY K.J., LIN J., *Nitrate removal from groundwater using catalytic reduction*, Water Research, 2000, Vol. 34, No. 3, 995–1001.

[6] PAWEŁCZYK A., *Badania nad usuwaniem azotanów ze ścieków przemysłowych metodą redukcji do wolnego azotu*, Ochrona Środowiska, 2008, Vol. 30, No. 4, 45–48.

[7] MAĆKIEWICZ J., DZIUBEK A.M., *Usuwanie azotanów z wód podziemnych na selektywnych żywicach anionowymiennych IONAC*, Ochrona Środowiska, 2005, Vol. 27, No. 4, 45–47.

[8] SAWINIAK W., *Badania skuteczności selektywnej wymiany jonowej przy usuwaniu azotanów z wód podziemnych*, Ekoinżynieria, 1998, No. 2.

USUWANIE AZOTANÓW Z WÓD W PROCESIE SELEKTYWNEJ WYMIANY JONOWEJ

Omówiono wyniki badań nad możliwością usuwania azotanów z wód podziemnych przeznaczonych do spożycia. W badaniach określono przydatność procesu wymiany jonowej na selektywnych żywicach anionowymiennych do usuwania azotanów z wody. Uwzględniono wpływ chlorków (50 g Cl^-/m^3) i siarczanów (90 g SO_4^{2-}/m^3) oraz prędkości procesu (10–25 m/h) na jego skuteczność. Wyznaczono zdolność wymienną żywicy w stosunku do azotanów na poziomie 0,5 val/dm^3. Ustalono także, że wydajność procesu wymiany jonowej do momentu wyczerpania zdolności jonowymiennej żywicy, wyrażona jako stosunek objętości oczyszczonej wody do objętości żywicy, wynosiła 200–280.