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## APPLICATION OF ION EXCHANGE FOR POTABLE WATER PREPARATION PART I. REMOVAL OF NITRATES

Application of anion exchange resins for removal of nitrates from drinking water is discussed. Commercial resins were found to be suitable for removal of nitrates, when ratio of sulfates to nitrates is low. Biological regeneration of ion exchange bed leads to minimization of a problem of disposal of regeneration effluent.

### 1. INTRODUCTION

Nitrates were found to be harmful to health and therefore recently their maximum admissible concentrations in drinking water decreased in many countries (i.e., E. C. Council Directive (1980) decreased an admissible level of nitrates in drinking water from 22.6 mg N-NO<sub>3</sub>/dm<sup>3</sup> to 11.3 mg N-NO<sub>3</sub>/dm<sup>3</sup>). On the other hand, mostly due to extensive use of fertilizers, there is observed a continuous increase in nitrate concentration in many countries. Therefore, the number of places, in which a standard water treatment system must be supplemented by nitrate removal, is growing. A concentration of nitrates can be decreased by application of denitrification, reverse osmosis, and ion exchange.

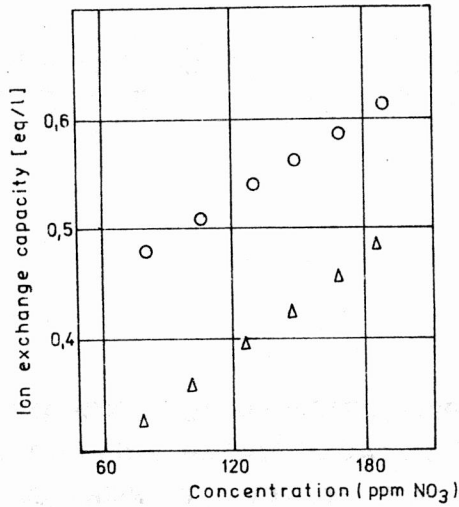
In the case of denitrification, contamination of a treated water by nitrites and bacteria can create some problems. Application of reverse osmosis allows us to decrease nitrate concentration only by 25-40%. The most effective is ion exchange.

### 2. APPLICATION OF CONVENTIONAL ANION EXCHANGERS

It is possible to use conventional anion exchangers for removal of nitrates. Usually their capacities amount to ca 0.4 eq/dm<sup>3</sup> of resin and decrease with an increase of sulfate content since the sulfates have higher affinity to resin. An increase in nitrate concentration increased

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○ concentration of  $\text{NO}_3^- + \text{HCO}_3^- + \text{SO}_4^{2-} + \text{Cl}^- = 4,3 \text{ meq/l}$   
 Δ concentration of  $\text{NO}_3^- + \text{HCO}_3^- + \text{SO}_4^{2-} + \text{Cl}^- = 8,6 \text{ meq/l}$

Fig. 1. Effect of nitrates concentration on ion exchange capacity

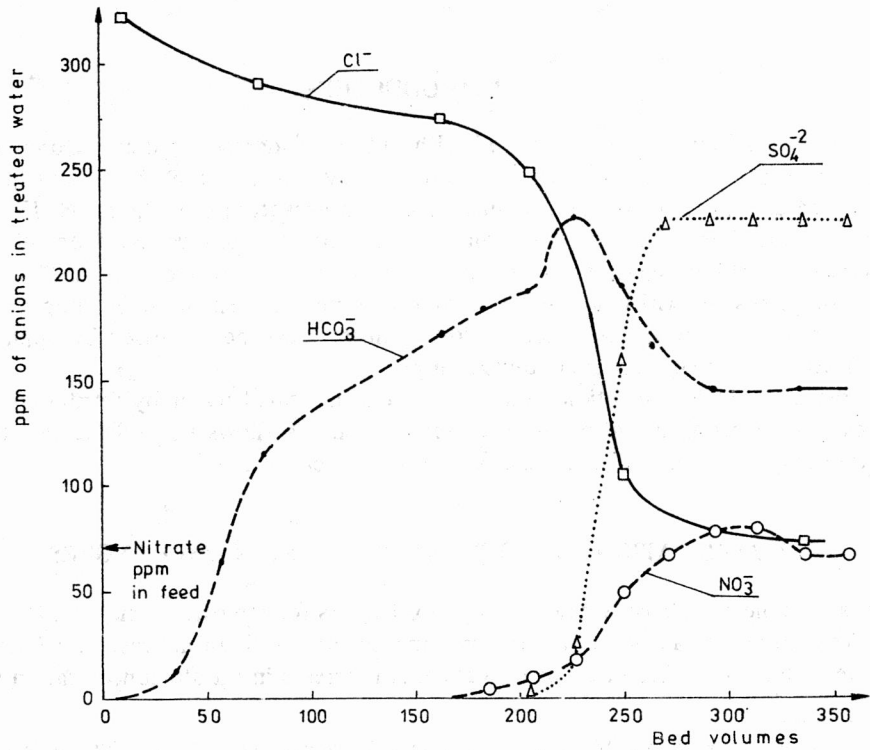


Fig. 2. Characteristics of concentration profiles of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  in treated water

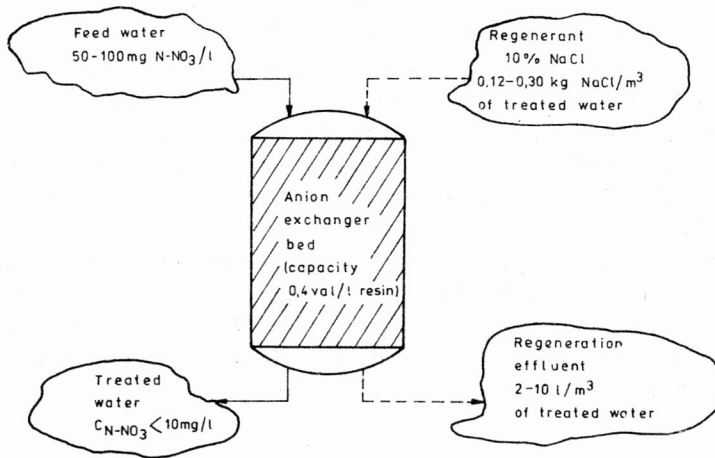


Fig. 3. Flowsheet of an ion exchange process for nitrate removal

the resin capacity for nitrate (fig. 1). An ion composition of the purified water is not uniform. A content of chlorides gradually decreases, and content of bicarbonates increases.

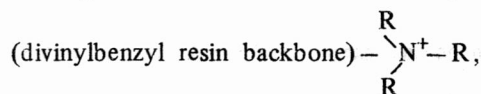
Since in an effluent from an ion exchange bed a total content of ions (in equivalents) is always constant, thus appearance of sulfates and nitrates in the treated water must be accompanied by a decrease in chloride and bicarbonate contents.

A characteristics of concentration profiles of different anions in the treated water is shown in fig. 2. A flowsheet presented in fig. 3 depicts an idea of a removal of nitrates with use of conventional anion exchangers. Disadvantages of that process are low ion exchange capacity and relatively high volume of regeneration effluent which is difficult for disposal in inland area.

### 3. SELECTIVE ANION EXCHANGERS

Sorption in other major ions (mostly sulfate) found in water exhausts ion exchange capacity and thus reduces nitrate removal efficiency of the resin and increases quantity of sodium chloride used for regeneration. It is therefore understandable that various investigators seek some idea of "nitrate-selective anion exchangers" as a remedy for the observed process inefficiencies.

Various researchers were making attempts to synthesize nitrate selective resins. Noticeable results were obtained by Guter, who has found a striking correlation between nitrate-to-sulfate selectivity and the molecular structure of the alkyl substituents of the quaternary ammonium ion. For anion exchange resins, at normal groundwater concentrations, the series of ion selectivity is as follows: bicarbonate < chloride < nitrate < sulfate. As the number of carbon atoms in the R-groups around the nitrogen increases in the resin structure,



the increasing series of ion selectivity is changed to bicarbonate, chloride, sulfate, nitrate. When the radicals are of methyl or ethyl nature, the  $K_S^N$  values (a measure of nitrate-to-sulfate selectivity) are ca 100 and 1000, respectively. Thus, in column tests with triethyl resin and aqueous solution of nitrate and sulfate of a concentration equal to ca 10 meq/dm<sup>3</sup>, nitrate is the last ion which passes. Other resins with a total of four and five carbon atoms show intermediate  $K_S^N$  values. The effect of introducing OH<sup>-</sup> groups into the alkyl substituents is to decrease the  $K_S^N$  value. For example, if the K groups are the ethoxy ones, the  $K_S^N$  value is approximately 10.

These structural effects on  $K_S^N$  value are ascribed to steric strains set up in the resin by the spatial (or steric) requirements of the alkyl R groups with nitrate having capability of decreasing the steric strain while sulfate can increase strain. Poor effect on the  $K_S^N$  values is noted. All resins are easily regenerated with chloride brins. This effect of molecular structure gives rise to a concept of structurally induced reversal of electroselectivity.

#### 4. RECYCLING OF REGENERATION EFFLUENT

A problem of brine disposal was solved by Van der HOEK et al. [1]–[5]. The process is based on recirculation of regeneration effluent via denitrification reactor of upflow sludge blanket (USB) type. A main idea of the process is depicted in fig. 4.

Nitrates are removed in ion exchange column, preferably on the nitrate selective resins, although less efficient, conventional, strongly basic resins can be also used. An efficiency of nitrate removal is a function of selectivity of the resins used and a regeneration level.

In most cases, a selectivity of normal, strongly basic anion exchanger resins is suitable for nitrate removal. However, when sulfate concentration is high, as it is often a case when ground water is treated, other resins of a higher nitrate selectivity should be used.

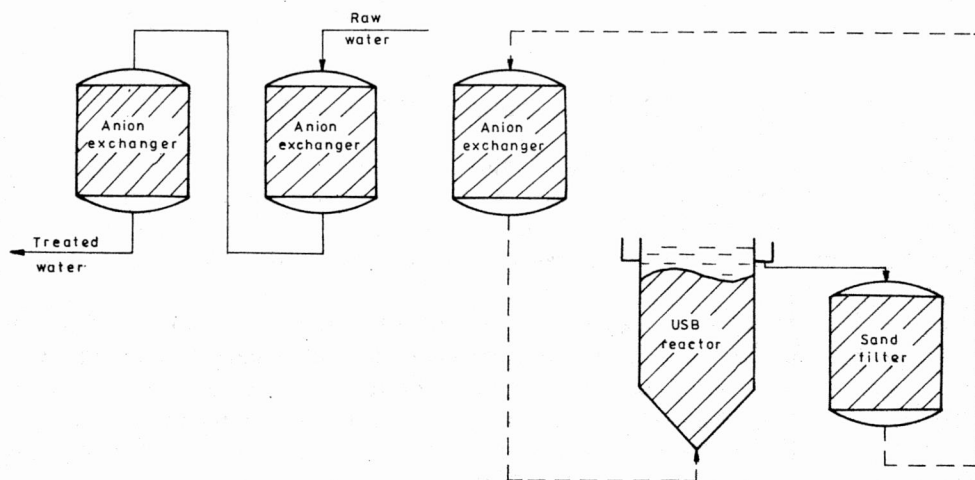


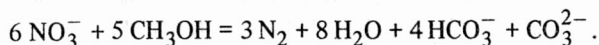
Fig. 4. Flowsheet of an ion exchange process for nitrate removal with bioregeneration of effluent

Regeneration of an anion exchanger exhausted by nitrates without recycling of the regeneration effluent does not present any problem. However, when recycling of the regeneration effluent via the USB reactor is performed, new, specific problems have arisen, i. e.:

impact of concentration of a regenerant used on denitrification reaction,  
disinfection of an ion exchange bed and its impact on an ion exchange capacity,  
efficiency of regeneration by the recycled regenerant.

#### IMPACT OF CONCENTRATION OF A REGENERANT USED ON DENITRIFICATION REACTION

In the USB reactor denitrifying bacteria reduce nitrates, and methanol used as a carbon and energy source is converted to bicarbonate, carbonate and water according to the following reactions [2]:



As one can see, a substantial amount of bicarbonates is formed in denitrification reaction. Therefore, when solution of NaCl is used for regeneration, during recycling there is practically formed a mixture of NaCl and NaHCO<sub>3</sub> instead of pure NaCl.

It is proved [2] that denitrification occurs in the presence of 10–30 g of NaCl, NaHCO<sub>3</sub> or their mixture per dm<sup>3</sup>, and the rise in pH values in the regenerant recycled will not inhibit severely the denitrification reaction. Waste production is minimal: firstly – brine production is low as a result of the regenerant recycling, and secondly – sludge production in the denitrification reactor is also low as a result of low sludge yield in high bicarbonate concentrations. The high bicarbonate concentration in the recirculated regenerant suppresses nitrite formation keeping its concentration low. One should remember that nitrite production is one of the main problems of direct biological denitrification of ground water.

#### DISINFECTION OF AN ION EXCHANGE BED

Sand filter shown on flowsheet (fig. 1) does not prevent an ion exchange bed from bacteria present in treated water. Therefore it is necessary to disinfect the ion exchange bed during its rinsing.

Two disinfectants were found to be efficient in the system [3]: peracetic acid at a concentration of 0.075% and contact time of 15 min. or hydrogen peroxide at a concentration of 0.20% and contact time 45 min. In both cases it was possible to keep a level of 30 cells/cm<sup>3</sup> of treated water.

However, application of peracetic acid leads to a significant decrease in an ion exchange capacity [4]. Therefore, only hydrogen peroxide may be used for disinfection of the exchange bed.

## REFERENCES

- [1] Van der HOEK J. P., Klapwijk A., *Nitrate removal from ground water*, Water Res., Vol. 21 (1987), No. 8, pp. 983-997.
- [2] Van der HOEK J. P., LATOUR P. J. N., Klapwijk A., *Denitrification with methanol in the presence of high salt concentrations and at high pH levels*, Appl. Microbiol., Vol. 27 (1987), pp. 199-205.
- [3] Van der HOEK J. P., VERHEIJE J., VIS P. I. M., Klapwijk A., *Disinfection of anion exchange resins in the combined ion exchange/biological denitrification process. Part I. Effect on water quality*, Z. Wasser-Abwasser-Forsch., Vol. 20 (1987), pp. 155-160.
- [4] Van der HOEK J. P., Van der VEN P. J. M., Klapwijk A., *Disinfection of anion exchange resins in the combined ion exchange/biological denitrification process. Part II. Effect on resin capacity*, Z. Wasser-Abwasser-Forsch., Vol. 20 (1987), pp. 155-160.
- [5] Van der HOEK J. P., Klapwijk A., *The use of a nitrate selective resin in the combined ion-exchange/biological denitrification process for nitrate removal from ground water*, Wat. Supply, Vol. 6 (1988), pp. 57-62.

#### ZASTOSOWANIE WYMIANY JONOWEJ W OTRZYMYWANIU WODY PITNEJ CZĘŚĆ I. USUWANIE AZOTANÓW

Przedstawiono zastosowanie żywic anionitowych w usuwaniu azotanów z wody pitnej. Handlowe żywice okazały się przydatne w usuwaniu azotanów pod warunkiem, że wartość stosunku siarczanów do azotanów była mała. Biologiczna regeneracja złoża jonitowych zmniejsza do minimum problem usuwania odcieku regeneracyjnego.

#### ПРИМЕНЕНИЕ ИОНООБМЕНА ДЛЯ ПОЛУЧЕНИЯ ПИТЬЕВОЙ ВОДЫ. ЧАСТЬ I. УДАЛЕНИЕ НИТРАТОВ

Представлено применение анионитных смол для удаления нитратов из питьевой воды. Смолы, встречаемые в торговле, оказались пригодными для удаления нитратов при условии, что значение отношения сульфатов к нитратам было малым. Биологическая регенерация ионитных залежей уменьшает до минимума проблему удаления регенерационного оттока.