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NITRATE REMOVAL FROM GROUND WATER

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Abstract—A new technique is described for nitrate removal from ground water. This technique is a combination of ion exchange and biological denitrification. Nitrate is removed by ion exchange. Regeneration of the resin in a closed circuit is achieved with a denitrification reactor. In contrast with traditional denitrification procedures there is no direct contact between ground water and denitrifying bacteria. Also brine production and regeneration salt requirements are minimal as compared with conventional regeneration of ion exchange resins. The basic design criteria and the first pilot plant results are presented. The pilot plant results show that the process is very attractive when compared with ion exchange and biological denitrification as separate techniques. Ground water with a relatively high sulfate concentration can be treated when a nitrate selective resin is used.

Key words—nitrate removal, drinking water, ground water, denitrification, ion exchange, biological regeneration, nitrate selective resin

INTRODUCTION

Increased nitrate concentrations in public water supplies is becoming an important problem in several countries, especially as the maximum admissible concentration of nitrate in drinking water is decreased from 22.6 to 11.3 mg NO_3^-–N l^{-1} according to the E.C.-Council Directive (E.C. 1980). In The Netherlands it is estimated that about 25% of the ground water wellfields exploited by the waterworks may experience problems, either with nitrate itself or with the reaction products of nitrate reduction (Van Beek, 1985). As about two-thirds of the drinking water in The Netherlands originates from ground water it is obvious that many problems are expected in the coming years (Scheltinga, 1985).

Several techniques are available for the removal of nitrate from ground water. Some of these techniques are summarized in Table 1 (Sorg, 1979; Sontheimer and Rohmann, 1984). Only ion exchange and biological denitrification are considered feasible and practical for full-scale treatment of drinking water. However, both processes have serious disadvantages.

Biological denitrification is a process by which nitrate is converted to nitrogen gas by denitrifying bacteria. A direct contact is created between ground water, which is generally free of microorganisms, and bacteria. In the case of heterotrophic denitrification also a carbon-source has to be added to the ground water. Both cause a serious risk of a bacteriological contamination of the ground water, and extensive post-treatment is necessary to safeguard the drinking water quality (Sorg, 1979; Barlog, 1980; Leprince and Richard, 1982; Sontheimer *et al.*, 1982; Haberer, 1984). Also the production of nitrite, an intermediate product of denitrification, is a serious risk. Further, at the normal ground water temperature of ±10–12°C the activity of denitrifying bacteria is rather low, which means that relatively large reactors are needed.

Table 1. Nitrate removal techniques

Ion exchange
Biological denitrification
Chemical reduction
Reverse osmosis
Electrodialysis

Ion exchange is a physical–chemical process. By means of an anion exchange resin nitrate is exchanged for chloride or bicarbonate. A problem is the regeneration of the resin. It is customary to use a highly concentrated NaCl solution (50–100 g l^{-1}) at a flowrate of 2–4 BV h^{-1} (BV = bed volumes) for a period of 30–45 min (Gauntlett, 1975; Deguin, 1982; Guter, 1982; Richard and Leprince, 1982; Partos and Richard, 1985). Hence, a large excess of salt is needed, producing a voluminous brine with high nitrate, sulfate and chloride concentrations. Brine disposal can be very difficult. Both aspects cause financial and environmental problems.

A NEW PROCESS: BIOLOGICAL/PHYSICAL CHEMICAL NITRATE REMOVAL FROM GROUND WATER

By combining ion exchange and biological denitrification into one process (van der Hoek, 1985; van der Hoek and Klapwijk, 1985, 1986) most problems connected with the separate techniques can be avoided. This new process is shown schematically in

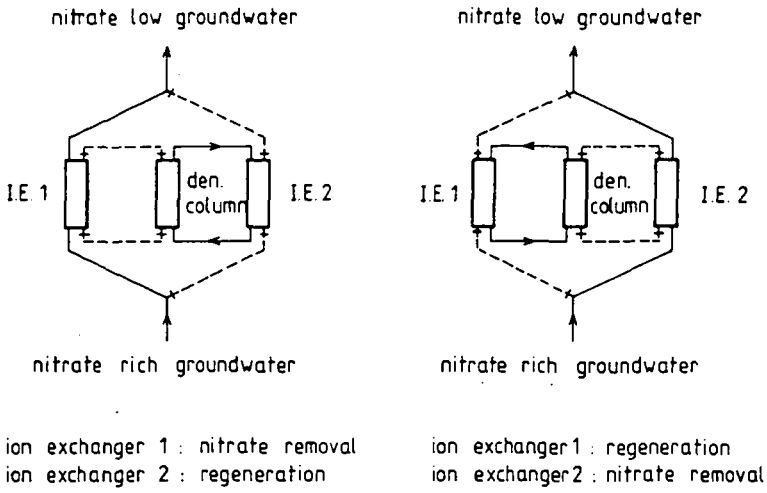

Fig. 1. Combination of ion exchange and biological denitrification: biological/physical chemical nitrate removal from ground water.

Fig. 1. Nitrate is removed from the ground water by ion exchange and for the regeneration of a nitrate loaded resin a denitrification reactor is used.

In the simplest form one ion exchange column (column 1) is used for production of potable water while another ion exchange column (column 2) is regenerated. When ion exchange column 1 is exhausted and ion exchange column 2 is regenerated the denitrification reactor is connected with the exhausted ion exchange column 1 and the regenerated resin (column 2) is used for potable water production. Depending on the ratio of run time and regeneration time more ion exchange columns can be used in this process.

The regeneration process itself is schematically shown in Figs 2 and 3. It can be carried out with a NaCl solution (Fig. 2) or a $NaHCO_3$ solution as regenerant (Fig. 3). The regenerant, for example a

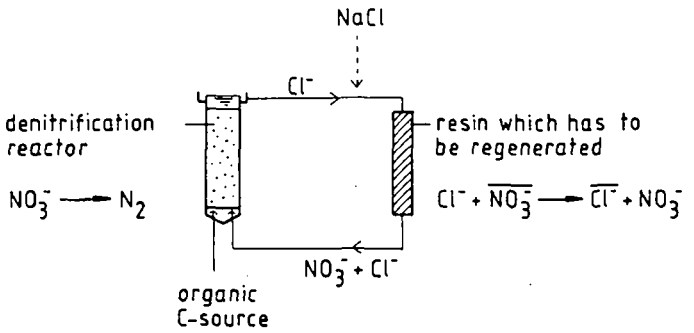

Fig. 2. Regeneration of a nitrate-loaded resin into the chloride form with a denitrification reactor.

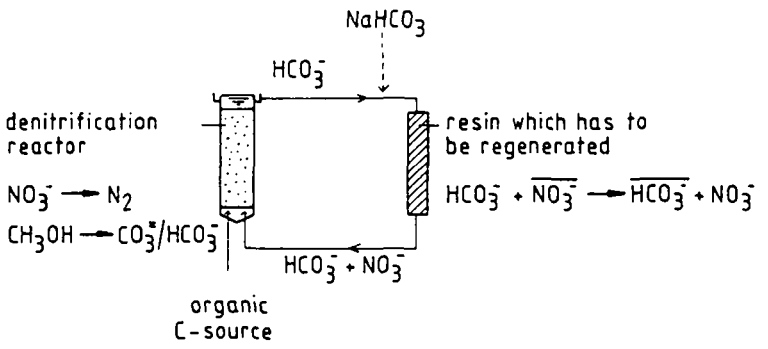

Fig. 3. Regeneration of a nitrate-loaded resin into the bicarbonate form with a denitrification reactor.

$NaHCO_3$ solution, passes over the ion exchange column to exchange nitrate ions for bicarbonate ions. After passage the nitrate rich regenerant is led through a denitrification reactor where denitrifying bacteria convert nitrate to nitrogen gas. The organic C-source (methanol) which has to be added is converted into bicarbonate, carbonate and water. The regenerant is recirculated through the ion exchange column and the denitrification reactor, until the ion exchanger has reached a sufficient bicarbonate loading. The regeneration thus takes place in a closed system.

Compared with separate ion exchange or biological denitrification the most important advantages of this new process are:

(1) The regeneration is carried out in a closed system in which the production of a voluminous brine can be avoided and the salt requirements are minimized. The use of $NaHCO_3$ as regenerant has the advantage that the system itself produces the salt necessary for regeneration because bicarbonate is an endproduct of biological denitrification. When NaCl is used as regenerant only the stoichiometric required amount has to be dosed.

(2) As the biological process does not take place in direct contact with the ground water there is no risk that nitrite production will affect the water quality.

(3) There is no direct contact of bacteria and the C-source with the ground water and concomitant contamination. Still pollution of the resin by carry-over of suspended material from the denitrification reactor to the ion exchange column is possible. However, measures against this can be taken in the regeneration circuit itself, so there is no need for an extensive post-treatment.

MATERIALS AND METHODS

Ion exchange experiments

Breakthrough and regeneration experiments were conducted in columns with i.d.s of 1.9 or 3.2 cm and a height of 14, 19 or 40 cm.

The total anion exchange capacity of resins was measured by potentiometric titration of resins in the chloride form in water with a $AgNO_3$ solution after addition of excess KNO_3 to the water–resin mixture, or by pH titration of resins in the bicarbonate form in water with a HCl solution after addition of excesss NaCl to the water–resin mixture.

Selectivity coefficients and binary equilibrium isotherms were determined at a total anion concentration of 0.012 equiv l^{-1} in liquid phase.

Resin disinfection experiments were performed with ion exchange columns (resin Duolite A 165) with an i.d. of 1.9 cm and a height of 40 cm.

Denitrification experiments

The effect of high sodium bicarbonate concentrations on denitrifying sludge was studied in 5 l. batch reactors. To avoid accumulation of bicarbonate, one of the end products of denitrification with methanol, the effect of high sodium chloride concentrations on denitrifying sludge was studied in an upflow sludge blanket denitrification reactor with a working volume of 2.5 l.

Pilot plant experiments

Design and dimensions of the pilot plant are described in "Results and Discussion".

Analyses

Nitrate was analyzed either through the salicylate method according to the *Dutch Normalized Standard Methods* (NNI 1981) or by liquid chromatography with a Chrompack HPLC column, packing material Ionospher tmA (dim: 250 × 4.6) and u.v. detection at 205 nm (Spectroflow 773 u.v. adsorbance detector). Alkalinity was determined according to the *Dutch Normalized Standard Methods* (NNI, 1966). Sulfate was analyzed by liquid chromatography with the same column as used for nitrate and a Knauer differential refractometer. Chloride was analyzed potentiometrically using a Mettler DL 40 RC memotitrator and a Mettler DM 141 combined Ag electrode, or by liquid chromatography along with sulfate.

Standard plate counts were performed at 22°C on glucose yeast extract according to the *Dutch Normalized Standard Methods* (NNI, 1982).

The accumulation of organics fouling the ion exchange resins was measured by extracting samples of resin with a solution containing 2% NaOH and 10% NaCl. The optical density of the extract at 435 nm was related to the optical density of a standard humic substance. For this purpose a solution of commercially available humic acids was used, which was prepared by adding NaOH to a 0.25% solution of sodium humate (Fluka) in deionized water until pH 11 was reached. After stirring for 24 h the suspension was neutralized with HCl to pH 5.5 which resulted in partial precipitation of the humic compounds. This solution was filtered over a 0.45 μm membrane filter and used as standard humic substance solution.

RESULTS AND DISCUSSION

Basic design criteria

Salt concentration of the regenerant. The optimal salt concentration of the regenerant is controlled by two factors. Very high salt concentrations can have an inhibiting effect on the biological denitrification, but the salt concentration must be high enough to produce sufficient regeneration of the resin within a reasonable time.

Claus and Kutzner (1985) demonstrated that 20 g NaCl l^{-1} has no effect on autotrophic denitrification. Denitrification has also been observed in marine sediments (Sørensen, 1978, 1979). Our experiments on the effect of NaCl and $NaHCO_3$ on the capacity of denitrifying sludge with methanol as C-source are summarized in Fig. 4. It is clear that with $NaHCO_3$ concentrations of 25–30 g l^{-1} and NaCl concentrations of 10–15 g l^{-1} the dentrification capacity is still present for about 80%.

Figure 5 shows that regeneration of a nitrate loaded resin is possible with a solution containing 30 g $NaHCO_3$ l^{-1} (357 m-equiv l^{-1}). Compared with the usual regeneration procedure with 50–100 g NaCl l^{-1}, a flowrate of 2–4 BV h^{-1} and a period of approx. 30–45 min (Gauntlett, 1975; Deguin, 1982; Guter, 1982; Richard and Leprince, 1982; Partos and Richard, 1985) more time and a higher flowrate are needed. However, with 30 g $NaHCO_3$ l^{-1} and a flowrate of 10 BV h^{-1} almost complete regeneration is possible in 3.5 h.

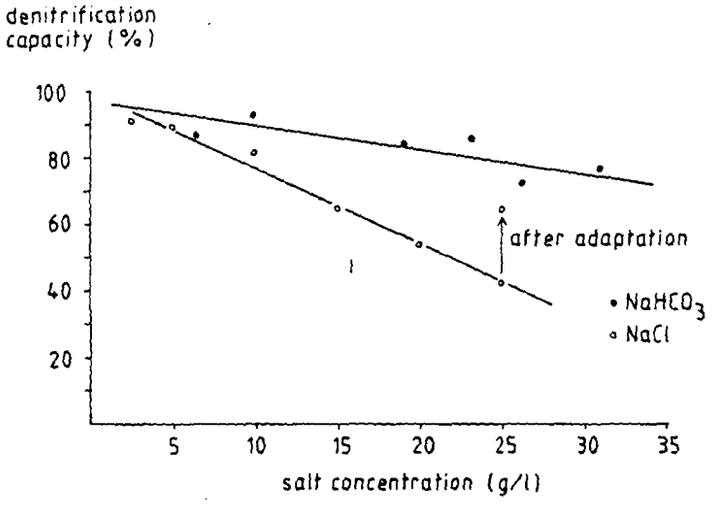

Fig. 4. Effect of high NaCl and $NaHCO_3$ concentrations on denitrification.

In Table 2 the selectivity coefficients $K_{NO_3}^{Cl}$ and $K_{NO_3}^{HCO_3}$ of some strong base anion exchange resins are shown. The coefficients are defined as

$$K_{NO_3}^{A} = \frac{[\overline{A^-}]\cdot[NO_3^-]}{[\overline{NO_3^-}]\cdot[A^-]}$$

with

$[\overline{A^-}]$, $[\overline{NO_3^-}]$ = concentration of A^- and NO_3^- on the resin (equiv l^{-1})

$[A^-]$, $[NO_3^-]$ = concentration of A^- and NO_3^- in solution (equiv l^{-1}).

Because $K_{NO_3}^{Cl}$ is about twice $K_{NO_3}^{HCO_3}$ it is possible to use a NaCl solution as regenerant with a concentration which is only half of the $NaHCO_3$ concentration. So, regeneration can also be carried out in 3.5 h with 10.4 g NaCl l^{-1} (178 m-equiv l^{-1}) and a flowrate of 10 BV h^{-1}.

Selection of denitrification reactor type. The denitrification reactor in this process must fulfill a number of conditions:

(1) Hydraulically it should fit in the process: this means that the flowrate through the denitrification reactor must equal the regeneration flowrate through the ion exchange column, otherwise a bypass would be necessary.

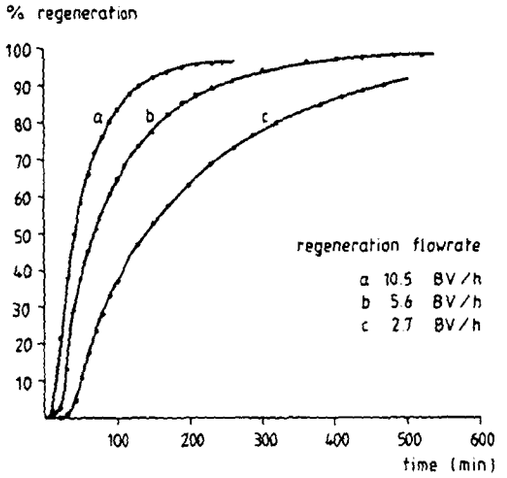

Fig. 5. Regeneration of a nitrate-loaded resin (Duolite A 161) with a solution containing 30 g $NaHCO_3$ l^{-1} (regeneration percentage = regeneration as percentage of total ion exchange capacity).

(2) The reactor must be capable to treat solutions with very high nitrate concentrations without re-

Table 2. Capacity and selectivity coefficients $K_{NO_3}^{Cl}$ and $K_{NO_3}^{HCO_3}$ of strong base anion exchange resins

Anion exchange resin	Capacity (equiv l^{-1})	$K_{NO_3}^{Cl}$	$K_{NO_3}^{HCO_3}$
Macroporous resins			
Duolite A 161	1.11	0.30	0.16
Duolite A 162	1.19	0.24	0.12
Duolite A 165	1.19	0.35	0.17
Bayer Lewatit MP 500	1.09	0.36	0.18
Bayer Lewatit MP 600	1.14	0.30	0.15
Amberlite IRA 996	1.01	0.11	0.04
Gel resins			
Bayer Lewatit M 500	1.36	0.33	0.18
Bayer Lewatit M 600	1.29	0.35	0.18

circulation, because nitrate concentrations up to 700 mg NO_3^-–N l^{-1} can be expected in the regenerant (van der Hoek, 1985).

(3) It should be possible to develop and maintain a high sludge concentration in the reactor. By this a constant high volumetric capacity can be obtained and the reactor dimensions can be small.

(4) Sludge washout must be minimal to prevent organic fouling of the ion exchange resin.

(5) Maintenance and process control must be minimal.

In most experiments on denitrification of potable water fluidized bed reactors (Richard *et al.*, 1980; Hall *et al.*, 1985) or fixed bed reactors (Frick and Richard, 1985; Philipot *et al.*, 1985) have been used. The five conditions mentioned are not met completely with these reactors. The flowrate through a fluidized bed reactor is much higher than the flowrate through the ion exchange column, and this type of reactor cannot treat high nitrate-concentration water without recirculation. Also it needs a good control and balancing of the flowrate to avoid washout of sludge/sand particles. The disadvantages of fixed bed reactors are that backwashing is necessary to avoid clogging (Frick and Richard, 1985; Philipot *et al.*, 1985; Roennefahrt, 1985) and that the volumetric capacity is low compared with fluidized bed reactors (Roennefahrt, 1985).

The best suited denitrification reactor in this process is the Upflow Sludge Blanket (USB) reactor. Much experience has been obtained in recent years with such reactors in the field of denitrification (Klapwijk *et al.*, 1979; Klapwijk *et al.*, 1981) and in anaerobic treatment of waste water (Lettinga *et al.*, 1980). In this type of reactor the biomass is not present on a carrier material as in the fluidized bed reactor and fixed bed reactor, but the biomass grows in pellets or grains with favorable settling characteristics depending on the chemical, physical and biological conditions. In the case of denitrification pellet formation (2–3 mm) is promoted by precipitation of $CaCO_3$ as is a result of the rise in pH due to biological denitrification. So a sludge concentration up to 30–40 g VSS l^{-1} can be maintained (van der Hoek, 1985) with superior settling characteristics, and superficial velocities as high as 2–4 m h^{-1} are possible (Lettinga *et al.*, 1980; Klapwijk *et al.*, 1981).

With the USB denitrification reactor the above mentioned conditions can be fulfilled. Hydraulically it is possible to use the same flowrate through the USB reactor as in the ion exchange column. A USB denitrification reactor is able to treat water with very high nitrate concentrations without recirculation, and a volumetric denitrification capacity of 400–500 g N m^{-3} h^{-1} can be attained (Klapwijk *et al.*, 1981; van der Hoek, 1985). Sludge washout is very low due to good settling characteristics and can be minimized when the reactor is equipped in the upper part with a gas–solids separator as shown in Fig. 6. Operation

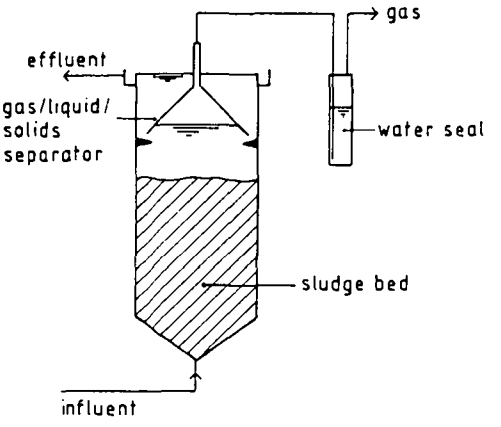

Fig. 6. Schematic diagram of a USB denitrification reactor.

of this reactor is very simple and backwashing is not necessary.

Influence of sulfate and selection of resin type. Most strong base anion exchange resins are more selective for sulfate than for nitrate (Clifford and Weber, 1978; Clifford, 1982; Guter, 1982). Most ground waters contain both sulfate and nitrate. Sulfate in the ground water influences the process in two ways:

—the effective nitrate capacity of the resin decreases with increasing sulfate concentration of the ground water (Deguin, 1985).

—sulfate is readily removed from the resin during regeneration into the regeneration circuit (van der Hoek, 1985). The sulfate will accumulate in the regeneration circuit, and it may be possible that after several regenerations the resin will remain partly loaded with sulfate due to the high sulfate concentration in the regenerant. This further decreases the effective nitrate capacity of the resin.

When treating a Dutch ground water with 19.2 mg NO_3^-–N l^{-1} and 29.5 mg SO_4^{2-} l^{-1} no problems were encountered with a normal resin, Duolite A 165 (see results of pilot plant). However, sulfate concentrations can be much higher in ground water. In such cases other resins should be used with a higher nitrate selectivity.

Recently some nitrate selective resins have been developed (Guter, 1982), including the resin Amberlite IRA 996 of Rohm and Haas. This is evident from the binary equilibrium isotherm in Fig. 7 for the equilibrium between nitrate and sulfate. At all equivalent fractions of sulfate in the liquid phase ($X SO_4^{2-}$ = sulfate concentration in liquid/total anion concentration in liquid) the concomitant equivalent fraction of sulfate on the resin ($\bar{X} SO_4^{2-}$ = sulfate on resin/total ion exchange capacity) is lower. The breakthrough curve in Fig. 8 shows that even at a very high sulfate concentration in the ground water (139.4 mg SO_4^{2-} l^{-1}) nitrate will break through after sulfate.

After nine repeated regenerations with a solution containing 30 g $NaHCO_3$ l^{-1} and sulfate concen-

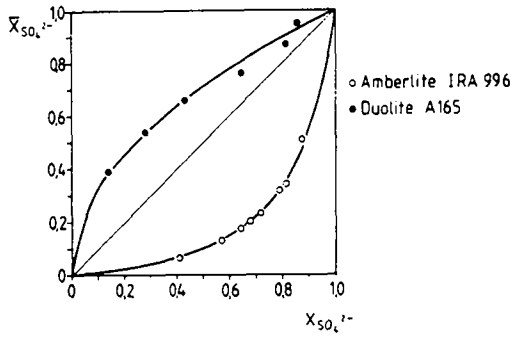

Fig. 7. Binary equilibrium isotherm of nitrate and sulfate for a sulfate selective resin (Duolite A 165) and a nitrate selective resin (Amberlite IRA 996) (total anion concentration in liquid phase 0.012 equiv l^{-1}).

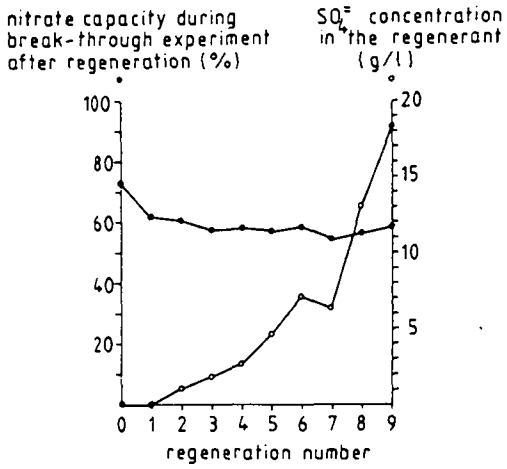

Fig. 9. Effect of sulfate in the regenerant on nitrate capacity of the nitrate selective resin Amberlite IRA 996 (nitrate capacity expressed as percentage of total ion exchange capacity). Ground water composition during breakthrough experiments 18 mg NO_3^-–N l^{-1}, 30 mg SO_4^{2-} l^{-1}, 25 mg Cl^- l^{-1} and 58 mg HCO_3^- l^{-1}; flowrate 35 BV h^{-1}; runtime 17 h. Regeneration flowrate 10 BV h^{-1}; regeneration time 3.5 h. ○, SO_4^{2-} concentration (g l^{-1}); ●, nitrate capacity (%).

trations varying from 0 g SO_4^{2-} l^{-1} in the first up to 18.4 g SO_4^{2-} l^{-1} in the ninth regeneration the nitrate capacity of this resin in the service mode after each regeneration turned out to be almost independent of the sulfate concentration in the regenerant (Fig. 9).

This means that the proposed process is also suitable for ground water with high sulfate concentrations when nitrate selective resins, such as Amberlite IRA 996, are used.

Use of a sandfilter and a disinfectant in the process. Although sludge washout can be minimized with a USB denitrification reactor, the resin can still become polluted by carry-over of suspended solids from the denitrification reactor to the ion exchange column. Also humic and fulvic acids, which can accumulate in a closed regeneration circuit with a biological process, can cause organic fouling of the resin (Wilson, 1959; Frisch and Kunin, 1960; Ungar, 1962; Abrams, 1982; Pelosi and McCarthy, 1982). This pollution of the resin can affect the bacteriological quality of the treated water because after regeneration the resin is in contact with drinking water.

To overcome these problems a sandfilter can be placed in the regeneration circuit between the USB denitrification reactor and the ion exchange column to remove suspended solids from the regenerant before they reach the resin. Secondly, the ion exchanger can be disinfected in the process. After regeneration the ion exchange column is rinsed with water. It is advisable to use a disinfectant during the first minutes of this rinsing. Especially peracetic acid is often used for disinfection of ion exchange resins (Ballmoos and Soldavini, 1979; Flemming, 1984).

In a pilot plant for nitrate removal from ground water the ion exchange columns are used for 9 h for

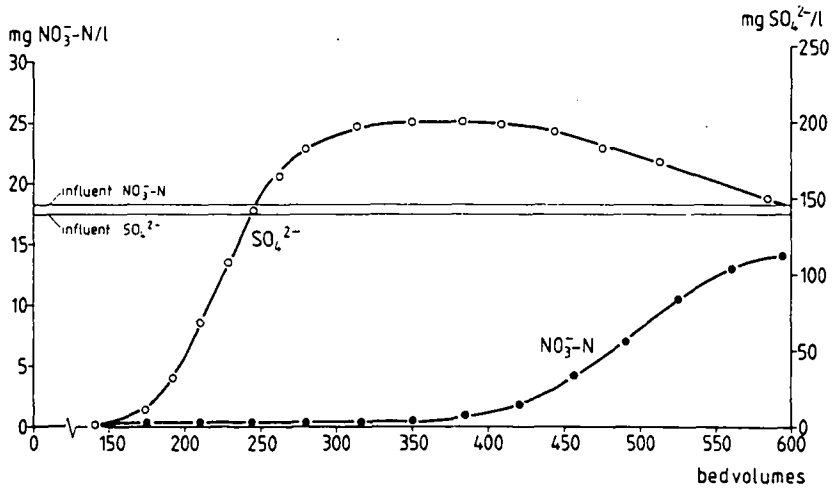

Fig. 8. Breakthrough profile of ion exchange resin Amberlite IRA 996. Influent concentrations 18.1 mg NO_3^-–N l^{-1} and 139.4 mg SO_4^{2-} l^{-1}, flowrate 35 BV h^{-1}, resin in HCO_3^- form.

Table 3. Standard plate counts in biological regenerant, in water treated with a non disinfected resin and in water treated with a disinfected resin (resin disinfected with peracetic acid)

	Standard plate counts (No. of bacteria ml^{-1})
Regenerant (effluent from USB denitrification reactor)	100,000–1,000,000
Water treated with a non disinfected resin	50,000–100,000
Water treated with a disinfected resin	0–30

potable water production after which they are regenerated for 3.5 h and rinsed for 1 h (see "Design of the pilot plant"). To study the effect of the use of a disinfectant during rinsing on the bacteriological water quality this sequence was simulated in a laboratory experiment with two ion exchange columns. After regeneration with a bacteriologically contaminated regenerant (see Table 3) one column was rinsed with water, containing 0.15% peracetic acid during the first 15 min, and the other column was rinsed without peracetic acid. For the next 9 h both columns were run with sterilized water. In the water, leaving the ion exchange columns, the number of bacteria was measured. This procedure was repeated several times. In Table 3 the results are presented. It can be seen that a bacteriologically reliable water [standard plate counts $< 100\ ml^{-1}$ according to the E.C. Council Directive (1980)] can be produced when 0.15% peracetic acid is used the first 15 min during rinsing.

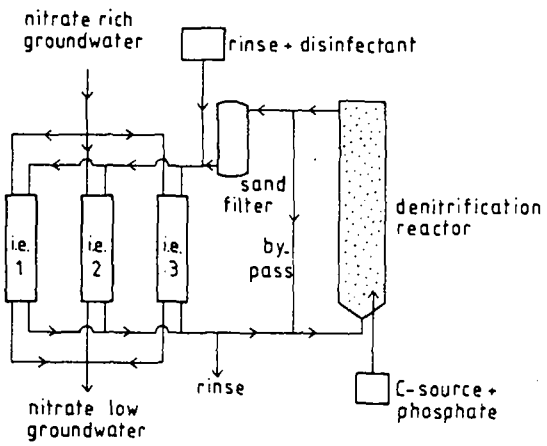

Fig. 10. Lab-scale pilot plant for nitrate removal from ground water using the biological/physical chemical process.

Table 4. Dimensions of the pilot plant and ground water composition

Volume ion exchange columns	0.95 l.
Volume denitrification reactor	5 l.
Ground water flowrate	$65.7\ l\ h^{-1}$ ($2 \times 32.9\ l\ h^{-1}$)
Regeneration flowrate	$9–12\ l\ h^{-1}$
Rinse flowrate	$9–12\ l\ h^{-1}$
Ground water composition	
NO_3^--N	$19.2\ mg\ l^{-1}$
SO_4^{2-}	$29.5\ mg\ l^{-1}$
Cl^-	$26.1\ mg\ l^{-1}$
HCO_3^-	$98.3\ mg\ l^{-1}$
pH	7.8
Regenerant $NaHCO_3$	$10.5–23.7\ g\ l^{-1}$

Pilot plant study

Design of the pilot plant. With the conditions mentioned above a lab-scale pilot plant was designed. The pilot plant is shown schematically in Fig. 10. It consists of three ion exchange columns filled with resin Duolite A 165, a sand filter and a USB denitrification reactor. Methanol is used as substrate for the denitrification reactor.

Two ion exchange columns are used simultaneously for production of potable water with a run time of 9 h each, but a phase shift of 4.5 h. The third ion exchange column is connected with the denitrification reactor and is regenerated for 3.5 h followed by 1 h rinsing with water that contains a disinfectant (peracetic acid) during the first 15 min. During rinsing, water is recirculated through the denitrification reactor by means of a bypass. In this way every 4.5 h a regenerated ion exchange column is put into service for nitrate removal from ground water. The pilot plant is controlled by a programmable logic controller (PLC).

Table 4 summarizes the dimensions of the plant and the ground water composition. During the experimental period $NaHCO_3$ was used as regenerant. No disinfectant was used and the sand filter was used only temporarily.

Operation of the pilot plant. In Fig. 11 the nitrate concentration in the treated ground water is shown.

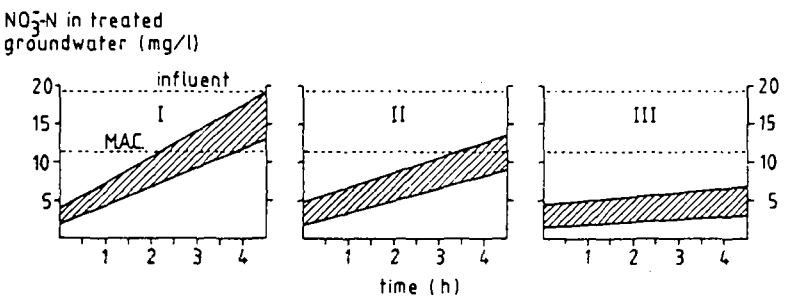

Fig. 11. Nitrate concentration in the treated ground water. I—Denitrification reactor capacity $525\ mg\ N\ h^{-1}$; II—denitrification reactor capacity $625\ mg\ N\ h^{-1}$; III—denitrification reactor capacity $840\ mg\ N\ h^{-1}$ (denitrification reactor vol 5 l., influent concentration $19.2\ mg\ NO_3^-$-N l^{-1}, maximum admissible concentration $11.3\ mg\ NO_3^-$-N l^{-1}).

All measurements concern the process-cycle of 4.5 h. During the experimental period three different denitrification reactor capacities were tested with: 525 (I), 625 (II), and 840 mg NO_3^-–N h^{-1} (III) respectively. A higher denitrification reactor capacity results in a better regeneration of the resin which means that a lower nitrate concentration in the treated water can be reached. At each capacity a sort of breakthrough profile was visible in the 4.5 h process-cycle. This is caused by the fact that at the start of every 4.5 h process-cycle one ion exchange column is switched into service for water production, while the other is already 4.5 h in operation. At the end of the 4.5 h process-cycle one ion exchange column has been 4.5 h in service and the other 9 h, resulting in a higher nitrate concentration in the treated water.

At the lower denitrification reactor capacity (I) sulfate was present in the treated water ranging from 3.4 to 5.8 mg SO_4^{2-} l^{-1}. At capacities II and III only occasionally sulfate was present in the treated ground water in very low concentrations. Chloride concentrations in the treated water varied between 4.4 and 39.7 mg Cl^- l^{-1}. Bicarbonate concentrations in the treated water were always higher than influent concentrations due to a $NaHCO_3$ regenerant. The highest measured concentration was 238 mg HCO_3^- l^{-1}. The pH ranged from 7.70 to 8.60.

In order to control and prevent sulfate accumulation in the regenerant the latter was replaced every 6 days. In Fig. 12 the course of sulfate concentrations

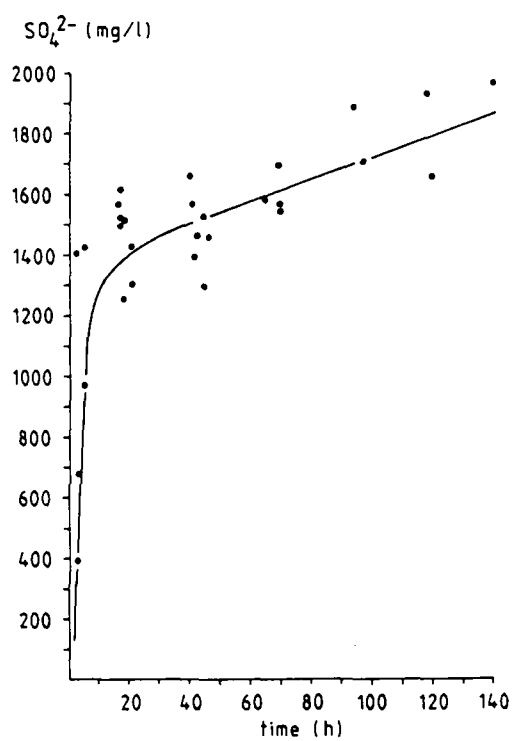

Fig. 12. The course of sulfate concentrations in the regenerant.

Table 5. Organic fouling of the resin after 44 and 111 days

Ion exchange column (0.95 l.)	Extractable organics (mg organics/g resin)	
	After 44 days	After 111 days
1	6.31	11.51
2	6.57	12.62
3	5.21	11.13

Table 6. Loss of resin capacity by organic fouling after 44 and 111 days of operation

Resin in column	Relative capacity (%)	
	After 44 days	After 111 days
1	90.1	91.0
2	90.1	90.9
3	89.2	90.6

in the regenerant during these 6 day periods is shown. The brine volume produced by renewing the regenerant every 6 days is only 13–20% of the brine which would be produced if the ion exchange columns are regenerated in the conventional way without a closed system.

As said before, in a closed system with a biological process, accumulation of humic and fulvic acids can occur. These substances can be absorbed by the resin and influence resin capacity (Wilson, 1959; Frisch and Kunin, 1960; Ungar, 1962; Abrams, 1982; Pelosi and McCarthy, 1982). For this reason the extractable organics were measured for each ion exchange column and also the capacity of the resin in each column. This was done after 44 and 111 days of operation.

The results are presented in Tables 5 and 6. The capacity is expressed as percentage of the capacity of an unpolluted resin which is 1.19 equiv l^{-1} for Duolite A 165. Although pollution of the resin increased from 44 to 111 days the capacity did not decrease. This is in good accordance with earlier observations (van der Hoek, 1985). In 11 regeneration cycles with effluent of a USB denitrification reactor the capacity of an anion exchange resin (Duolite A 165) decreased only 8% and this decrease was already reached after three regenerations. Already Harries *et al.* (1984) stated that there is no apparent link between deterioration in resin performance and the degree of organic fouling of the resin.

CONCLUSION

The described biological/physical chemical process is a very attractive technique for nitrate removal from ground water. Compared with ion exchange brine production is very low and regeneration salt requirement is minimal. Compared with direct biological denitrification of ground water the production of bacteriologically reliable drinking water is possible by means of simple measures, without the need of extensive post-treatment. Also ground water with a

high sulfate concentration can be treated with this technique when a nitrate selective resin is used, for example Amberlite IRA 996.

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