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Catalytic denitrification: direct and indirect removal of nitrates from potable water

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Abstract

A nitrate removal process that drastically reduces salt consumption and waste discharge has been developed on a bench scale. Nitrate is removed by chloride ion exchange, and the strong-base anion resin is completely regenerated at mild reaction conditions (i.e., ambient temperature, atmospheric pressure) in a closed circuit containing a single-flow fixed-bed reactor packed with a Pd–Cu/γ-Al_2O_3 catalyst. The combined treatment system avoids direct contact between the denitrification reactor and the water to be treated, and minimizes operational problems associated with each separate technique. No dissolution of Pd and Cu metallic-phases was observed at the given operating conditions.

Keywords: Combined process; Ion exchange; Catalytic hydrogenation; Nitrate removal; Pd–Cu bimetallics; Potable water purification

1. Introduction

Nitrate concentrations in surface water and especially in groundwater have increased in many locations in the world. Man-made or man-caused sources of nitrogen introduction into the subsurface environment include agricultural fertilizers, septic tank systems, and animal waste disposal. Since nitrates cause methaemoglobinaemia in infants, increased nitrate concentrations in groundwater have led to the shutdown of wells and rendered aquifers unusable as water sources. Communities with closed nitrate-contaminated wells now need them to meet the increased water demand. Surface waters have also experienced seasonal nitrate violations. As a result, there is renewed interest in the removal of nitrates from raw water. Technology development has occurred in this area, but there is still a need to further optimize the current treatment techniques and to develop the emerging processes for nitrate remediation.

State-of-the-art of treatment methods for the removal of excessive quantities of nitrates from drinking water is discussed by Kapoor and Viraraghavan [1], and various treatment options are compared in terms of their effectiveness, ease of operation, and cost. Physicochemical methods allow effective removal of nitrate ions from contaminated groundwater by concentrating them in a secondary waste stream. Among these methods, the capital and operating costs are the lowest for the ion exchange process; nevertheless, it is very difficult and costly to dispose off large quantities of spent regenerant brine in noncoastal locations where natural evaporation is impossible. The most promising techniques for nitrate removal, without any occurrence of wastewater, are biological digestion and catalytic denitrification by using noble metal catalysts [2,3]. The main reasons for the slow transfer of biological denitrification to drinking water purification

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Nomenclature

c_{NaCl}	sodium chloride concentration (g/l)
$c_{NO_3^-}$	nitrate concentration (mg/l)
d_p	average catalyst particle diameter (mm)
L	total length of packed bed in ion exchange column (cm)
$m_{cat.}$	mass of catalyst in bed (g)
m_{resin}	mass of IMAC HP-555 resin in bed (g)
pH	pH value of aqueous solution of the regenerant (–)
$p(H_2)$	hydrogen partial pressure (bar)
$P_{tot.}$	total operating pressure (bar)
T	reaction temperature (K)
$V_{saturator}$	volume of aqueous solution in saturator (ml)
z	axial coordinate in ion exchange column (cm)

Greek symbol

$\Phi_{vol.}$	volumetric flow rate (ml/min)

Subscripts

feed	feed solution
L	liquid-phase

are concerns over the possible bacterial contamination of treated water, the presence of residual organics in treated water, and the possible increase in chlorine demand of purified water. Furthermore, the presence of old sludge could lead to the formation of nitrites.

The reduction of aqueous nitrate solutions by using hydrogen over a solid Pd–Cu bimetallic catalyst offers an alternative process to biological treatment as a means of purifying drinking water streams. The reaction is carried out in a two- or three-phase reactor operating under mild reaction conditions (e.g., $T = 278$–298 K, $p(H_2)$ up to 7 bar), and obeys a consecutive reaction scheme in which nitrite appears as an intermediate, while nitrogen and ammonia are the final products. To maintain electroneutrality of the aqueous-phase, the consumed nitrates are replaced by hydroxide ions. Supported Pd–Cu and Pd–Sn bimetallic catalysts exhibit the highest activity for nitrate reduction and chemical resistance, but still inadequate selectivity towards nitrogen production. Permanent hardness of drinking water exhibits no inhibitive impact either on the extent of nitrate removal or on reaction selectivity [4]. On the other hand, the nitrate disappearance rate as well as the nitrogen production yield decrease appreciably in the presence of hydrogencarbonates in tap water.

Recently, catalytic nitrate reduction was investigated in continuous-flow reactors [5]. Experiments carried out in a bubble-column fixed-bed reactor in the presence of distilled water as a reaction medium demonstrated that nitrates could be efficiently removed from the liquid-phase, and that the maximum contaminant level for ammonium ions in drinking water (0.5 mg/l) was not exceeded. The measured nitrate conversions were considerably influenced by the variation of volumetric flow rate of either the gas- or liquid-phase. The order of magnitude analysis of apparent rate constant and mass transfer coefficients confirmed that the observed reaction rate was governed by the mass transfer of hydrogen from the gas-phase into the bulk liquid-phase. Due to the maldistribution of the liquid-phase and consequently shorter mean residence times, lower nitrate conversions were measured in a trickle-bed reactor [5]. At the given reaction conditions, catalyst particles were directly exposed to the gas-phase in this reactor system, which drastically enhanced ammonia production. However, when drinking water was used as a reaction medium instead of distilled water, the nitrate disappearance rate as well as reaction selectivity decreased appreciably, which was attributed to the presence of dissolved ionic species in the feed solution. Additionally, nitrite was detected in the reactor effluent at levels higher than the maximum admissible concentration (0.02 mg/l). These observations indicate that the use of up-to-date bimetallic catalysts for direct treatment of contaminated drinking water with a high level of temporary hardness does not allow selective nitrate removal [5].

To overcome the operational problems associated with the regeneration of exhausted ion exchange resins and direct purification of drinking water by means of catalytic hydrogenation, an integrated process was invented [6], which efficiently combines a conventional single-bed ion exchange unit with a catalytic denitrification reactor in such a way that drawbacks of each separate technique are effectively eliminated, i.e. (i) the production of secondary waste stream containing high concentrations of nitrate, sulfate and chloride

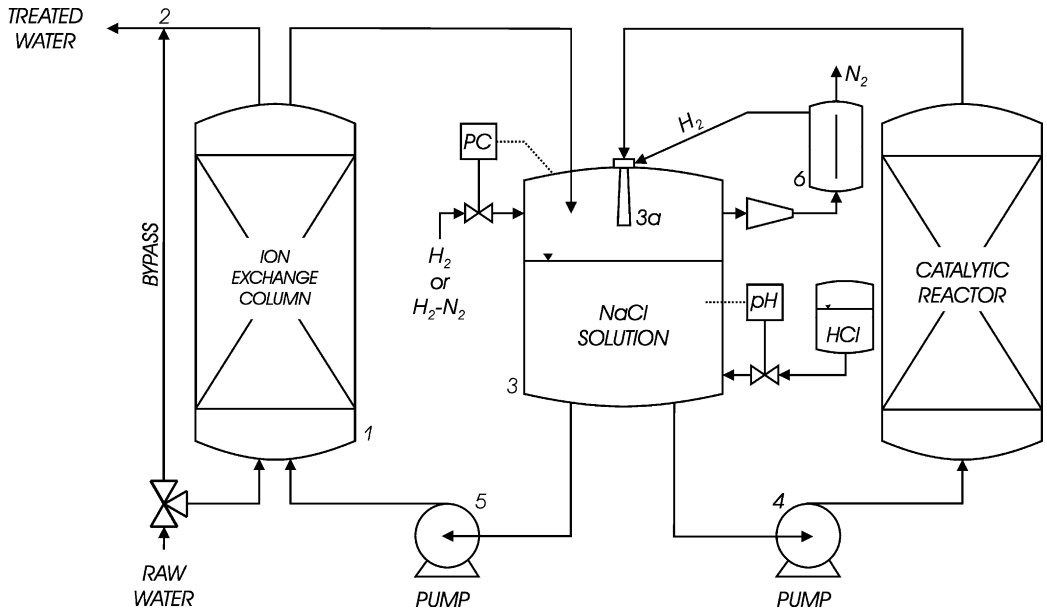

Fig. 1. Schematic layout of the combined ion exchange/catalytic denitrification process for nitrate removal: (1) column with the packed bed of ion exchange resin; (2) mixing point of the treated and untreated water; (3) saturator; (3a) mixing nozzle; (4, 5) pump; (6) separator.

ions; (ii) the contamination of purified water with the produced ammonium ions, which are formed due to the unsatisfactory selectivity of Pd–Cu bimetallic catalysts in the presence of hydrogencarbonate ions. A schematic layout of the combined process is illustrated in Fig. 1.

The objective of the present work was to examine the catalytic hydrogenation of aqueous nitrate solutions in the combined process with respect to the total remediation and the reaction products formed during the reaction course in the presence of a Pd–Cu/γ-Al_2O_3 bimetallic catalyst. An additional goal was to monitor the recovery of ion exchange capacity for nitrate loading in subsequent exhaustion–regeneration cycles. The stability of a catalyst composed of supported Pd and Cu metallic-phases was also studied by means of bulk chemical analyses and catalytic tests carried out in a batch-recycle reactor.

2. Experimental

The ion exchange step made use of a packed-bed of anion resin in the chloride form. In this work, a macroporous strongly basic anion exchange resin IMAC HP-555 (Rohm and Haas), which is nitrate selective, was used to remove nitrate ions from groundwater. Total exchange capacity of the employed resin determined by means of both breakthrough curves (not shown here) and potentiometric titration with a $AgNO_3$ solution was found to be equal to 0.00286 mol/g (i.e., 0.92 eq/l). In a typical run, removal of nitrates by ion exchange was conducted in the upflow mode at $T = 298\,\mathrm{K}$, $P_{\mathrm{tot.}} = 1\,\mathrm{bar}$ and $\Phi_{\mathrm{vol.,L}} = 8.0\,\mathrm{ml/min}$. Fig. 1 shows that the nitrate-free effluent can be blended with a predetermined fraction of bypass raw water to produce a water stream of acceptable nitrate concentration; however, no bypass was used in this study.

When the resin was saturated with nitrate ions, column exhaustion was terminated. Meanwhile, H_2 was introduced into the saturator (3), which operated at atmospheric pressure and was filled with 700 ml of aqueous solution of NaCl with the initial concentration of 5.0 g/l. A centrifugal pump (4) recirculated the solution of chloride ions through the saturator and upflow catalytic reactor at a flow rate of 5.3 l/min. The saturator was equipped with a heating–cooling coil ($T = 298\,\mathrm{K}$) and a mixing nozzle (3a), which

provided good contacting between the gas-phase and the liquid-phase. When the latter was saturated with H_2, a peristaltic pump (5) started to recirculate the regenerant through the bed of the ion exchange resin and the saturator at a flow rate of 10.0 ml/min. The chloride ions from the regenerant substituted the nitrate ions on the ion exchange resin. Due to the continuous recirculation of the aqueous solution of chloride ions through the two-phase catalytic reactor, packed with an egg-shell type Pd(1.0 wt.%)–Cu(0.3 wt.%) bimetallic catalyst, nitrate ions from the regenerant solution reacted with H_2 chemisorbed on the catalyst surface and converted into nitrogen (and ammonia).

The neutralization agent, i.e., the aqueous solution of HCl (0.25 M), was applied by means of an autotitrator (Metrohm, model 751 GPD Titrino) in order to keep the pH value of the regenerant constant at 5.5. The use of HCl had the advantage that no further make-up of the regenerant with NaCl was required, since the stoichiometric amount of chloride ions required for a subsequent regeneration cycle was simultaneously introduced to the process via the neutralization of hydroxide ions produced during the liquid-phase nitrate reduction. The regenerant continued to be recirculated through the ion exchange column and the denitrification reactor, until both nitrate and nitrite ions were completely consumed. The regenerant free of these species was used in subsequent regeneration cycles.

In the catalytic reactor, the catalyst layer was formed from γ-Al_2O_3 spherical particles ($d_p = 1.7$ mm) on which metallic Pd and Cu-phases were deposited in such a sequence that the catalyst surface was enriched with Pd clusters. A detailed preparation of the catalyst used in this process is described elsewhere [7].

3. Results and discussion

It was found out in this study that regeneration of nitrate loaded IMAC HP-555 resin is possible with a diluted solution containing 2.5–10.0 g/l NaCl (see Fig. 2). Compared to the conventional regeneration procedure with 50–100 g/l NaCl, a flow rate of 2–4 BV/h and a period of approximately 30–50 min, more time and a higher flow rate are needed. However, with 5 g/l NaCl and a flow rate of 3.0 ml/min (i.e., 25 BV/h) complete regeneration of the resin is possible in 240 min; one should note that prolonged time of regeneration does not represent any drawback for an integrated process.

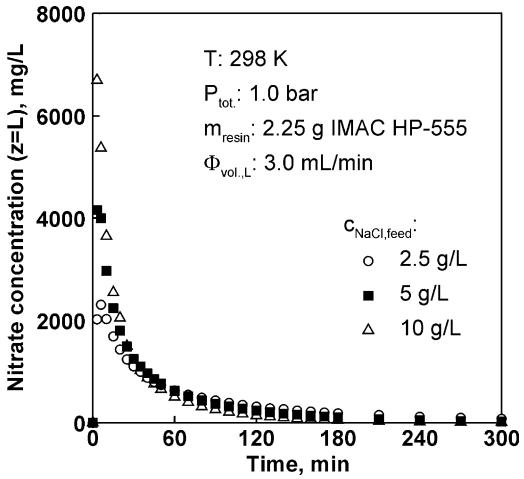

Fig. 2. Nitrate concentration as a function of time in brine discharge during regeneration with aqueous NaCl solutions of different concentrations.

Although small amounts of NaCl were consumed in the performed regeneration runs, the regeneration efficiency, defined as the ratio of equivalents of nitrate removed from the resin during regeneration to the equivalents of regenerant used, is rather low and found in the range of 0.07–0.15 eq nitrate/eq chloride. Low regeneration efficiency is not a serious problem in a closed regeneration system, because the excess of NaCl remains in the system and is not lost in the disposed brine. In other words, the value of regeneration efficiency can easily be increased by reusing the regeneration solution. This is particularly true when it has been made free of nitrates, which can be achieved, e.g., by means of the combined process shown in Fig. 1. Of course, all the advantages of the process described above come at the price of increased capital cost and process complexity.

The breakthrough curves (or effluent histories) for nitrate from the IMAC HP-555 resin bed with regenerant reuse are shown in Fig. 3. The breakthroughs are nearly identical and do not suggest any trend to shorter or longer nitrate removal runs. It can thus be concluded that reusing the denitrified regenerant containing 5.0 g/l NaCl did not negatively influence the column performance. A major concern when a

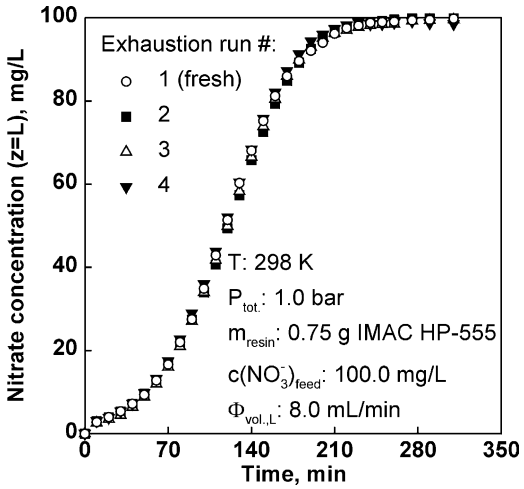

Fig. 3. Nitrate breakthrough curves for different exhaustion runs during regenerant reuse. Groundwater composition during breakthrough experiments: 100.0 mg/l nitrate (spiked with KNO_3), 44.4 mg/l sulfate, 6.0 mg/l chloride and 276.6 mg/l hydrogencarbonate.

spent regenerant is reused is the accumulation of ions stripped from the resin during regeneration. These include the nitrate, the sulfate and the hydrogencarbonate. The nitrate (and nitrite) should be eliminated by denitrification, hydrogencarbonate by neutralization with HCl in the saturator, but the sulfate can accumulate during reuse when there is a net removal of these ions during exhaustion. It was found in this study that only a small amount of sulfate ions is accumulated in the regenerant solution (about 8 mg/l sulfate per regeneration cycle), which suggests that more than one-half of the sulfate has been dumped from the resin during exhaustion. The results depicted in Fig. 3 demonstrate that in each run the nitrate capacity in the exhaustion mode was found to be unaffected by the amount of the sulfate in the regenerant beforehand. After the fourth exhaustion–regeneration cycle of resin with regenerant recycling, it was found out by means of argentometric titration that the IMAC HP-555 resin maintains 99% of its initial capacity for nitrate loading.

Experimental results of regeneration of ion exchange resin saturated with a nitrate and the simultaneous removal of the nitrate ion from the regeneration solution using catalytic hydrogenation in a two-phase fixed-bed reactor are presented in Fig. 4. The temporal course of the destructive nitrate reduction obtained in the presence of Pd(1.0 wt.%)–Cu(0.3 wt.%)/γ-Al_2O_3 was followed by measuring the instantaneous concentrations of nitrate, nitrite and ammonium ions in the regenerant solution by means of flow-injection analysis (Perkin-Elmer). At the given reaction conditions, the contacting time of the liquid-phase in the single-flow reactor was equal to 30 ms, and the latter operated in the kinetic regime. Although the volumetric flow rate of regenerant solution through the ion exchange column was rather low (10.0 ml/min), nitrate disappearance rate was not affected by the rate of nitrate desorption from the ion exchange resin. It is evident from Fig. 4a that by employing this process, total removal of stripped nitrate ions from the regenerant is attained, which means that the latter can be used in subsequent regeneration cycles.

One can see that the activity of the catalyst for nitrate removal decreases with the number of exhaustion–regeneration cycles. This cannot be attributed to the dissolution of Pd and Cu metallic-phases, since no metal ions were detected in the regenerant solution by means of ICP-AES examination. The chemical analysis of fresh and used catalyst samples confirmed that no dissolution of active components took place during the above-described experiments. Furthermore, no catalyst deactivation was observed in a series of nitrate reduction runs carried out in a batch-recycle reactor, when distilled water was used as the reaction medium [8]. Thus, the observed decline of catalyst activity in the combined process is due to the following reasons: (i) concentration of chloride ions in the regenerant solution increases with the number of regeneration cycles (see below); (ii) isoelectric point of the catalyst decreases during the liquid-phase nitrate reduction, which was confirmed by the "mass-titration" analysis. The latter effect is attributed to the consumption of weakly bound protons on the catalyst surface with the hydroxide ions formed [9]. It should be stressed that when the used catalyst was soaked in distilled water for about 3 h, its surface became reprotonated and the initial activity for nitrate reduction was replenished.

Although the catalytic nitrate reduction was carried out at pH = 5.5, considerable quantities of nitrite ions were accumulated in aqueous-phase during the regeneration (Fig. 4b). This is ascribed to the low contacting time of liquid-phase in the reactor and much higher affinity of nitrate ion towards the Pd–Cu active sites

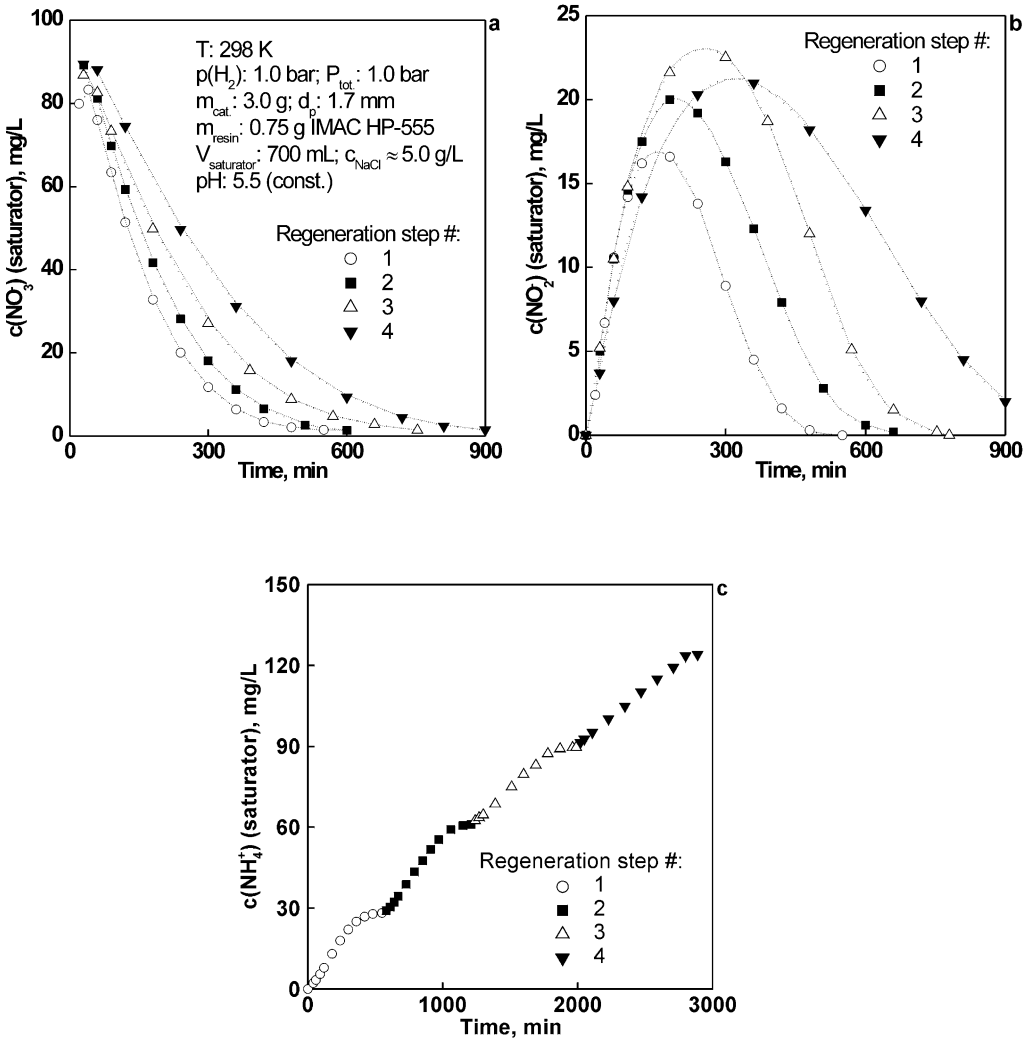

Fig. 4. Temporal course of nitrate (a), nitrite (b) and ammonium (c) ions for consecutive regenerations of IMAC HP-555 resin by means of catalytic denitrification.

on the catalyst surface in comparison to nitrite. The concentration of nitrite ion in the regenerant, after the regeneration process of saturated ion exchange resin and simultaneous destructive hydrogenation had been finished, was lower than that prescribed by the regulation of the law (i.e., 0.02 mg/l). However, it is obvious from Fig. 4b that longer reaction time is needed to achieve this goal in subsequent regeneration cycles. This is again attributed to the fact that in each reduction run the catalyst surface becomes more negatively charged, which consequently increases the repulsion between intermediate nitrites and the active sites on the catalyst surface. The mechanism of catalyst deactivation observed in the process of liquid-phase nitrite reduction is described in detail by means of the theory of electrical double layer [9].

In Fig. 4c the concentration of ammonium ions produced is shown as a function of time for various regeneration cycles. Based on these data, about 70 mol% of nitrate stripped from the ion exchange

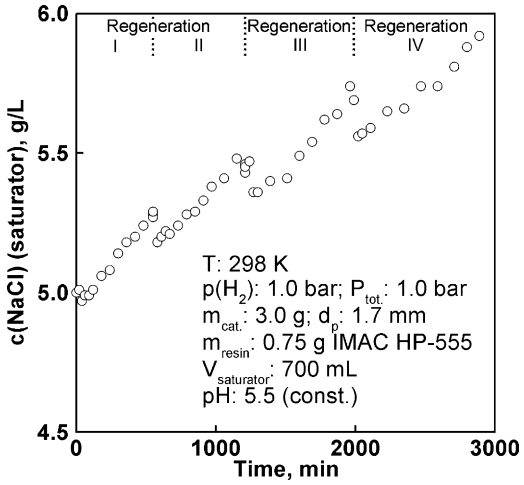

Fig. 5. Concentration of chloride ions (expressed as NaCl) as a function of time in the reused regenerant solution.

resin is transformed to ammonia. However, this value can easily be minimized to, e.g., 15 mol% by carrying out the catalytic nitrate reduction at lower hydrogen partial pressures. As the denitrification process does not take place in direct contact with groundwater, there is no risk that ammonia production would affect water quality. The data shown in Fig. 4c confirm that no ammonia was transferred into the gas-phase at the given reaction conditions.

Fig. 5 shows the concentration–time profile of chloride ions in the regenerant for different regeneration cycles. It can be seen that the concentration of chlorides measured in the saturator increases with time, which arises from the: (i) favorized formation of ammonium ions, which accordingly to the reaction stoichiometry increases the consumption of HCl by a factor of 2; (ii) neutralization of stripped hydrogencarbonate ions from the ion exchange resin by means of HCl; (iii) reference electrolyte (3 M KCl) outflow from the pH electrode. Additional experiments of liquid-phase nitrate reduction carried out in a batch-recycle reactor in the presence of the same catalyst as used in this study show that the nitrate (and nitrite) disappearance rate decreases by increasing the concentration of sodium chloride in the aqueous solution. Also, the inhibitive impact of the produced hydroxide ions on the catalyst activity is more pronounced in the presence of chlorides. Due to the synergistic effect of these species on the reaction behavior, no kinetic analysis of data shown in Fig. 4a is possible. However, the results depicted in Fig. 5 demonstrate that no make-up of the regenerant solution is required between exhaustion–regeneration cycles. In this work, no organic fouling of either the ion exchange resin or the catalyst, which can be caused by humic and fulvic acids accumulated in a closed regeneration circuit, was observed. This implies that after the exhaustion–regeneration cycle has been completed, no disinfection of the unit with a solution of, e.g., peracetic acid is needed. In this respect, the denitrification process shown in Fig. 1 is advantageous over the combined ion exchange/biological denitrification techniques [10,11].

4. Conclusions

The described catalytic-physicochemical process is a very attractive technique for nitrate removal from groundwater. Compared to ion exchange, brine production is very low and regeneration salt requirement is minimal. As the denitrification process does not take place in direct contact with groundwater, there is no risk that nitrite and ammonia production would affect water quality; thus, the production of reliable drinking water is possible without the need of extensive post-treatment. Also groundwater with a high sulfate content can be treated with this technique, when a nitrate selective resin, e.g., IMAC HP-555, is used. Further work is needed in order to diminish the effect of chlorides and the produced hydroxide ions on the activity of Pd–Cu/γ-Al_2O_3 bimetallic catalysts.

It is believed that scaling up of the combined process for the removal of nitrates from contaminated drinking water would be straightforward, since the process equipment for large-scale operation either of ion exchange treatment or liquid-phase hydrogenation reactions (e.g., Buss loop reactor technology) is already available. To make the combined process even more economically attractive, it would be advantageous to incorporate in situ generation of hydrogen into the process scheme.

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