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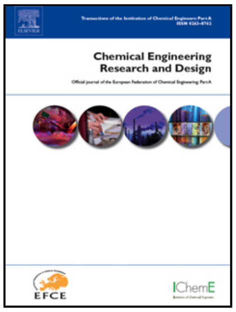

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Authors: Gustavo Mendow, César I. Grosso, Agustina Sánchez, Carlos A. Querini

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Hybrid Process for the Purification of Water Contaminated with Nitrites: Ion Exchange plus Catalytic Reduction.

Gustavo Mendow, César I. Grosso, Agustina Sánchez, Carlos A. Querini*.

Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE)-(FIQ-UNL, CONICET), Santiago del Estero 2654, (3000) Santa Fe (Argentina)

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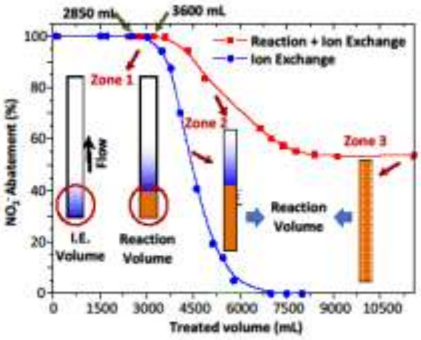
*** Corresponding Author:**
Carlos Querini
Santiago del Estero 2654
(3000) Santa Fe
e-mail: querini@fiq.unl.edu.ar
Phone: +54-342-4533858
Fax: +54-342-4536861

Graphical abstract

Graphical Abstract



Highlights

- Catalytic resins Pd/WA30 can exchange nitrites and/or reduce them to nitrogen.
- The performance of the Pd(2%)/WA30 catalyst in a hybrid process (reaction and ion exchange) proved to be very good.
- The ammonium concentration generated by nitrites over-reduction never exceeded 0.2 mg/L.
- A new methodology for regenerating the resin makes it possible to eliminate more than 99 % of the nitrites.
- A pilot plant scale reactor was used to verify this behavior.

Abstract

Water polluted with nitrites represents a big risk to human health. In this work, palladium supported on macroporous anionic exchange resin was used in the catalytic nitrite reduction. This process is compared with the traditional ion exchange procedure using the same catalytic resin. Both, the resin and the catalyst behaviour were evaluated in a fix-bed reactor, feeding water containing nitrites and other competitor ions, such as sulphate, bicarbonate, and chlorides, and adjusting the pH with carbon dioxide. When feeding water containing only nitrites, it was observed that the catalytic reduction makes it possible to treat 55% more water than when using the ion exchange process, at the same level of nitrites elimination. Moreover, in steady state it was possible to obtain a nitrite conversion to nitrogen of 54% with high selectivity, obtaining an ammonium concentration lower than 0.2 mg/L. In the case of having other ions present in the system, both the conversion and the selectivity decreased. A regeneration strategy is also developed, using a very low hydrogen flow rate at atmospheric pressure and room temperature. This treatment leads to the reduction of more than 99% of the nitrites present in the contaminated water. The catalyst was used in several consecutive cycles maintaining a very good performance, even in the presence of competitor ions. The process was scaled up to a pilot level obtaining identical results.

Keywords: Nitrites, ion exchange resin, palladium, catalytic reduction, regeneration.

1. Introduction

In recent years, a significant amount of surface water sources, mainly from groundwater, with high concentrations of nitrates have been detected, due to excessive use of fertilizers in intensive agriculture, leaking of septic tanks and waste disposal in breeding farms [1]. Chronic and excessive intake of nitrate through water can cause serious health problems in adults, such as ovarian or prostate cancer, as well as growth problems or diseases such as methemoglobinemia (blue baby syndrome) in infants [2-5].

Numerous processes for the removal of nitrates and nitrites from water have been developed. Among them are the ion exchange, biological denitrification, reverse osmosis, electrodialysis and catalytic reduction. The World Health Organization (WHO) recommends the biological denitrification and ion exchange as the most appropriate methods developed to date for the removal of nitrates from drinking water [6]. The biological denitrification is a very specific and selective process. However, it has as disadvantage the risk of contaminating the water with bacteria and metabolic substances. Therefore, it is necessary the filtration and disinfection with germicides of the treated water, which increases the process costs [7]. Meanwhile, technologies using ion exchange are more suitable for water decontamination, due to its simplicity, efficiency, selectivity, reusability, and relatively low cost [8]. The main disadvantage of this technology is the disposal of the effluent rich in nitrates or nitrites, which means that the problem is only transferred but not completely solved.

Catalytic reduction of nitrates or nitrites using heterogeneous catalysts is an alternative to remove these species from polluted streams. In these technologies, nitrates or nitrites are reduced to nitrogen using a reducing agent, which is usually hydrogen [9-12]. However, this technology presents a major constraint, which is the catalyst selectivity. Over-reduction of nitrate or nitrite leads to the formation of ammonia, being the maximum concentration allowed by the WHO 0.5 mg/L. For this reason, it is necessary to develop catalysts displaying not only good activity but also a very good selectivity to N_2.

Recently, polymers have being used as supports, with the purpose of stabilizing the bimetallic particles. Polymers such as poly (N-vinylpyrrolidone) (PVP) or poly (vinylalcohol) (PVA) were used to increase the stability and controlling the size and composition of the bimetallic particles [13-14]. A third type of polymers, such as functionalized resins or ion exchange resins have been successfully used in the synthesis of Pd-Cu and Pd-In bimetallic catalysts for their use in the catalytic reduction of nitrates [9,15-17]. These resins are constituted by a copolymer of styrene-divinylbenzene containing exchange functional groups such as $-N(CH_3)_3^+ Cl^-$ or $-SO_3^- H^+$, known as anionic or cationic resins respectively. The use of acid cationic resins as support for bimetallic catalysts was studied by different authors. Such resins are very attractive because they provide protons that can neutralize the OH^- generated during the nitrate reduction, maintaining the pH of the aqueous solution at acceptable values, thus increasing the N_2 selectivity [15,18-19].

No reports have been found about nitrite removal using monometallic catalysts supported on anionic resins. On the other hand, the effect of competing ions such as sulfates, chlorides and bicarbonates on the exchange capacity and catalytic activity of the resins, were addressed only in few studies [20-23], in spite of being a key issue in order to properly determine the real catalytic behavior [24].

Pintar et al. [11] proposed a process in which the nitrates were eliminated from the water using an ion-exchange resin. Once the resin was saturated, it was regenerated by eluting the nitrates using a sodium chloride solution (5%w/w). This stream containing high concentrations of nitrates and chlorides was them fed to a two-reactor system. In the first one, the nitrates were reduced to nitrites in a basic media (pH=12.5) using a $Pd-Cu/Al_2O_3$ catalyst. Then, in a second reactor, the nitrites were selectively converted to nitrogen in an acid media. In the present work, a catalytic process that can be applied to the second reactor of this purification strategy is studied. According to Pintar et al. [11] the presence of chlorides decreased the catalyst performance and induced ammonium formation. Also, they found that in the second reactor, the selectivity to ammonium was too high, due to pH gradient inside the catalyst pores.

Catalysts containing metals supported on ion exchange resins have the advantage of being bifunctional. On one hand, the palladium deposited on the resin is capable of reducing nitrites in the presence of H_2, and on the other hand, the support may adsorb nitrites by an ion exchange mechanism (IE). Thus, the decrease in the nitrites concentration observed at the reactor outlet is due to the sum of two contributions, the reaction and the ion exchange.

This work presents studies of the catalytic process performance for nitrite reduction of monometallic Pd catalyst, supported on a macroporous anionic resin using the process named as RIE: Reaction + Ion Exchange. The efficiency of this process is compared with that of the conventional ion exchange (IE) using the same catalytic resin. In addition, the resin regeneration is studied and the process was scaled up to pilot plant level. The overall performance of the process developed showed an excellent performance. Initial adsorption and reaction rates were also determined in a batch reactor, in order to have quantitative information regarding the contribution of each mechanism in the nitrites removal. In addition, the effects of competing anions on nitrites adsorption and reduction were also addressed.

2. Experimental

2.1. Catalyst preparation

The WA30 (Mitsubishi) resin used as catalytic support is a styrene divinylbenzene polymer matrix with tertiary amine functional groups. It is a weak macroporous anionic exchange resin, with an exchange capacity of 1.6 equivalent/L. Before metal impregnation, the resin was washed with HCl 5 wt.% for 1 h, filtered and washed with distilled water. The palladium was fixed on the resin by addition of a solution containing $[PdCl_4]^{2-}$, obtained by dissolution of $PdCl_2$ in an acidic media (HCl 0.01 wt.%). The palladium complex was exchanged with the chloride ions of the resin at room temperature, while stirring the resin in distilled water and N_2 bubbling. The system was kept under these conditions during 3 h after the addition of the palladium salt. The exchange was complete, not being possible to detect Pd in the final solution by atomic absorption spectroscopy. The amount of solution and concentration of palladium were selected in order to obtain the desired Pd content in the final catalyst, which was typically 2 w/v %, based on the wet resin. Afterwards, the catalysts were filtered and reduced in a basic hydrazine solution (35 v/v% of hydrazine in a solution of NaOH 20 wt.%). The reduction led to a neat color change of the resin to grey or black depending upon the metal loading. The palladium catalysts were then filtered and washed with distilled water. Afterwards, the catalyst was treated with a solution containing chlorides (as sodium chloride) to exchange the OH^- ions left in the resin during palladium reduction.

2.2. Reaction Studies

2.2.1.1. Fixed bed reactor. Laboratory scale.

The catalysts were evaluated in a continuous fixed bed reactor. The water was fed by a peristaltic pump (Cole Parmer), entering the reactor from the bottom. The flow rate was measured in a rotameter located upstream the reactor. The glass reactor had a diameter of 1 cm and a length of 30 cm. The catalyst was supported on glass wool. In all the experiments, 7 mL of solid catalyst were used. Before entering the reactor, both the water and the H_2 were flowed through a 1/16" diameter tube, 15 cm length, to achieve an intimate contact in order to obtain the water saturated with hydrogen. The water and the H_2 left the reactor through the top and entered a gas-liquid separator. The gas was vented to the atmosphere after dilution with nitrogen, while the water was collected for subsequent analysis. The feed solution was prepared using sodium nitrite salt. Aliquots of 10 mL were taken from the solution coming out of the reactor in order to determine the nitrite and ammonia content. The initial concentration of nitrite was 76.8 mg NO_2^-/L. The competitor ions concentrations were 125 mg/L, 100 mg/L and 135 mg, for chlorides, sulfates and bicarbonates, respectively. In all cases, sodium salts were used. The feed solution was saturated with carbon dioxide in order to obtain a buffered system with acid pH. The amount of bicarbonates formed upon CO_2 dissolution was calculated using the equilibrium constants reported in the literature. In the presence of the competing ions it was very small (0.8 ppm), and did not modify the amount of bicarbonates added as competing ion. The carbonate concentration in this case was also negligible.

Since the reaction occurs in parallel with the ion exchange, this process is named using the acronym RIE (Reaction + Ion Exchange). In the case in which no hydrogen was fed to the reactor, only the ion exchange took place.

The regeneration process was carried out after the RIE process or after nitrites adsorption by ion exchange. The water flow was stopped, and hydrogen was flowed at atmospheric pressure and room temperature using a flow rate between 0.5 and 1.5 mL/min. At the end of this step, the hydrogen flow was stopped and a NaCl solution (5 g/L) was fed with the objective of exchanging the non-converted nitrites, sulphates, bicarbonates and ammonium (formed by nitrites over-reduction), thus leaving the resin in proper conditions for a next RIE or Ion Exchange cycle. The stability was studied repeating the cycle five times.

2.2.1.2. Fixed bed reactor. Pilot plant.

The reactor was made of acrylic with an internal diameter of 54 mm and a length of 110 mm. At the reactor outlet, a gas-liquid separador was included. The flow of water saturated with CO_2 was controlled using a peristaltic pump. The CO_2 was bubbled at

250 mL/min from the bottom of the vessel while water was pumped with a flow rate of 270 mL/min, obtaining a pH of 5.4. The amount of catalyst loaded in the reactor was 500 mL. Tap water was used in this study, adding nitrites (82 mg/L), sulphates (103 mg/L), chlorides (137 mg/L) and bicarbonates (170 mg/L). Hydrogen was fed from the bottom of the reactor, using a flow rate of 35 mL/min during the regeneration. In order to elute the ions from the resin, the solution of NaCl 5 g/L was pumped from the bottom of the reactor.

2.2.2. Batch reactor.

The catalytic test was carried out in a pyrex glass reactor equipped with a magnetic stirrer and three inlets for N_2, CO_2 or H_2 bubbling. All the reaction tests were carried out at atmospheric pressure and 25°C. Experiments were carried out with 0.1 g of Pd (2%)/WA30, added to 200 mL solution of known nitrites concentration. Before the reaction test, the aqueous medium was purged with N_2 to remove dissolved oxygen. The N_2 flow rate was 100 mL/min during 10 min. Afterwards, H_2 and CO_2 were bubbled during 10 min. at 200 mL/min and 100 mL/min respectively, in order to saturate the water. The reaction started when Pd(2%)/WA30 catalytic resin was added to the vessel. Samples were taken at pre-set time intervals and the nitrites and ammonium concentrations were measured. The duration of a typical catalytic run was 2 h.

Initial rates measurements: Experiments to determine the initial reaction and adsorption rates were carried out using 0.1 g of Pd (2%)/WA30 and 100 mL of solution containing nitrites concentration of 21.7, 42.1, 82.5 and 117.6 mg/L. The solution was saturated with CO_2 and H_2, by bubbling at 100 mL/min during 10 min. Zero time was taken as the moment in which the catalyst was added to the reaction media. In order to determine initial reaction rates, short experiments were carried out. After 7 minutes of reaction the H_2 bubbling was stopped, and 5 g of NaCl were added in order to elute the nitrites adsorbed on the resin. Finally, the nitrites concentration in the liquid phase was measured. The mass of nitrites converted due to the chemical reaction were calculated as follows:

$(C_o - C_F).V = M_{NO2}$

Where C_o is the initial nitrites concentration (mg/L)

C_F is the nitrites concentration after the addition of NaCl (mg/L)

V is the volume of solution used in the experiment (L)

M_{NO2} is the mass of nitrites converted in the chemical reaction (mg)

2.3. Adsorption Isotherms.

The adsorption isotherms were determined in batch mode, using a 250 mL Erlenmeyer flask with magnetic stirring. Different amounts of the Pd (2%) catalyst, supported on macroporous anionic resin WA30, were used. The catalyst was added to 200 mL of solution with a known nitrites concentration. To maintain a constant pH during the experiment, CO_2 was bubbled continuously. Stirring was maintained for 2 hours, since preliminary experiments showed that in this time the system reached equilibrium. Nitrites concentrations were measured in the initial solution and at equilibrium.

2.4. Batch adsorption studies.

Using a procedure similar to that described in section 2.2.2, experiments were carried out with 0.1 g of Pd (2%)/WA30, added to 200 mL solution of known nitrites concentration, but without H_2 bubbling. Samples were taken at preset time intervals and the nitrites concentration was measured. To maintain a constant pH, the solution was conditioned with CO_2 bubbling. The effects of temperature, particle diameter, competing ions and initial concentration were studied.

2.5. Breakthrough curves

The determination of the breakthrough curves was carried out in a continuous fixed bed reactor, loaded with 7 mL of Pd(2%)/WA30 catalytic resin. The solution flow rate used in all experiments was 3 mL/min. The pH of the solution of known nitrites concentration was conditioned by bubbling CO_2. Samples were taken at preset time intervals and the nitrites concentration was measured. The results were plotted on a graph of C/Co vs. treated volume, where Co is the initial concentration of nitrite and C is the concentration at the reactor outlet. The initial concentration of nitrite in all the experiments was 100 mg/L. The competitor ions concentrations used for each of the experiments were 125 mg/L, 100 mg/L and 135 mg, for chlorides, sulfates and bicarbonates, respectively. The salts used to prepare each of these solutions were NaCl, Na_2SO_4 and $NaHCO_3$.

2.6. Analytical methods.

Nitrite and ammonium were analyzed using visible spectroscopy with a Cole Palmer Spectrophotometer, combined with colorimetric reagents. Ammonium was analyzed by the adapted Berthelot method. The concentrations of other anions (sulfate, bicarbonate and chloride) were measured using the Standard method of water analysis [25-27].

2.7. Catalyst characterization.

Total exchange capacity determination was performed by titration of the resins in the HO^- form with hydrochloric acid. The X-ray diffractograms were obtained with a Shimadzu XDD1instrument with a monochromator using CuK radiation at a scan rate of 4 °/min, in the range 10° - 100°. The sample morphology of the different catalysts was examined with a Jeol JSM-35C scanning electron microscope operated at accelerating voltages of 20–25 kV. Samples were glued to the sample holder with Ag paint and then coated with a thin layer of Au in order to improve the quality of the images. The metal distribution inside the catalyst was analyzed by X-ray spectra with the EDAX software. Semi quantitative results were obtained with the theoretical quantitative method, which does not require standards. X-ray spectra were obtained with an acceleration of 20 kV. Nitrogen adsorption was employed to determine BET surface areas, using a Quantachrome Autosorb 1 analyzer. The determinations were carried out by pre-treating the catalysts under vacuum at 150°C for 3 h. The metallic dispersions were determined by dynamic CO chemisorption. The sample was reduced with H_2 and then purged with N_2 in order to desorb any hydrogen remaining on the metal. After this treatment, pulses of 250 μl of 2.5% CO in Ar were sent to the catalyst at room temperature. The gas coming out of the cell was fed to a methanation reactor, in order to increase the system sensitivity. In this reactor, CO reacts with H_2 over a Ni catalyst producing CH_4, which is fed to a flame ionization detector (FID). For dispersion calculations a 1:1 stoichiometry for the CO chemisorption on the metal atoms was assumed.

3. Results and discussion

3.1. Influence of process variables on adsorption.

3.1.1. Effect of particle size.

Figure 1 shows the variation of nitrite concentration with time for different particle sizes (P_s) of the catalytic resin, obtained in experiments carried out as described in section 2.4. It can be seen that the rate of nitrites exchange increases with decreasing particle size. Therefore, the internal diffusive effects have a non-negligible effect on the adsorption rate. The commercial particle diameter of WA30 resin is in the 20 - 40 mesh (841 – 420 μm) range, which presented the lowest exchange rate. The use of particle sizes smaller than 841 – 420 μm on a fixed bed reactor would cause an excessive pressure drop. Moreover, the generation of very small particles will cause their dragging and hence, subsequent filtering stages will be required increasing the process costs. It can be seen that in all cases the same equilibrium concentration was achieved, regardless of the particle diameter. Initial exchange rates were determined for each case, resulting that for commercial particle sizes (841 – 420 μm) the initial adsorption rate was 435.8 mg $NO_2^-/g_{resin}.h$, while in the case of smaller particles (177 - 149 μm) this initial rate was three times higher, showing a value of 1308.9 mg $NO_2^-/g_{resin}.h$.

3.1.2. Effect of competing anions on adsorption.

Ions normally present in natural waters may compete with nitrites for the exchange sites, leading to a decrease in the process efficiency. Therefore, before selecting a resin for a process for nitrite removal, its adsorption selectivity should be evaluated. The concentration of competing ions commonly found in groundwater (sulfates, bicarbonates and chlorides) is very variable. To evaluate the performance of the catalytic resin Pd(2%)/WA30 in the presence of different anions, a concentration equal to half of the maximum value specified by the quality standards for drinking water was used.

On the other hand, to properly compare the adsorption selectivity among ions, it is necessary to do the experiments using the same equivalent concentrations. Therefore, ion exchange experiments were also performed using the same normality of nitrite and competing ions. The results are shown in Figure 2. The amount of nitrites removed by adsorption was 65% when no competing ions were present, and this value decreased to 38% in the presence of sulfates, showing the important effect that other ions have on nitrites adsorption. These effects will be used to explain the results obtained in the fixed bed reactor activity experiments (see section 3.5.2). It can also be clearly seen that there is no significant variation in the removal of nitrites between the experiments carried out using two different levels of concentrations of competing ions. For this reason, breakthrough and adsorption isotherms studies were performed using the same competing ion concentrations as those used in the catalytic reduction experiments (sections 3.2 and 3.3).

Nitrite concentration as a function of time, in the presence of different competing ions (concentration equal to half of the maximum value specified by the quality standards for drinking water) was evaluated, as described in Section 2.4. Figure 3 shows these results obtained with nitrites and using all the competing ions simultaneously. The curves corresponding to the individual competing ions bicarbonate and chloride (not shown) were almost superimposed on each other. Furthermore, these two curves of nitrites removal were very close to that obtained when no competing ions were present. When the competitors were chloride and bicarbonate ions, initial exchange rates were 339.5 and 335.2 mg $NO_2^-/g_{resin}.h$, respectively; whereas when no competing ions were present, the observed rate was 358.7 mg $NO_2^-/g_{resin}.h$. In addition, it was observed that the equilibrium concentration/initial concentration ratio (at 70 minutes exchange time), was 0.46.

In the case that all the ions were present, the initial exchange rate decreased to 229.1 mg $NO_2^-/g_{resin}.h$, while the equilibrium/initial concentration ratio increases to 0.71. Thus, it can be concluded that both the ion exchange rate and the nitrites equilibrium concentration are impaired by the simultaneous presence of the competing ions sulfates, bicarbonates and chlorides.

3.2. Breakthrough curves

The effect of different competing ions in nitrite adsorption was also studied using a continuous fixed-bed flow reactor, measuring the breakthrough curves, as indicated in section 2.5. These curves were obtained by flowing the solution to be treated through the catalytic resin Pd(2%)/WA30. The operating conditions used were those found to be optimal for the purposes of removing nitrites. When the catalytic resin approaches the saturation state with the ions entering the solution, there is an increase in the concentration of these ions in the solution leaving the column. This is called "breakthrough". When the concentration of these ions in the leaving solution equals the inlet concentration, the resin has reached its exchange capacity at the operating conditions employed. As it was shown in Section 3.1.2., the presence of competing ions significantly decreases the amount of nitrites ions extracted from water. For this reason, the nitrites breakthrough curves evaluation was conducted in the presence of each competing ion individually, without competing ions and with all of the ions simultaneously. The concentrations used were presented in Section 2.5. These results are shown in Figure 4. In the case that no competing ions were present, the volume of treated water at the moment in which the nitrite ions were first observed in the outlet was 3000 mL, and corresponds to 430 volumes of water per volume of resin. However, when all of the competing ions were present simultaneously (Cl^-, $SO_4^=$ and HCO_3^-), the amount of treated water decreaseed to 800 mL, i.e. 115 times the resin volume employed. This significant reduction in the water treatment capacity can be analyzed in terms of the effects that each individual ion has on nitrite adsorption, as shown in Figure 3. The breakthrough curve obtained in the presence of sulfates is very similar to that obtained in the presence of all ions. In this particular case, approximately 1000 mL were treated (equivalent to 143 resin volumes), until observing the presence of nitrites at the column outlet. In this way, it can be concluded that sulfate was the ion that more strongly competed with nitrites for the resin exchange sites.

Figure 4 shows that the breakthrough curves obtained for nitrites in the presence of chloride and bicarbonate ions are very similar, but the effect is not as strong as in the case of the sulfate ions. However, it is observed that when the solution presents chlorides or bicarbonates, the treated volume was approximately 1750 mL (equivalent to 250 resin volumes), which was slightly more than half the treated volume when no competing ions were present. It can be concluded that both chlorides and bicarbonates strongly compete with nitrite ions for the exchange sites. Nevertheless, sulfate ions have the highest effect on decreasing the nitrites adsorption.

3.3. Adsorption isotherms

As discussed in the previous sections, there are significant differences among different competing ions in the effect of nitrite adsorption. In order to quantify these effects, the adsorption isotherms were determined [35].

Figure 5 shows experimental nitrites adsorption isotherms at 23 ºC, both with and without acidification of the aqueous phase with CO_2, in the presence of different competing ions, using Pd(2%)/WA30 catalytic resin. These conditions are the same as those used for catalytic reduction (section 3.4). In this figure, q_e is the adsorption capacity at equilibrium; C_e is the equilibrium concentration in the liquid solution. These isotherms are in agreement with results presented above, showing that the sulfates are the ions that more strongly affects the nitrites adsorption. It is very important to highlight in these results, the impact that the pH adjustment has on the nitrite adsorption capacity of the resin. Note that when no CO_2 was bubbled, the nitrite adsorption was even lower than when all the competing ions were present in the system and the pH adjusted by CO_2 bubbling. These results show the high impact that the pH has in the ion exchange capacity of the WA30 resin, and consequently in the process design for nitrites removal.

The Langmuir isotherm is a well-known and widely used model in the literature. According to this model, a single adsorbate is retained in only one molecular layer. The Langmuir isotherm model can be expressed as Eq. 1:

$$q_e = qo*b*Ce / (1+b*C_e) \qquad \text{Eq. 1}$$

where qe is the adsorption capacity at equilibrium, Ce is the equilibrium concentration in the liquid solution, and qo and b are the Langmuir constants related to the maximum adsorption capacity and equilibrium constant. Maximum adsorption capacity qo represents the monolayer coverage of sorbent with adsorbate and b represents the enthalpy of adsorption.

While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on sorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and this model can be expressed as Eq. 2:

$$q_e = k_f *(Ce)^{1/n} \qquad \text{Eq. 2}$$

where k_f and 1/n are the Freundlich constant and adsorption intensity, respectively [36].

The parameter k_f related to the adsorption density increased with a decrease of adsorbent amount. The parameter n is always higher than 1.0 [37].

Equilibrium parameters have been calculated by Micromath Scientist using the linear regression method. Comparing the two models, the linear correlation coefficients (r^2) indicated that the Langmuir equation fitted the experimental data better than the Freundlich equation. The parameters corresponding to the Langmuir and Freundlich equations are shown in Table 1.

Very good r^2 values were obtained by adjusting the experimental data with the Freundlich model. However, the physical meaning of the constants k_f and n is not consistent with that determined by Langmuir model or the other experiments. Table 1 shows that the higher exchange capacity (high k_f) is observed when the competitor is the sulfate ion, and this is contrary to the experimental results. The same happens when all competing ions are in solution. Thus, it is concluded that although the adjustment obtained with these isotherms is good, the results are not descriptive of the real process. It should be noted that the Freundlich isotherm is limited in its adjustment ability at intermediate surface coverage ranges, not presenting an asymptotic behavior for coverage degrees close to 1. Therefore, the parameters obtained from this equation are not useful. Therefore, the catalytic behavior of the Pd(2%)/WA30 resin can only be described satisfactorily by the Langmuir model. This is because the resins have a homogeneous distribution of exchange sites, which can be considered identical, and the adsorption occurs in a monolayer.

3.4. Batch reactor: Catalytic reduction vs. ion exchange: without competitors ions

As above mentioned, the catalyst used in this study is bifunctional, in the sense that it can eliminate nitrites both by ion exchange and catalytic reduction. Each of these mechanisms has different rates. In order to determine the individual contributions to the global nitrites elimination rate, initial nitrite disappearance rate were measured as explained in section 2.2.2. These data improve the understanding of the mechanism by which nitrites are eliminated with the Pd(2%)/WA30 resin. Figure 6 shows the nitrites concentration as a function of time, obtained both with and without chemical reaction. It is very interesting to observe that at low times both curves are very similar. However, after approximately 7 minutes the nitrites concentration is clearly lower in the case of the Reaction + Ion exchange (RIE) process. This means that at the beginning of the process, the main path for nitrites elimination is the ion exchange, and this masks the catalytic reduction. As described in section 2.2.2, short experiments were carried out to determine the initial reduction rate. Figure 7 shows the results. It can be observed that the initial nitrites reduction rate is low compared to the ion exchange rate. This difference is higher at higher nitrites initial concentration. In addition, the initial reduction rate is linear as a function of the concentration, and therefore, the catalytic reduction follows a first order law. The global rate follows the same pattern as the adsorption rate, being this the faster contribution to decrease the nitrites concentration at the beginning of the process. Using the linear relationship between the initial reaction rate and the initial nitrite concentration shown in Figure 7, the kinetic constant for nitrites reduction was calculated assuming first order in hydrogen partial pressure. It resulted to be 0.18 L/g_{cat}.h.atm.

3.4.1. Kinetics of the ion exchange process

The characteristic kinetic parameters of the ion exchange process were obtained for a pseudo-first and pseudo-second order model [22,29-33].

The pseudo-first order model is very simple and has the following form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{Eq. 3}$$

and

$$q_t = (C_o - C_t)\frac{V}{m} \qquad \text{Eq. 4}$$

Where C_o and C_t (mg/L) are the concentrations at time zero and t, respectively, of solute in the volume V (mL) of solution; and m is the mass of catalytic resin used in the experiment (g); k_1 is the pseudo-first order adsorption rate constant (min^{-1}) and q_e (mg/g) represents the amount of ions adsorbed at equilibrium. By solving the differential equation using the following boundary conditions: at t = 0, q_t = 0, and at t = t, q_t = q_t, gives:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1.t}{2.303} \qquad \text{Eq. 5}$$

A plot of log (q_e - q_t) vs. t, makes it possible to obtained k_1, from the slope.

The pseud-second order model has the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \text{Eq. 6}$$

Where k_2 is the pseudo-second order adsorption rate constant (g $(mg.min)^{-1}$). Solving the differential equation using the following boundary conditions: at t = 0, q_t = 0, and at t = t, q_t = q_t, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{1}{q_e}t \qquad \text{Eq. 7}$$

It must be noted that by using this equation, q_e and k_2 can be obtained from the intercept and the slope of the line obtained plotting t /q_t vs. t.

A set of experiments was performed, systematically varying the initial nitrites concentration, using the catalytic resin Pd(2%)/WA30. The results are shown in Figure 8. The parameters presented in Table 2 were obtained using the SCIENTIST software v2.01. Such parameters were used to perform the simulations, which are shown in Figure 8 with solid lines (only pseudo-second order).

Table 2 summarizes the kinetic parameters and the correlation coefficient r^2 obtained when adjusting the experimental data to pseudo-first and pseudo-second order model. Both of models adjust relatively well the ion exchange kinetics, but the second order model is slightly better. It can be observed that the kinetic constants obtained in each of the experimental series are not constant, even though the adjustment of the models to the experimental data is good. As above discussed, there is an effect of the particle size in the adsorption rate. Therefore, the changes found in the kinetic constant upon variations in the initial nitrites concentration may be due to this diffusion limitation. Similar results were found by Chabani et al. [34], in the study of nitrates adsorption. Therefore, it can be concluded that the pseudo-second-order model can be used to describe the kinetics of nitrite exchange in the catalytic resin Pd(2%)/WA30. However, it has to be emphasized that using the resin in its commercial form, i.e. without crushing, only apparent kinetic constants can be obtained.

3.5. Fixed bed reactor.

3.5.1. Nitrites catalytic reduction in a fixed bed reactor vs. Ion Exchange: without competitor ions.

Figure 9 shows the nitrites percentage removal during RIE and IE experiments, and the corresponding ammonia generation in the case in which the reaction was carried out (RIE experiments). In both cases, water saturated with CO_2 was used as feed, with a concentration of nitrites of 76.8 mg/L, hydrogen flow of 1 mL/min, water flow of 3.1 mL/min, and pH = 3.89. The difference between these experiments is that in the IE procedure no H_2 was bubbled through the catalyst bed, and therefore no chemical reaction occurred, taking place only the ion exchange. The saturation curve that corresponds to the IE experiment displays three characteristic zones. In the first zone (zone 1) the exchange was complete, then in the second section the resin began to saturate (zone 2), and finally in the third part of the curve (zone 3) there was not exchange, because the resin was saturated. However, the curve corresponding to the experiment called (Reaction + Ion Exchange) presents a marked difference. The area corresponding to total elimination of nitrites (zone 1) is broader. This is because some of the nitrites fed were reduced, while another fraction was exchanged. Thus, the resin can treat a larger amount of water before reaching saturation.

From the data shown in Figure 9, it can be calculated that when only ion exchange occurred, the amount of nitrites removed from time zero to the time when the resin reached saturation was 31.4 mg NO_2^-/mL resin (treated volume 2850 mL), while when performing (Reaction + Ion exchange), the amount of nitrites eliminated was 39.5 mg NO_2^-/mL resin (treated volume 3600 mL). This indicates that 20.1% of the nitrites were eliminated by chemical reaction during the first part of the process, i.e. in zone 1..

The experimental curve corresponding to (Reaction + Ion Exchange) also presented three zones. In the first one, 20.1% of the nitrite ions were transformed mainly into $N_{2,}$ and the rest (79.9%) was exchanged with the chloride ions. These values were calculated assuming that during this experiment, the ion exchange process was the same as during the IE experiment. In the second zone, the resin began to saturate, although the (reaction + exchange) phenomenon still occurred. This is evident when comparing the slope of the saturation zones of the two curves. It can be seen that in the case where there was only exchange, the slope is more pronounced than that observed in the case where the two phenomena occur simultaneously: exchange and reaction. It is important to note that the higher the slope of the second region of the curves, the more quickly the resin becomes saturated. The third zone has a different meaning than the one explained for the exchange curve. In this case, the stabilization value represents the nitrites conversion due to the reaction with hydrogen.

Note that the conversion due to chemical reaction increases from 20.1% in the first part of the process to the constant value of 54% in the third zone. The explanation for this change is based on the mechanism of the resin saturation [28] shown in Figure 10. In zone 1, the bed volume occupied by nitrites is relatively low, being these adsorbed only in a part of the catalyst bed. Since the resin is saturated with nitrites in this zone, there are nitrites ions in the solution that can react before reaching the virgin resin. When H_2 flows, the chemical reaction will only occur in this area, i.e., the effective volume of catalyst involved in the reaction is a small fraction of the total bed. For this reason, the percentage disappearing by chemical reaction is only 20.1%. However, as the fraction of saturated resin increased, the system reached zone 3 of the process (Figure 10). Under these conditions, the entire bed is saturated with nitrite ions, and therefore the hydrogen can react at any point throughout the reactor with the nitrites that are available in the liquid phase and can be adsorbed in the Pd, thereby increasing the effective volume of bed in which the reaction occurs, and therefore the conversion increases.

The better performance of the RIE process compared to the IE one can be seen comparing the volume of water that can be treated at an intermediate nitrate removal percentage. For example, to have 70% of nitrate removal during the RIE process the volume of water treated was 6200 mL, while during the IE process, it was 4000 mL (see Figure 9). This means that the RIE process makes it possible to treat 55% more volume than when using ion exchange, making it possible to decrease the reactor volume. These results agree with those shown in Section 3.4 obtained with batch reactor.

It is important to note that during the entire course of the reaction, the ammonia concentration at the reactor outlet was below 0.2 mg/L, except in the first point, which shows a high ammonia concentration due to the decomposition of the resin functional groups that occurs during its storage. Thus, it can be concluded that the catalytic removal of nitrites using a continuous fixed bed reactor with a Pd(2%)/WA30 catalyst is feasible, obtaining good conversions and very high selectivities.

3.5.2. Nitrites catalytic reduction in a fixed bed reactor vs. Ion Exchange: with competitor ions.

Figure 11 shows the results obtained during the nitrites reduction in presence of competitor ions, as indicated in section 2.2. It can be observed that the volume of water treated with 100% nitrites elimination is smaller than in the case of not having competitor ions (compare with Figure 9). The amount of nitrites removed in the IE process (zone 1) was 8.9 mg NO_2^-/mL resin, and 10.5 mg NO_2^-/mL resin in the RIE process. These values are significantly lower than those obtained when water contained only nitrites, and is obviously caused by the presence of chlorides, bicarbonates and sulfates, that compete with nitrites by the adsorption sites.

From the data presented in Figure 11, it is possible to calculate that 15.2% of the nitrites was removed by reduction in the first part of the curve (zone 1) before they can be detected in the water at the reactor outlet. This amount is smaller than that obtained without competitor ions, which was 20.1%. This is due to the contribution of two effects. First, the competitor ions adsorb on the metal competing with the nitrites adsorption thus decreasing the reduction rate. Second, the pH of the water saturated with CO_2 is higher in the presence of these competitor ions. This increase in the pH leads to a decrease in the nitrite conversion.

Finally, it can be observed that at the stabilization stage (zone 3) the nitrite conversion was 31%, which is a smaller value than that obtained in the case of feeding only nitrites in the water, for the same reasons.

Another important consequence of the presence competitor ions, is that the selectivity to nitrogen decreases (compare Figures 9 and 11), with a higher ammonium production. This is mainly due to the different pH observed in these situations. As above mentioned, the pH in the system when there were only nitrites ions was 3.89, while in the presence of competitor ions it was 5.15.

In the presence of competitor ions, the RIE process also has better performance than the IE. For example, using the RIE process, and with 70% of nitrates removal, it was possible to treat 25% more water than in the IE. (see Figure 11).

These results are very important regarding the design of processes for nitrate and nitrites removal, and show that it is necessary to study the catalytic behaviour using the real water composition, and not only model systems containing the nitrites as unique ions.

3.5.3. Resin regeneration process. (RIE + Regeneration)

The process described in the previous section (RIE) has a disadvantage, which is the fact that the fraction of nitrites eliminated by reduction to nitrogen during the reaction is relatively low, being the main path for nitrites elimination the ion exchange. Because of this, a large amount of nitrites remains adsorbed in the resin and its regeneration must be developed. After the RIE process, the water flow is stopped while hydrogen is flowed thorough the reactor. After the regeneration, a NaCl (5 g/L) solution is fed in order to elute the ions that remained adsorbed (sulphates and bicarbonates), that decrease the ion exchange capacity of the resin for the next reaction cycle. With this procedure, it is possible to eliminate the ammonium formed during the regeneration, and leave the resin exchange only with chlorides ions.

The RIE process was run using a solution containing 89.5 mg NO_2^-/L saturated with CO_2. The pH of this solution was 3.89. The volume of Pd(2%)/WA30 catalyst loaded in the reactor was 7 mL, and the water and hydrogen flow rates were 3.37 mL/min and and 0.6 mL/min respectively. The volume of water contaminated with nitrites treated during the RIE process was 3000 mL maintaining the nitrites concentration at the reactor outlet in negligible values (undetected), with an ammonium average concentration during the whole experiment below 0.2 mgNH_4^+/L. After this step, the water flow was stopped and hydrogen was flowed at 1.4 mL/min. After 16 h of regeneration, the catalytic bed was eluted with NaCl solution (5 g/L), measuring the amount of nitrites present in this solution. The total amount of nitrites fed to the reactor was 38.4 mg NO_2^-/mL_{resin}, and the mass that remained in the resin after the regeneration was 0.03 mg/ mL_{resin}. In order to determine the percentage of nitrites eliminated during the process, the following equations were used:

$$\text{Inlet } (mgNO_2^-/mL_{resin}) = \text{ Outlet } (mgNO_2^-/mL_{resin}) + \text{Ch.R} + \text{I.E. } (mgNO_2^-/mL_{resin})$$

% NO_2^- Removal = (Ch.R/Inlet)*100

where:

Inlet: mass of NO_2^- per mL resin fed to the reactor during the RIE process.

Outlet: mass of NO_2^- per mL resin that came out of the reactor during the RIE process.

Ch.R: mass of NO_2^- per mL resin reduced during the RIE and regeneration processes.

I.E.; mass of NO_2^- per mL resin that remained in the resin after the regeneration.

Using these equations it was calculated that 99.9% of the nitrites ions fed to the reactor were eliminated in the RIE and regeneration processes.

Influence of competitor ions

A similar experiment to the previous one was carried out, including competitor ions in order to evaluate its influence on the performance of the (RIE + regeneration) processes. The water saturated with CO_2 contained 102.4 mgNO_2^-/L and 94 mg/L of sulphates, 130 mg/L of chlorides and 170 mg/L of bicarbonates. The pH of this solution was 5.28, the volume of Pd(2%)/WA30 catalyst loaded in the reactor was 7 mL, and the water and hydrogen flowrates were 3.2 and 0.6 mL/min respectively.

During the RIE step, the concentration of nitrites at the reactor outlet was again undetectable, and the ammonium average concentration during the whole run was 0.20 mgNH_4^+/L. After treating 800 mL of water, the catalytic bed was regenerated with 1.5 mL/min of hydrogen. After 16 h of regeneration the bed was eluted with NaCl (5 g/L) measuring the amount of nitrites that were not converted. It was determined that 99.3% of nitrites fed to the reactor were reduced during the RIE and regeneration steps.

Therefore, the process was not affected in its efficiency by the presence of competitor ions.

3.5.4. Ion Exchange and Catalytic Regeneration.

This is an alternative to the RIE + regeneration process. It consists on purifying water by ion adsorption, but then the adsorbed nitrites are reduced by flowing hydrogen. The advantage of this option as compared to the RIE+regeneration process is that during water potabilization there is no formation of ammonium ions since no chemical reaction occurs. On the other hand, since the nitrites are finally reduced during the regeneration, no concentrated effluent in this contaminant is generated, as it occurs during conventional ion-exchanged processes for water treatment.

A solution containing 114 mg NO_2^-/L saturated in CO_2 was fed to the reactor that contained 7 mL of the Pd(2%)/WA30 catalyst. The volume of water treated was 1925 mL, and during this treatment the nitrites concentration at the reactor outles was undetectable. The water flow was stopped and the hydrogen flow was set at 1.4 mL/min After 16 h of regeneration, the NaCl solution (5 g/L) was circulated to elute the nitrites that remained in the resin, resulting to be 0.07 mgNO_2^-/ mL$_{resin}$. The total amount of nitrites fed to the reactor was 31.5 mgNO_2^-/mL$_{resin}$. With these values and the equations above presented it can be calculated that 99.8% of the nitrites were reduced during the regeneration. Therefore, this procedure makes it possible to eliminate practically all the nitrites from water without contaminating the water with ammonium.

Influence of competitor ions

The effect of the competitor ions was evaluated in this process using water saturated with CO_2 containing 83.1 mgNO_2^-/L, and 103.7 mg/L of sulphates, 127.4

mg/L of chlorides and 140 mg/L of bicarbonates. The pH of this solution was 5.28. The volume of the Pd(2%)/WA30 catalyst loaded in the reactor was 7 mL. After treating 630 mL of water, it was determined that the concentrations of ions in this water were 1 mg/L of sulphates, 144 mg/L of chlorides, 150 mg/L of bicarbonates, and it did not contain nitrites. After this step the catalyst was regenerated flowing 1.4 mL/min of hydrogen during 16 h. As in the previous experiments, it was measured that 99.8% of nitrites were reduced.

These results make it possible to conclude that this process is adequate to purify water contaminated with nitrites without forming ammonium in the treated water, even in the presence of competitor ions. It has to be emphasized, that the nitrites are effectively reduced to nitrogen during the regeneration step.

Both, the process presented in Section 3.5.3 (RIE + Regeneration) and the one described in Section 3.5.4 (Ion Exchange and Catalytic Regeneration) make it possible to purify water contaminated with nitrites. The first one, has the advantage of treating larger water volume before regeneration, but has the disadvantage of generating small amounts of ammonium. Nevertheless, the concentration of this compound was below the limit of 0.5 mg/L recommended by the WHO. On the other hand, the process Ion Exchange and Catalytic Regeneration assure water free from ammonium, although the volume of treated water between regenerations is smaller than in the first process.

Catalyst Stability

Consecutive cycles of ion exchange and regeneration were carried out. It was found that after 5 cycles the catalyst maintained its performance without loosing exchange capacity. In each of these cycles, the regeneration with hydrogen during 16 h eliminated more than 99.5% of the nitrites. It can be concluded that the catalyst has a very good stability in this combined process of ion exchange and regeneration.

3.5.5. Pilot Plant. Ion Exchange and Catalytic Regeneration.

The pilot plant studies were carried out as described in section 2.2.1.2. During this experiment, 20 liters of water contaminated with nitrites were purified. The concentration of nitrites in the water collected was 0.09 mg/L, while the concentration of sulphates was undetectable, and there were 204 mg/L y 145 mg/L of chlorides and bicarbonates respectively. After the ion exchange step, the catalyst was regenerated flowing hydrogen at 35 mL/min during 16 h, and then the ions left in the resin were eluted with NaCl solution (5 g/L). It was not possible to detect nitrites in this solution. This means that 100% of the nitrites present in the catalyst at the end of the ion exchange process were eliminated during the regeneration with H_2.

Therefore, there is an excellent agreement between the results obtained in the laboratory experiments and those obtained in pilot scale plant.

3.6. Catalyst Characterization.

The Pd(2%)/WA30 catalyst was characterized by different techniques. The exchange capacities of the resin used as support and of the catalyst were determined by titration with NaOH. The exchange capacity of the resin was 1.6 meq and that of the catalyst was 1.54 meq/g . Therefore the procedure used to incorporate the metal on the resin did no change the ion exchange capacity of the support.

Similar results were obtained in the BET area analyses. For the resin it was measured a value of 17.94 m^2/g and for the catalyst it was 17.85 m^2/g.

The fresh catalyst, and the catalyst used in 5 consecutive cycles were analyzed by SEM. Results are presented in Figure 12. Both in the external surface (Fig. 13A) and in the internal part of the resin, there are not significant modifications in the morphology visible with this technique.

The metallic dispersion measured by CO dynamic chemisorption was 43% in the fresh catalyst, which is a high value taking into account that the metal loading was 2%. After 5 cycles or ion exchange and regeneration, the palladium dispersion dropped to 10.2%. There is an important increase in the palladium particle size as indicated by this decrease in dispersion. Nevertheless, this change in dispersion has not impact on the catalytic activity for nitrites reduction in the process used in this work. This means that the controlling step in the regeneration mechanism does not involve the metallic sites.

Figure 13 shows results of XRD analyses. It can be observed a peak at 40.1 ° that corresponds to the Pd^0 (JCPDS card # 05-0681), both in the fresh and used catalysts. The peak displayed at low angles corresponds to the resin. The relative intensity of the peak that corresponds to the Pd^0 and the peak at low angle is higher in the case of the used catalyst. This indicates that the Pd^0 crystals are bigger in the used catalysts, in agreement with the CO chemisorption results that showed that there was Pd sinterization during operation.

Figure 14 shows the results obtained by EPMA. Values shown in Figure 14 are relative to the chloride ions present in the resin. In the fresh catalyst, the Pd content is practically constant in the first 65 microns, and then, at approximately 100 microns from the surface, the Pd concentration decreased sharply, and at 150 microns no signals due to Pd are detected. In the case of the used catalyst, the Pd concentration in the outer surface increased up to 90%, a higher value than in the fresh catalyst. This result indicates that there is a migration of Pd particles towards the outer surface of the resin particle. At 100 microns there is a relative concentration of Pd of 10%. Therefore, the analyses carried out with the EPMA technique indicate that there is a migration of Pd particles from the interior of the resin towards the external surface, resulting in metal sinterization. It is interesting to highlight that the Pd sinterization occurs in this system at room temperature, being this deactivation mechanism usually associated with high temperatures. However, it must be recall that the reaction is carried out in liquid phase, and this facilitates the diffusion of the Pd nanoparticles from the inside of the resin particle, towards the external surface. Similar behaviour has been previously observed in a Pd-Cu catalyst supported on resin [17]. On the other hand, it was not possible to detect Pd in the water either by atomic absorption spectrometry and inductively coupled plasma analyses. If there is leaching during the reaction and/or regeneration steps, the resulting Pd concentration in water is below the detection limits of the techniques used to perform the analyses.

4. Conclusions

Important diffusive effects were observed during the ion exchange process. However, decreasing the particle size would bring about problems of fine particles dragging and over-increase the pressure drop throughout the reactor. Taking into account the results obtained in the breakthrough and batch ion exchange experiments, it is concluded that sulfate is the competing ion which causes the larger alterations in the ion exchange ability. The selectivity and activity for nitrite reduction decrease in the presence of competitor ions. These results show that in order to evaluate the catalytic performance in the nitrite or nitrate reduction, the presence of other ions in the reaction media must be taken into account.

The performance of the Pd(2%)/WA30 catalyst in the process called Reaction + Ion Exchange (RIE) proved to be very good. It was found that using this process; it was possible to treat 55% more water than when using only ion exchange. Moreover, the conversion due to chemical reaction varies from 20.1% at the reaction beginning to 54% when the resin is saturated with nitrite ions. The ammonium concentration generated by nitrites over-reduction never exceeded 0.2 mg/L.

A new methodology for regenerating the resin is presented, and simply consists of flowing hydrogen in the catalytic bed. This process makes it possible to eliminate more than 99 % of the nitrites, without forming ammonium ions in quantities above those specified by the international quality standards. This good performance was also verified including the most common ions present in the water, and also the stability was proved using the same catalyst in several consecutive reaction and regeneration cycles. Also, a pilot plant scale reactor was used to verify this behaviour.

The process for treating water contaminated with nitrites is developed in order to be used in the elimination of nitrates in a two-step strategy, as above described.

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Legends to figures

Figure 1: Nitrite concentration as a function of time, obtained using different sizes of resin particles. Initial nitrite concentration: 82 mg/L. Catalyst mass: 0.2 g, solution volume: 200 mL. pH = 3.89. Temperature 23 ºC.

Figure 2: % Nitrite Removal during ion exchange process (Pd(2%)/WA30). ▨ The ions concentration is equal to half of that specified by the quality standards for drinking water; □ The equivalents of nitrite ions is equal to the equivalents of the competing ion. Initial nitrite concentration: 2.17 meq/L (100 mg/L). Resin mass: 0.2 g, solution volume: 200 mL. Ion exchange time: 70 min. Temperature 23 ºC.

Figure 3: Nitrite concentration as a function of time, in the presence of different competing ions. Initial nitrite concentration: 63 mg/L. Catalyst mass: 0.2 g, solution volume: 200 mL. Particle size: 20 – 40 mesh. Temperature 23ºC. Initial competing ions concentration Cl^- : 125 mg/L, $SO_4^=$: 100 mg/L, CO_3H^- : 135 mg/L.

Figure 4: Breakthrough curves obtained with different competing ions. Nitrite initial concentration: 100 mg/L. Temperature: 23 ºC. Catalyst volume: 7 mL. Particle size: 20 – 40 mesh. Initial competing ions concentration Cl^- : 125 mg/L, $SO_4^=$: 100 mg/L, CO_3H^- : 160 mg$CaCO_3$/L. Solution flow rate: 3 mL/min.

Figure 5: Experimental adsorption isotherms for nitrite removal using Pd(2%)/WA30 catalyst. Temperature 23 ºC. Nitrite initial concentration: 100 mg/L. Particle size: 20 – 40 mesh. Initial competing ions concentrations: Cl^- : 125 mg/L, $SO_4^=$: 100 mg/L, CO_3H^- : 135 mg/L.

Figure 6: Nitrite concentration profiles, obtained with Reaction + Ion Exchange (RIE) and Ion Exchange (IE) processes at different nitrites initial concentrations. Temperature 23 ºC. pH = 3.89.

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Figure 7: Initial rate of nitrites elimination. (experimental conditions: see section 2.2.2).

Figure 8: Experimental and simulated nitrite adsorption profiles, with different initial nitrite concentrations. Simulation performed with SCIENTIST v 2.01. using pseudo second-order model.

Figure 9: Nitrites percentage removal in the Ion Exchange processes (IE) and Reaction + Ion Exchange (RIE). Catalyst volume: 7 mL. Initial nitrite concentration: 76.8 mgNO_2^-/L. Feed pH = 3.89. Hydrogen flow : 1 mL/min. Feed flow : 3.1 mL/min. Temperature 23ºC. Other experimental conditions: see section 2.2.

Figure 10: Ions concentration evolution in an ion exchange bed. V.R.: Virgin Resin, M.T.: Mass Transfer Zone, S.R.: Saturated Resin

Figure 11: Nitrites percentage removal through Ion Exchange processes (IE) and Reaction + Ion Exchange (RIE) with competitor ions. Catalyst volume: 7 mL. Initial nitrite concentration: 83.1 mg/L. Feed pH = 5.15. Hydrogen flow: 1 mL/min. Feed flow: 3.1 mL/min. Temperature 23 ºC. Other experimental conditions: see section 2.2.

Figura 12: SEM analyses of the Pd(2%)/WA30 catalyst, fresh and used in 5 cycles.A: External surface;. B: Transversal cut (12000 X). C: Transversal cut (6000 X).

Figure 13: XRD profiles. Used Pd(2%)/WA30., fresh Pd(2%)/WA30 and WA30 resin.

Figure 14: Pd radial profile determined by EPMA, A: Fresh catalyst, B: catalyst used in 5 consecutive reaction-regeneration cycles.

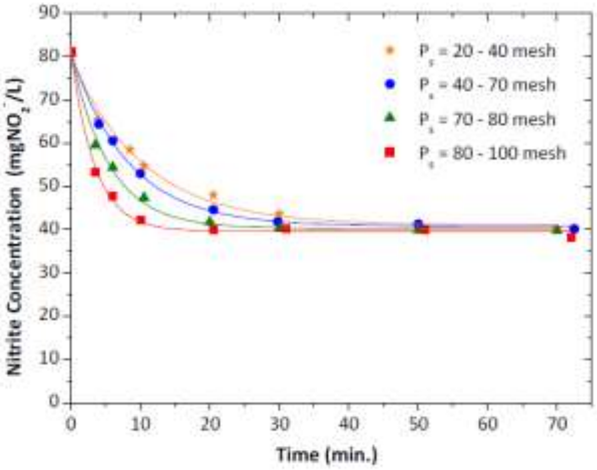


Figure 1

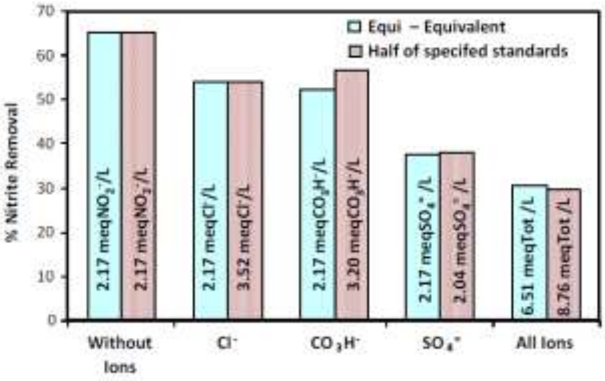


Figure 2

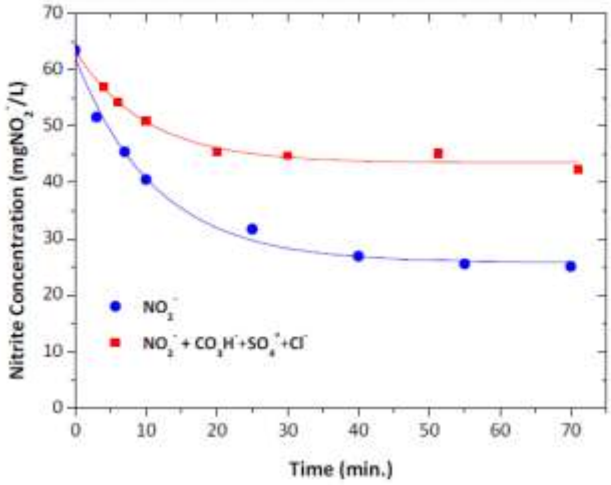
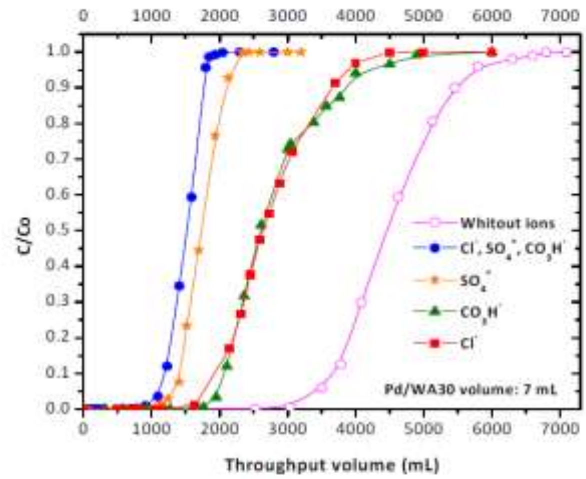


Figure 3



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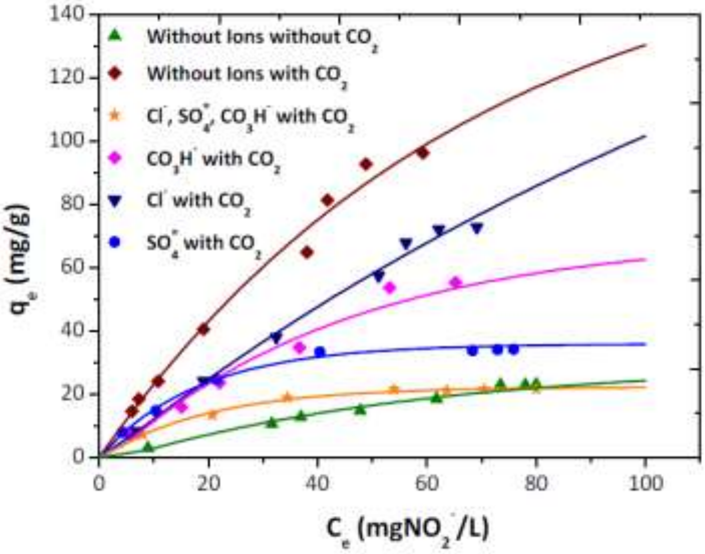
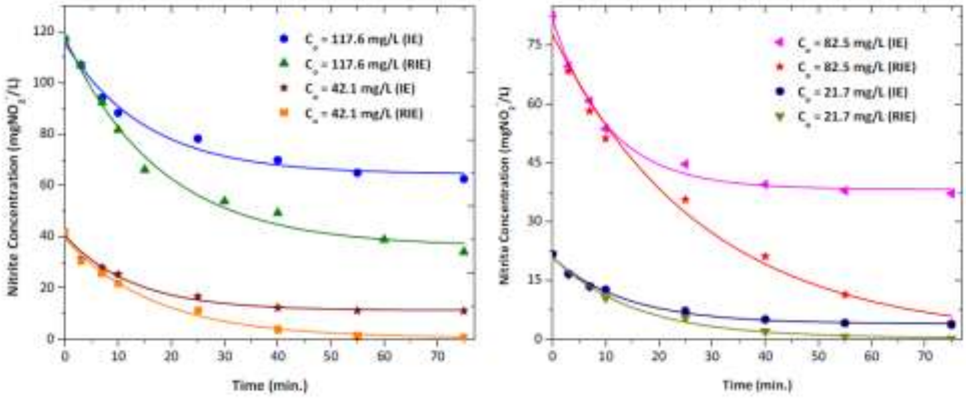


Figure 5



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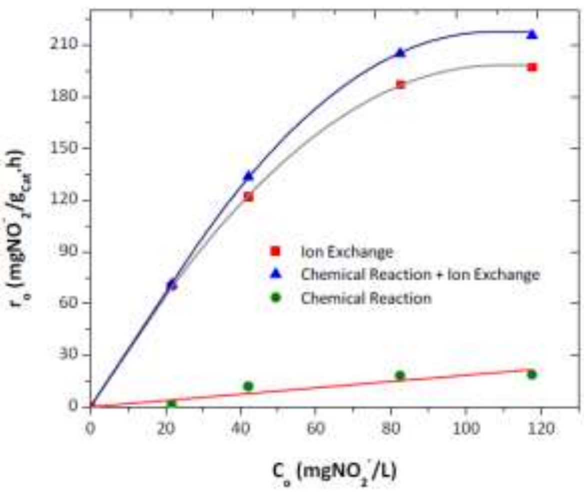

Figure 7

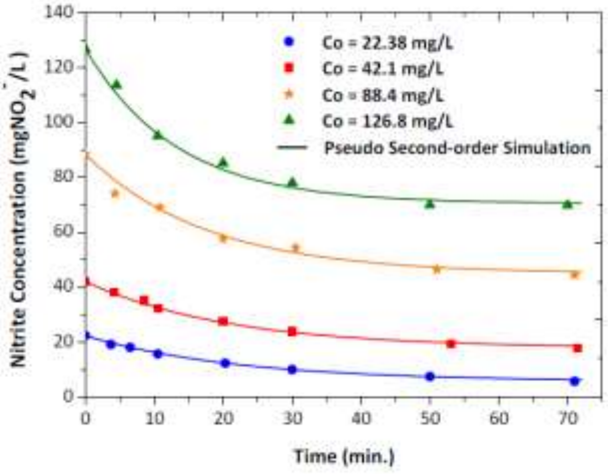

Figure 8

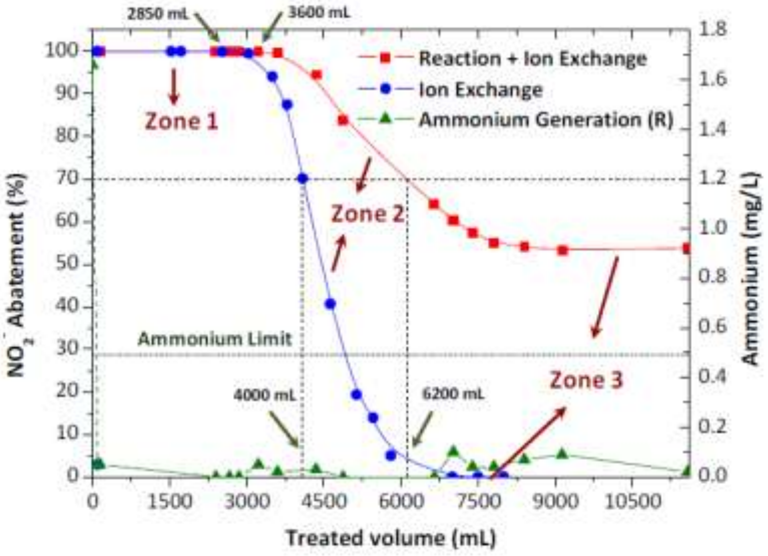

Figure 9

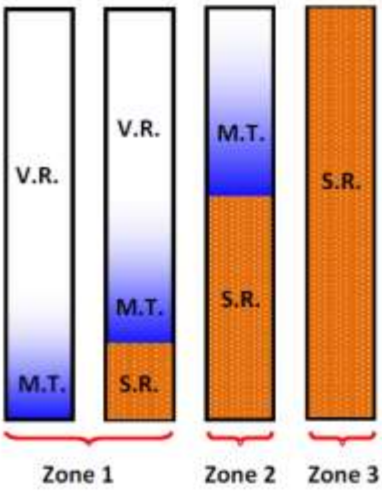

Figure 10

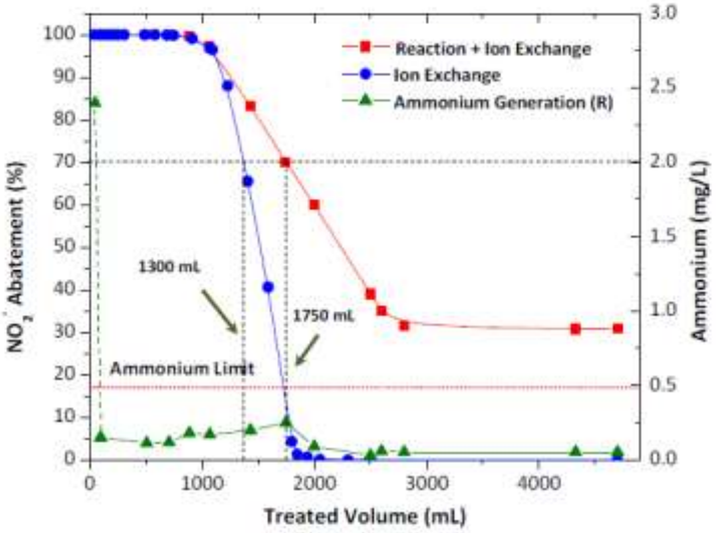
Reaction + Ion Exchange
Ion Exchange
Ammonium Generation (R)
1300 mL
1750 mL
Ammonium Limit
NO_2^- Abatement (%)
Ammonium (mg/L)
Treated Volume (mL)
0
10
20
30
40
50
60
70
80
90
100
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
1000
2000
3000
4000

Figure 11

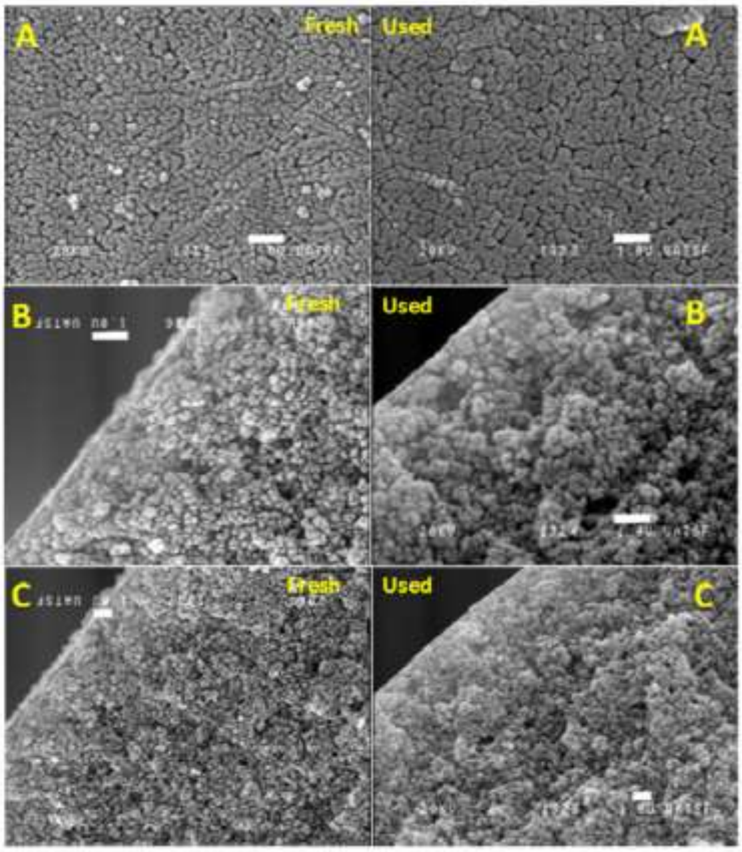

Figure 12

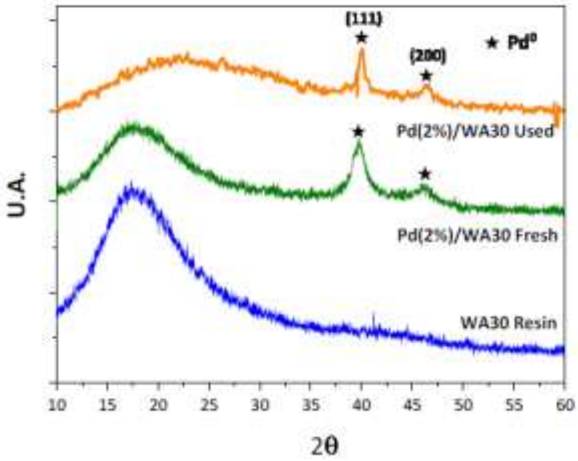

Figure 13

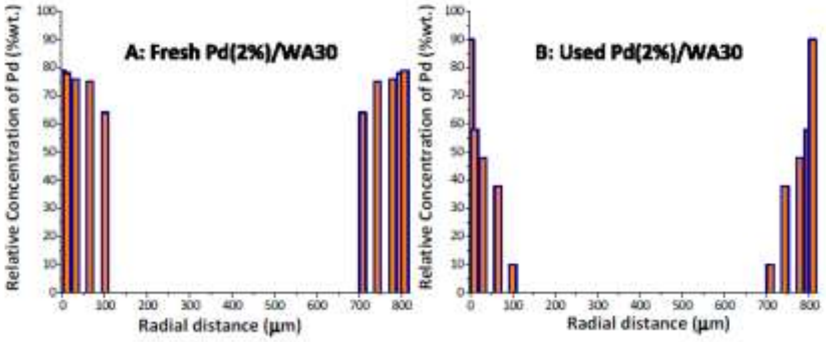
A: Fresh Pd(2%)/WA30
B: Used Pd(2%)/WA30
Relative Concentration of Pd (%wt.)
Radial distance (µm)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800

Figure 14

TABLES

Table 1 - Langmuir (Eq. 1) and Freundlich (Eq. 2) constants. q_o [meq/g], b [cm^3/mg].

	Langmuir			**Freundlich**		
	q_o	b	r^2	n	k_f	r^2
No Ions - No CO_2	2.2	0.0038	0.98	1.17	0.56	0.98
No Ions - With CO_2	5.6	0.0100	0.99	1.21	3.51	0.99
Bicarbonates - With CO_2	2.2	0.0144	0.99	1.20	1.76	0.99
Chlorides - With CO_2	2.4	0.0030	0.99	1.10	1.67	0.99
Sulfates - With CO_2	1.0	0.0491	0.99	2.03	4.52	0.93
All Ions - With CO_2	0.7	0.0397	0.99	1.99	2.81	0.94

Table 2: Kinetic parameters obtained with Pseudo-First and Pseudo-Second Order models for nitrites adsorption at different initial concentrations.

	Pseudo-First Order		**Pseudo-Second Order**	
C_o (mgNO_2^-/L)	**k_1**	**r^2**	**k_2**	**r^2**
22.4	0.045	0.985	9.1E-04	0.996
42.1	0.048	0.972	4.5E-04	0.985
88.4	0.057	0.976	6.0E-04	0.987
126.8	0.076	0.970	4.8E-04	0.982