



A novel process for nitrate reduction in water using bimetallic Pd-Cu catalysts supported on ion exchange resin

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ABSTRACT

In this work, a Pd-Cu catalyst supported on a macroporous anion exchange resin was used in two novel processes to treat water contaminated with nitrates. The catalytic performance was evaluated in a continuous fixed bed reactor. The process (Reaction + Ion Exchange) – Regeneration, named RIE-R, has two steps: 1- reaction and ion exchange (RIE); 2- Regeneration (R). It was found that a hydrogen flow rate increase does not affect the nitrate removal efficiency during the RIE step, while the selectivity to nitrogen decreased. The presence of competing ions (sulphate, bicarbonate, chlorides) led to a decrease in the nitrate removal efficiency. In any case, the water obtained in the process meets the limits established by the World Health Organization. During the regeneration step, carried out by bubbling hydrogen to the catalytic bed, 100% of nitrates present in the resin at the end of the RIE cycle were eliminated.

The other process, named IE-R, has a first step in which only ion exchange of nitrates occurs, and a second one during which the catalyst is regenerated. This process has worse performance compared to the RIE-R. Only 36.7% of the nitrates present in the resin at the beginning of the regeneration were eliminated.

The catalyst was characterized by CO chemisorption, SEM, EPMA, TEM, and XRD. Pd migration towards the external surface occurs during the reaction, and also a decreased in dispersion takes place, leading to a small decrease in activity detected in consecutive reaction-regeneration cycles.

A regeneration mechanism is presented.

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1. Introduction

Nitrates are among the most commonly found pollutants in surface and underground water, as a consequence of the intensive use of nitrogen fertilizers and the discharge of residual water [1–4]. Nitrate consumption may lead to different health problems. Normally, once the nitrates are consumed they are eliminated throughout the kidneys before being converted to nitrites [5], but it has been reported that high levels of nitrates consumption by pregnant women may cause spontaneous abortion or birth defects [6,7]. Nitrates ions are converted to nitrites by microbial reduction. The reaction between nitrites and secondary or tertiary amines in acid media, such as that of the human stomach, may result in the formation of N-nitroso compounds, which are well known for being mutagenic, teratogenic, and carcinogenic [7–9]. However, the most important problem caused by nitrates is the methemoglobinemia, which is a potentially fatal disorder for babies up to the age of 6 months. This disease is commonly known as the blue baby syndrome. The Health World Organization established that the maximum allowed concentration of nitrates and nitrites in drinking water are 50 mg/L and 3 mg/L respectively [10]. The most common technologies used to treat water contaminated with nitrates are the reverse osmosis, ion exchange, and the biological

denitrification [11–13]. However, the reverse osmosis and the ion exchange present environmental problems due to the generation of effluents concentrated in nitrates [14,15]. On the other hand, the biological denitrification presents the disadvantages of needing long times to start-up the potabilization system, and risk of biological contamination [16]. For these reasons, the catalytic reduction of nitrates is a very attractive technology, since the nitrates are transformed in nitrogen [17–19].

The use of polymers as catalysts support has been used by several research groups in order to stabilize the bimetallic particles. The Poly(*N*-vinylpyrrolidone) (PVP), and Poly(vinylalcohol) (PVA) have been used to increase the stability and to control the size and composition of bimetallic particles [20–22]. Other types of polymers, such as functionalized resins, have been used with very good results in the preparation of Pd-Cu and Pd-In bimetallic catalysts for the nitrate reduction [23–26]. These resins contain a styrene-divinylbenzene copolymer, which contains exchange functional groups, such as for example $-\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ and $-\text{SO}_3\text{H}^+$, corresponding to anionic and cationic resins, respectively. These catalysts were evaluated in batch reactors and showed low conversion but very good selectivity to nitrogen, and for this reason they are very interesting in order to be used in continuous reactors. Gašparovičová et al. [24,27] studied the nitrate reduction using bimetallic Pd-Cu catalysts supported on ion-exchange resins, both of the anionic and cationic types. They found that the catalysts prepared using anionic resins were 4 times

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more active than those prepared using cationic resins. Comparing with Pd-Cu catalysts supported on inorganic materials such as alumina (Al_2O_3), the activity was lower, but the selectivity to nitrogen was better. The use of cationic resins as supports of bimetallic catalysts have been also studied by other research groups, since this support provides protons that neutralizes the OH^- generated during the nitrates reduction reaction, maintaining the pH of the system, and therefore increasing the selectivity to N_2 [23,28]. The anionic resins present the advantage of having a dual functionality: ion exchange and catalytic reduction. Kim et al. [29] developed an interesting integrated process that combines the catalytic reduction and the ion exchange of nitrates, similarly to the process described in the present work. The process of Kim et al. [29] used a strong anionic resin containing 1% Pd and 1% Cu. In a first step, nitrates are adsorbed in the resin, and then the nitrates were reduced in a static process with a mixture CO_2/H_2 1:1 at 6 barg. They observed that under these conditions the nitrates conversion and selectivity to nitrogen were 100%. Both the ion exchange and the reduction steps were carried out in a batch configuration.

On the other hand, there are only few studies of this reacting system (nitrates reduction in water) using a continuous fixed-bed reactor [30–33]. Palomares et al. [41] studied Pd-Cu/ Al_2O_3 in fixed bed reactor, but obtained a low selectivity to N_2 , with selectivity to NH_4^+ higher than 40%. In most cases, the catalysts showed low conversion or selectivity to N_2 , but there are no studies using catalytic resins in these reactors. This is surprising, since in order to apply this technology in large scale, the catalysts must be used in continuous fixed-bed reactor.

For these reasons, in this work the objective was to study the catalytic performance of Pd-Cu catalyst supported on a macroporous anionic resin, using a fixed-bed reactor. Two new processes based on this catalyst were developed, and named Reaction + Ion Exchange – Regeneration (RIE-R) and Ion Exchange-Regeneration (IE-R) [34]. Studies of activity and selectivity in different conditions were carried out, demonstrating that it is possible to reduce the nitrates even in the presence of the most commonly anions present in the groundwater, using a continuous process.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared following the procedure previously described [25]. Pd-Cu bimetallic catalysts were supported on the WA30 macroporous ion-exchange resin, manufactured by Mitsubishi. The Pd was loaded on the resin by ion-exchange at room temperature; using a solution of PdCl_2 (8571 mg/L) dissolved in NaCl 0.01 M and HCl 0.01 M. During this exchange, nitrogen was bubbled in the solution. The quantity of solution used in the ion-exchange was calculated in order to obtain the desired loading of Pd in the catalyst. At the end of this step, the solution is colourless. The catalyst is filtrated, and a 35 wt.% hydrazine solution with a pH = 14 is added to reduce the palladium. After 5 min, the catalyst is filtrated and washed with a NaCl (20 g/L) until de liquid has a neutral pH.

In order to incorporate the copper in this Pd/WA30 catalyst, the controlled surface reduction method was used. This method was selected in order to have the copper on the palladium particles. In this procedure, the reduced Pd/WA30 catalyst was suspended in water and hydrogen was bubbled for 2 h. Then, the solution containing the copper ($\text{CuNO}_3 \cdot 3\text{H}_2\text{O}$) was added maintaining the hydrogen bubbling for 2 h. After this, the catalyst was filtered and then reduced using the solution of hydrazine sulphate in basic media. Finally, the catalyst was filtered and washed with a 20 g/L of NaCl until neutral pH in the

liquid was observed. In this way, the catalyst supported on an anionic macroporous resin saturated with chlorine ions, containing 2 wt.% Pd and 0.5 wt.% Cu, was obtained.

The metals contents on the final catalysts were verified by Energy-dispersive X-ray fluorescence (XRF), using a Shimadzu equipment, model EDX-720, by energy dispersion.

2.2. Catalytic tests

The catalyst evaluation was carried out in a fixed-bed plug flow continuous reactor. The water, containing nitrates (KNO_3 , 100 mg/L of NO_3^-), was fed using a peristaltic pump. The water also contained chlorine, sulphate, and bicarbonate as competing anions (NaCl , Na_2SO_4 and NaHCO_3), with concentrations of 125 mg/L, 100 mg/L and 135 mg/L, respectively. In all the experiments, 7 mL (apparent volume) of the wet solid catalyst were used. Samples of 15 mL were taken from the solution coming out of the reactor. The concentrations of nitrates, nitrites, and ammonium were determined. The nitrates removal efficiency represents in this study the sum of the fractions converted and adsorbed in the resin (X, %), and the selectivities to nitrites ($S_{\text{NO}_2^-}$, %), ammonium ($S_{\text{NH}_4^+}$, %) and nitrogen (S, %), were calculated as follows:

$$X (\%) = [1 - (C/C_0)] \times 100 \quad (1)$$

$$S_{\text{NO}_2^-} (\%) = [C_{\text{NO}_2^-}/(C_0 - C)] \times 100 \quad (2)$$

$$S_{\text{NH}_4^+} (\%) = [C_{\text{NH}_4^+}/(C_0 - C)] \times 100 \quad (3)$$

C_0 is the concentration of nitrates in the water fed to the reactor (mmol/L $\text{N}-\text{NO}_3^-$), C is the concentration in the reactor outlet at time t , and $C_{\text{NO}_2^-}$ y $C_{\text{NH}_4^+}$ are the concentrations of nitrites and ammonium (mmol/L $\text{N}-\text{NO}_2^-$ and mmol/L $\text{N}-\text{NH}_4^+$) at time t , respectively. It was assumed that there were only three main products: N_2 , NO_2^- y NH_4^+ . This assumption was used in many investigations [4,13,17,18,20,25,29] since it was demonstrated that the yield of NO_x species is negligible. Therefore, the selectivity to nitrogen was calculated using Eq. (4).

$$S (\%) = 100 - S_{\text{NO}_2^-} - S_{\text{NH}_4^+} \quad (4)$$

The selectivities defined in Eqs. (2)–(4), represent the fraction of the total amount of nitrates removed from the water stream, as nitrite, ammonium and nitrogen respectively, and it is not referred to the amount of nitrates converted by reduction. Since the nitrates are removed from the water by two different mechanisms, i.e. reaction and ion-exchange, it is important to provide information regarding the overall process selectivity, but it has to be emphasized that it is not referred to the amount of nitrates converted, but to the total amount of nitrates removed from the water stream.

The water was pumped at different flow rates, in the range 2–15 mL/min. All the experiments were carried out at 20–22 °C and atmospheric pressure.

In order to adjust the pH, water was saturated with CO_2 previously to feed it to the reactor. The pH of the water containing only nitrates saturated with CO_2 was 3.9, while in the case of the water containing also the competing ions it was 5.3. The water was saturated by bubbling CO_2 at 80 mL/min in a 5 L tank. It was determined that the pH stabilized at the final value in approximately 90 s (results not shown), using the pH measured in the tank to verify that the wa-

ter was saturated with CO₂. The concentration of bicarbonate in the former case was calculated using the equilibrium constants obtained from physicochemistry handbooks for CO₂ dissolution and the formation of bicarbonate and carbonate species. It resulted to be 8 ppm, while the carbonate concentration was negligible. The presence of other ions changed the pH of the solution, both because of the sulphates hydrolysis and because there is a change in the Henry constant for the dissolution of CO₂. It is well known that the Henry's Law constant for gas dissolution decreases as the salinity increases. The estimation of the bicarbonates formed upon CO₂ dissolution in the presence of the competing ions 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.

2.2.1. RIE-R process: (reaction + ion exchange) – regeneration process

This process makes use of the two properties of the Pd-Cu/WA30 material: its catalytic activity and the ion-exchange capacity of the support. The advantage of this process as compared to that presented in the next section (see Section 2.2.2) is that it is possible to treat more water before the resin needs regeneration, since the two mechanisms for nitrates elimination are taking place simultaneously: ion exchange and chemical reduction. On the other hand, the disadvantage of this process is that the treated water may contain ammonium ions due to nitrates over-reduction. The water containing the nitrates is fed from the bottom of the reactor. Hydrogen is co-fed in this stream. This part of the process is called *Reaction + Ion Exchange (RIE)*. During this step, part of the nitrates is exchanged with the chloride ions of the resin, and other fraction is reduced to nitrogen on the active sites of the catalyst (Pd-Cu). Once the resin is saturated or the nitrates concentration at the reactor outlet reach the limit recommended by the WHO, the water flow is stopped but the hydrogen flow is maintained during a specified time. This part of the process is the regeneration step. In this step, the nitrates adsorbed in the resin are reduced to nitrogen or to ammonium. The final step of the process is the elution of the adsorbed ions using a NaCl solution (20 g/L) and washing with water in order to eliminate the ammonium and nitrites ions formed during the regeneration stage and also the other ions (sulphates and bicarbonates) adsorbed in the ion exchange sites of the resin. In these experiments water saturated with CO₂ with and without the competing ions, as indicated in Section 2.2, was fed. The water and hydrogen flow rates during the Reaction + Ion Exchange part of the process were 2.5 mL/min and 0.6 mL/min, respectively. The hydrogen flow rate during the regeneration was fixed between 0.3 and 1 mL/min.

2.2.2. IE-R process: ion exchange – regeneration process

The first part of this process consists of flowing contaminated water in a fixed bed reactor, fed from the bottom, using a Pd-Cu/WA30 catalyst. During this step only the ion-exchange takes place, since no hydrogen is fed to the reactor. This process presents the advantage that, since no chemical reaction occurs, the water comes out of the reactor free of ammonium and nitrites. On the other hand, since the adsorption is faster than the chemical reaction, the water flow-rate that can be fed is higher compared to the RIE-R process described in Section 2.2.1. Once the resin is saturated, the water flowrate is stopped and the hydrogen flow is started, thus reducing the nitrates adsorbed in the resin to nitrogen and/or to ammonium. This is the regeneration step. Finally, an elution with NaCl (20 g/L) and a water washing makes it possible to eliminate the ammonium and nitrites ions formed during this regeneration step, and the other ions (sulphates and bicarbonates) adsorbed in the ion-exchange sites of the

resin. In these experiments, a solution containing nitrates (100 mg NO₃⁻/L), sulphates (100 mg/L), chlorides (125 mg/L), and bicarbonates (100 mg/L), saturated with CO₂ was fed to the reactor. The pH of this solution was 5.3. The volume of Pd-Cu/WA30 catalyst loaded in the reactor was 7 mL. The water flow-rate used during the ion exchange step was 8 mL/min while the hydrogen flow during the regeneration was 1 mL/min.

This process is similar to that described by Kim et al. [29], although the present alternative has an important advantage, which is the fact that the regeneration is carried out at atmospheric pressure flowing hydrogen through the catalytic bed. In the work of Kim et al. [29], the regeneration was carried out using a mixture of H₂ and CO₂ (1:1), in a batch configuration at 6 barg, and this is a complication and a disadvantage for large scale water potabilization processes. On the other hand, the catalysts were prepared using different procedures. In the present work, Cu was loaded by catalytic reduction and the support was an anionic weak resin, while in the case of Kim et al. [29] Cu was introduced using an ethanol solution under reflux conditions using a strong anionic resin.

2.3. Mass balances

2.3.1. IE-R process

To determine the efficiency of the regeneration process, a mass balance for each compound was calculated, particularly for the nitrates, as follows:

$$\text{Inlet (mg NO}_3^-) = \text{Outlet (mg NO}_3^-) + \text{Adsorbed (mg NO}_3^-) \quad (5)$$

$$\text{Adsorbed (mg NO}_3^-) = \text{Rxn} + \text{Ion Exchange (mg NO}_3^-) \quad (6)$$

The Inlet corresponds to the total amount of nitrates fed to the reactor, and is calculated as the (volume fed × nitrates concentration). The water coming out of the reactor is collected in a vessel, and is used to measure the total volume of liquid treated in the reactor. The concentration of ions in this volume represents the average concentration that came out of the reactor during the entire experiment. The Outlet is calculated using the volume treated and the nitrate average concentration in this volume. The term Adsorbed represents the mass of nitrates adsorbed in the resin at the beginning of the regeneration. The amount Ion Exchange refers to the nitrate left in the resin after the regeneration, and is calculated with the volume of NaCl solution used to do the nitrates elution, and the nitrates concentration in this solution. It is important to highlight that during the elution, it was checked that in the last portion of solution collected at the reactor outlet, the nitrates concentration was zero, and thus, all the nitrates contained in the resin at the end of the IE-R experiment were desorbed. The Rxn amount corresponds to the amount of nitrates converted during the regeneration, and was calculated using Eqs. (5) and (6).

The percentage of nitrates reduced to NO₂⁻, N₂ and NH₄⁺ during the regeneration was calculated as follows:

$$\% \text{ Regeneration} = (\text{Rxn (mg NO}_3^-) / \text{Adsorbed (mg NO}_3^-)) \times 100 \quad (7)$$

2.3.2. RIE-R process

In the following equation (Eq. (8)), the term (Reduced_{RIE} + Adsorbed) represents the amount of nitrates reduced during the first step

(RIE) plus the amount of nitrates that remains adsorbed before the regeneration step.

(8) $\text{Reduced}_{\text{RIE}} + \text{Adsorbed (mg NO}_3^-) = \text{Inlet (mg NO}_3^-) - \text{Outlet (mg NO}_3^-)$

The amount of nitrates represented by the variable Adsorbed, is related to the amount of nitrates that are reduced during the regeneration (Rxn) plus the amount left in the resin at the end of the cycle after the regeneration (Ion Exchange) as indicated in Eq. (6). The amount Ion Exchange is experimentally determined as explained in Section 2.3.1.

The percentage of nitrates reduced during the complete cycle referred to the nitrates eliminated from the water, and is therefore calculated as follows:

$$\% \text{ Reduction} = (\text{Reduced}_{\text{RIE}} + \text{Rxn}) / (\text{Adsorbed} + \text{Reduced}_{\text{RIE}}) \times 100 \quad (9)$$

2.4. Sample analysis

The nitrates concentration was measured using the method of reduction with Cd combined with the Griess colorimetric method, while the nitrites concentration was determined with the Griess method [35]. The ammonium concentration was measured using the Berthelot method [36].

2.5. Catalyst characterization

In addition to the fresh catalyst, a sample of the Pd-Cu/WA30 catalyst used in a RIE experiment was also characterized.

2.5.1. X-ray diffraction (XRD)

The X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with a monochromator using CuK radiation at a scan rate of $4^\circ/\text{min}$, in the range 10° – 100° . The Scherrer's equation was used to calculate the palladium crystal size.

2.5.2. Scanning electron microscope (SEM)

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.

2.5.3. Electron probe microanalysis (EPMA)

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 (SEMIQ), which does not require standards. X-ray spectra were obtained with an acceleration of 20 kV.

2.5.4. Transmission electron microscopy (TEM)

TEM observations were carried out to compare the size of the metal particles before and after the reaction. The micrograph images of the samples were acquired with a JEOL 100CX model microscope with nominal resolution of 3 Å. The samples were analyzed at 100 kV, and magnification of 100,000 \times .

The mean volume diameters were calculated with TEM results, using Eq. (10):

$$D_V = \frac{\sum n_i \cdot d_i^4}{\sum n_i \cdot d_i^3} \quad (10)$$

2.5.5. BET surface

Nitrogen adsorption was employed to determine BET surface areas and pores volumes, using a Quantachrome Autosorb 1 analyzer. Micropores volumes were estimated by means of t-plots and Saito-Foley method was used to estimate the average micropore sizes. The determinations were carried out by pre-treating the catalysts under vacuum at 150 °C for 3 h.

2.5.6. CO chemisorption

The metallic dispersions were determined by CO chemisorption. The CO chemisorption experiments were carried out in a fixed bed reactor. The sample was reduced with H_2 and then purged with N_2 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 0.5:1 stoichiometry for the CO chemisorption on the metal atoms was assumed.

2.5.7. Optic microscopy

A Nikon Optiphot (50–400 \times) metallurgical microscope with halogen lamps was used to perform optical observations of the samples. The microscope had a Microflex AFX-DX photo-micrographic attachment with an FX-35 DX dark box.

3. Results and discussion

3.1. Catalyst characterization

The metals loadings on the catalysts determined by X-Ray Fluorescent (XRF), were very similar to the nominal values (2 wt.% Pd, 0.5 wt.% Cu). In addition, it was verified that the Pd and Cu contents in the preparation solution, after the ion exchange step were very small. The Pd that remained in solution was not detected by AA, and the Cu concentration was only 0.2 mg/L. Therefore, all the Pd and practically all the Cu were incorporated in the resin obtaining the nominal composition.

The BET areas of the catalytic resin Pd-Cu/WA30 and the WA30 resin were 18.47 y 17.94 m^2/g respectively. There is no surface loss due to the presence of the metals. It has been shown that the Pd is deposited on the resin particles in an egg-shell mode [25,37].

The WA30 resin is white, being easy to optically observe the region of the particle in which the metals are deposited. The resin particles were cut in half and observed in the microscope. Fig. 1 shows results obtained with two hemispheres of the Pd-Cu/WA30 catalysts, that correspond to a fresh sample and to a sample used in reaction. In the fresh catalyst (Fig. 1A) the Pd and Cu deposits can be clearly observed in an egg-shell mode. Obviously, it is not possible to distinguish Pd from Cu in this observation. The region in which the metals were deposited was very well defined. It is not possible to see a gradual change in colour that would indicate a gradual change in metal composition throughout the resin particle. The thickness of the region in which the metals were deposited was approximately 115–125 μm .

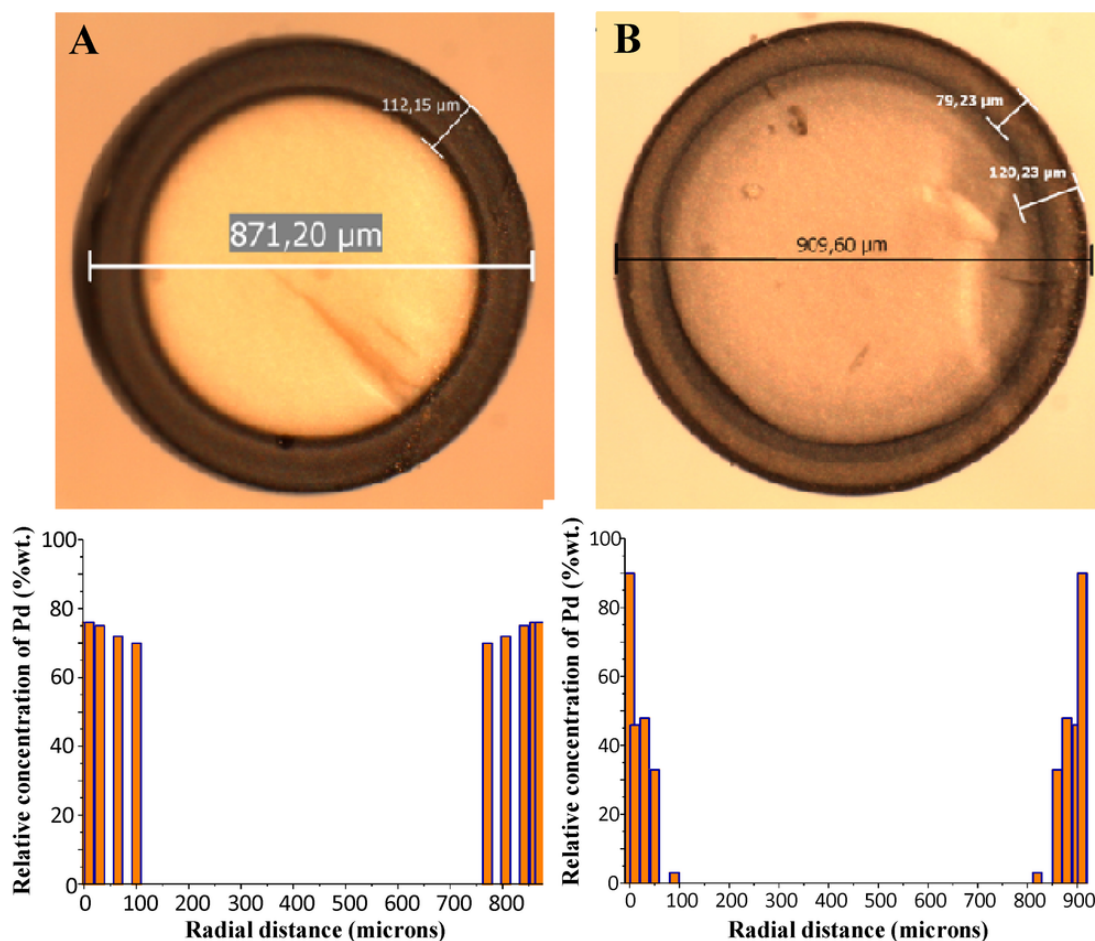


Fig. 1. Optical microscopy of a catalyst particle and radial distribution of Pd obtained by EPMA. A: Fresh Pd-Cu/WA30 catalyst. B: Pd-Cu/WA30 used in the reaction.

Fig. 1B shows the Pd-Cu/WA30 catalyst after it was used in a reaction cycle. It can be observed that the colour is darker in a thin layer in the outer part of the particle, suggesting that there is a migration of the Pd and/or Cu towards the exterior of the resin particle. In addition, the region in which the metals are present is not as well defined as in the fresh catalyst.

The technique used to prepare the bimetallic catalyst was the surface reduction, in which the Cu was deposited on the surface of the metallic Pd. In this way, both metals are initially concentrated in a thin layer in the outer part of the catalyst particle, as shown in Fig. 1A and B.

Pd and Cu relative concentrations were determined using the electron probe micro analysis technique (EPMA). The analysis was carried out using the resin saturated with chlorine ions that are detected by this technique, and therefore was used as reference to calculate the Pd concentration. It was assumed that the chlorine ions had a uniform distribution in the resin particle. The Pd concentration relative to the chlorine concentration is shown in Fig. 1. Copper was not detected by this technique due to the low concentration used for this metal. There is a good agreement between results obtained with EPMA and the images obtained with the optical microscope. In the fresh catalyst the Pd content slightly decreased from 76 to 70%, and at 110 μm from the surface, the concentration dropped to zero, as also observed in the optical microscope. In the used catalyst, it was found that the Pd concentration in a position very close to the external surface increased to 90%, what demonstrated that there was a Pd migration to-

wards the external surface during the reaction. At approximately 90 μm from the surface, the Pd relative concentration dropped to only 3%.

Fig. 2A and B shows SEM images of the Pd-Cu catalyst before and after its use in reaction, respectively. There are no differences in the morphology of the fresh and used resins that could be seen with this technique.

The TEM analyses results are shown in Fig. 3. The micrograph obtained with the fresh catalyst is shown in Fig. 3A. It can be observed isolated small metal particles. The graph shows the distribution of the particle sizes, from which an arithmetic mean diameter of 5.20 nm was calculated. Fig. 3B shows the micrographs obtained with the used catalyst. In this case, the arithmetic mean diameter was

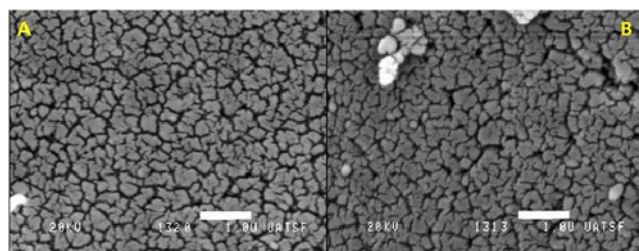


Fig. 2. SEM micrographs of the Pd-Cu/WA30 catalyst. A: Fresh, B: Used in reaction.

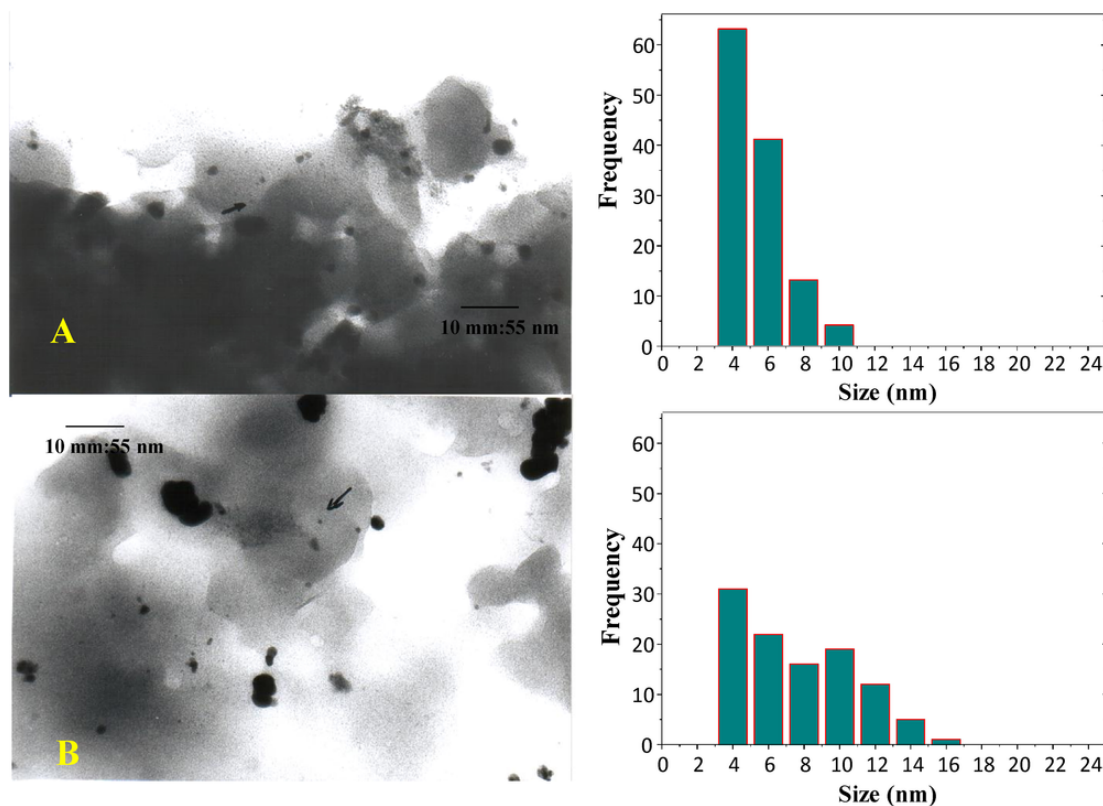


Fig. 3. TEM micrographs and particle size distribution of the Pd-Cu/WA30 catalyst. A: Fresh. B: Used in reaction (RIE experiment).

7.49 nm. These results clearly show that there was an increase in the metal particle size during the reaction. As it will be shown in Section 3.3, this change in the metal particle size led to an activity loss.

The change in dispersion during the reaction was also studied by CO chemisorption. The fresh Pd-Cu/WA30 catalyst had a dispersion of 30.8%. As reference, it is important to mention that the fresh monometallic Pd(2%)/WA30 catalyst had a dispersion of 43%. In the bimetallic catalyst, the CO chemisorption is affected by the interaction between the metals. Palladium chemisorbs CO at room temperature, while CO coverage on Cu(111) is negligible. The interaction between Cu and Pd modifies the electronic structure of the pure metals, moving the d-band centre position closer to the Fermi level, thus modifying the energy of the interaction with different adsorbates [40]. These results suggest that there might be an interaction between Pd and Cu, moreover taking into account that the TEM indicated that the mean particle size was small. After the reaction, the dispersion of the bimetallic catalyst decreased to 26%. There is a large uncertainty in the CO adsorption stoichiometry in a bimetallic catalyst such as Pd-Cu, therefore these values should only be used to compare trend of the changes that occur during the reaction.

The XRD results obtained with the fresh and used Pd-Cu/WA30 catalysts, the fresh Pd/WA30 and the WA30 resin, are shown in Fig. 4. The peak at 40.1° is characteristic of Pd⁰ (JCPDS card # 05-0681), and can be clearly observed both in the fresh and deactivated catalysts. The wide peak displayed at low angles corresponds to the resin. The relative intensity of the peaks that corresponds to the Pd⁰ relative to the wide peak at low angle is higher in the case of the used Pd-Cu/WA30. This suggests that the Pd crystal size are bigger in this catalyst, in agreement with results obtained by CO chemisorptions and TEM analyses, that also showed that there was sinterization during the reaction. The peak at 46.6° corresponds to the (200) peak of Pd metal. The used Pd-Cu/WA30 catalyst showed a peak at 36° that

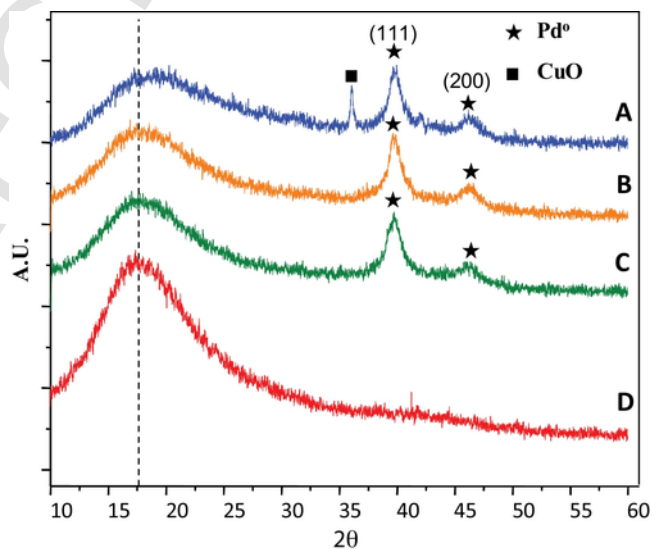


Fig. 4. XRD profiles. A: used Pd-Cu/WA30., B Fresh Pd-Cu/WA30, C: Pd(2%)/WA30, D: WA30 resin.

corresponds to CuO, while the fresh catalyst does not show this phase. This means that Cu is initially fully reduced and/or highly dispersed, and that it is partially oxidized and/or sinterized during the reaction, in agreement with the reaction mechanism originally proposed by Epron et al. [38]. Neyertz et al. [25] studied the Pd-Cu/resin catalysts by XPS, and found that even in the fresh catalyst a fraction of Cu was oxidized, while the XRD spectra did not show signals that corresponded to Cu species. In agreement with the present study,

these results indicated that initially the Cu is highly dispersed and presented both reduced and oxidized species. As catalyst deactivated, a part of CuO particles sintered, either on top of the Pd particles, or on the resin surface. Nevertheless, since the catalyst displays good activity for nitrate reduction, it is evident that enough amount of Cu remains on the surface or in close vicinity of Pd particles, thus participating in the bimetallic reaction mechanism. The mechanism by which the Cu forms large crystals of CuO that are observed in the XRD spectrum is a matter of further study.

The size of the Pd particles was estimated using the Scherrer's equation, and resulted to be 5.2 nm for the monometallic catalyst, and 5.7 and 6.4 nm for the fresh and used Pd-Cu/WA30 catalysts respectively. Using the TEM results and Eq. (10), the mean volume diameter were 6.8 and 10.8 nm for these two catalysts, in very good agreement with the XRD estimation.

These results clearly indicate that the metallic phase changes during the whole cycle, decreasing the dispersion and changing the level of interaction between Pd and Cu.

3.2. Reaction + ion exchange (RIE) – without competing ions

A monometallic Pd(2%)/resin catalyst was prepared, and its activity for nitrate reduction verified both in batch and continuous reactors. The conversion was zero in all cases, in agreement with previously reported data in many publications.

3.2.1. Effect of reaction variables

Fig. 5 shows the results obtained under different reaction conditions. It has to be emphasized that in the case of the catalyst used in this study, the decrease in the nitrate concentration in the reaction media is the combination of two different effects: the reaction and the ion exchange. The nitrates removal efficiency, the selectivity to nitrogen and the ammonium concentration at the reactor outlet are shown as a function of time. It is important to highlight that this removal efficiency is an apparent conversion, because a fraction of the nitrates that did not come out of the reactor, were just adsorbed in the resin. Nitrites were not detected at the reactor outlet during all the experiment. The water flow rate was maintained constant at 2.73 mL/min. There are 4 different zones in Fig. 5. In the first one (Zone 1) the hydrogen flow rate was 1.0 mL/min. The nitrates concentration at the re-

actor outlet was zero in this zone, due to the combined effect of reaction and ion exchange between the nitrates and the chlorides initially present in the resin. The initial ammonium concentration was high, but it rapidly decreased. This behaviour is due to the fact that the resin contains tertiary amines as functional groups that slowly decompose by the Hofmann's reaction, being this reaction the cause of the odour released by the strong base anion exchange resins. At the beginning of the reaction, these groups are washed from the resin and detected in the reactor outlet. Then, the ammonium ions concentration stabilized in an average value of 0.55 mg/L which is slightly higher than the limit fixed by the WHO standards (0.5 mg/L), indicated in Fig. 5 as the 'Ammonium Limit'.

Lemaigen et al. [39] proposed a mechanism for nitrate reduction on bimetallic catalysts. According to these authors, the nitrate is reduced to nitrite on the bimetallic sites, and then the nitrites are reduced on the monometallic sites. As above mentioned, during this process there were no nitrites at the reactor outlet. This means that once the nitrites were produced rapidly migrated to the monometallic sites where they were converted, or alternatively the nitrites were reabsorbed in the resin.

In the second zone of Fig. 5, the hydrogen flow rate was increased to 2.2 mL/min while keeping the other variables constant. Since the resin was not saturated with nitrates, the nitrates removal efficiency was 100%. When the treated volume was 4 L, the nitrates break through and appeared at the reactor outlet, because the resin was already saturated with nitrates. The fraction of nitrates eliminated from the water decreased to 45%, and stabilized in this value, without being possible to detect nitrites in the stream coming out of the reactor. This indicates that the nitrites were being reduced with a high reaction rate, and because of this, it was not possible to detect this compound in the product.

Another experiment was carried out, and stopped exactly at the end of zone 2, i.e. when the conversion was stabilized. In zones 3 and 4, the nitrates are eliminated from the water only by reaction (i.e. converted to nitrogen and ammonium); since the resin is already saturated with nitrates. The resin was treated with NaCl 20 g/L in order to elute the ions adsorbed in the resin. It was found that there were no nitrites in the eluted liquid. This demonstrated that the nitrites were being reduced before they were adsorbed in the resin.

The ammonium concentration slightly increased when the hydrogen flow was increased, reaching a value of 0.58 mg/L approximately. This lower selectivity to nitrogen upon an increase in the hydrogen flow rate was also observed by Hörold et al. [17].

In zone 3 the hydrogen flow rate was further increased up to 4.7 mL/min. The conversion did not change, but the ammonium concentration showed a significant increase up to 2.54 mg/L, which is almost 5 times higher than the value specified in the standards. Consequently, in this zone the selectivity to N₂ displayed a clear decrease, as shown in Fig. 5.

In zone 4 the hydrogen flow rate was lowered to 0.3 mL/min. It can be observed that the nitrates conversion did not change, but the ammonium concentration decreased to an average value of 0.24 mg/L, and no nitrites appeared in the product, therefore, the selectivity to N₂ increased again.

This experiment is very important in order to understand the nitrates reduction mechanism, and also to properly design a process to reduce the nitrates with a high selectivity to nitrogen. The results show that the hydrogen flow rate does not affect the rate of the nitrate reduction reaction which occurs on the bimetallic sites, but it strongly affects the nitrites reduction on the monometallic sites. This can be explained taking into account that hydrogen chemisorbs better on monometallic Pd than on the bimetallic system, and because of

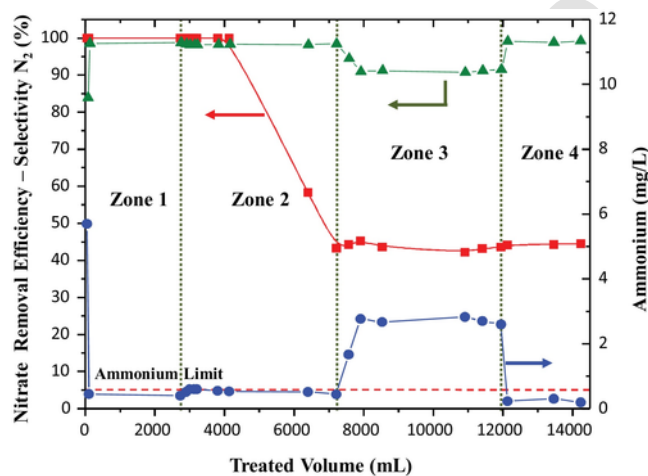


Fig. 5. Nitrate removal efficiency (■), nitrogen selectivity (▲) and ammonium generation (●). Water flowrate: 2.73 mL/min. Hydrogen flow: 1- 1.0 mL/min; 2- 2.2 mL/min; 3- 4.7 mL/min; 4- 0.3 mL/min.

this, the hydrogen flow rate has a major impact in the reduction of nitrites increasing the ammonium concentration in the treated water.

The water collected at the reactor output was analyzed by AA spectrometry to determine if there was leaching of Pd and Cu during the reaction. These metals were not detected in the water, meaning that the loss of metals from the catalyst during the reaction was below the detection limit of the AA spectrometry technique. Same result was obtained in all the experiments described in this work.

3.2.2. Effect of the acidifying agent

Table 1 shows results obtained using HCl or CO₂ to adjust the pH of the reaction media, compared with the results obtained without controlling the pH. The lowest selectivity to nitrogen was obtained when the pH was not adjusted, while when using HCl it was improved, but the ammonium concentration at the reactor outlet was too high. When using water saturated with CO₂, the inlet pH was higher than in the case of using HCl, but due to the buffer effect caused by the CO₂ the final pH was lower, and consequently, lower concentration of ammonium was produced, in agreement with Al Bahri et al. [19]. Therefore, it is very important to have into account, that in a plug-flow fixed bed reactor, the acidification with a buffer is necessary in order to obtain high selectivity to nitrogen.

3.2.3. Reaction + ion exchange vs. ion exchange

These experiments had the objective of comparing results obtained when reaction and ion exchange coexists with those obtained when only the ion exchange takes place. The experiment named as Reaction + Ion Exchange was carried out using water saturated with CO₂ with a nitrate concentration of 96.1 mg/L, 0.3 mL/min of hydrogen, and a flow of water of 2.6 mL/min. In other experiment, named Ion Exchange, the same conditions were used, except that no hydrogen was fed. Therefore, the main difference between these two experiments is that in the second one, there was no reduction reaction. Fig. 6 shows the results of the breakthrough curves.

The nitrates elimination during the Ion Exchange experiment shows three zones. In the first part (zone 1) there was a complete elimination of nitrates from the water. Then, the resin became saturated and nitrates are found in the water coming out of the reactor, and finally no nitrates were adsorbed by the resin.

The breakthrough curve obtained when the reaction takes place (Reaction + Ion Exchange) is similar in zone 1 to that obtained when only the Ion Exchange takes place. This means that during this stage, the nitrates reduction is practically zero, and most of these ions are adsorbed by the resin. The mass balance carried out as described in Section 2.3 shows that in the experiment shown in Fig. 6, the amount of nitrates that was reduced in the first part (zone 1) was 15.6%.

The experimental curve (Reaction + Ion Exchange) shows three characteristics zones. In the first one, 15.6% of the nitrates were transformed in N₂ and the rest (84.4%) was exchanged with chlorides ion present in the resin. In the second zone the resin gradually saturated although both phenomena (reaction and ion exchange) took place. This can be also inferred comparing the slopes of the curves obtained in both cases, since in the case that there was only Ion Exchange, the slope was higher than in the case in which (Reaction + Ion

Table 1
pH at the reactor outlet, ammonium generation and selectivity to nitrogen, with different initial pH.

Acidifying Agent	Inlet pH	Outlet pH	NH ₄ ⁺ Average Concentration (mg/L)	Nitrogen Selectivity (%)
CO ₂	3.9	5.22	0.24	98.8
Without acid	5.05	7.23	3.12	86.2
HCl	3.30	6.77	2.5	89.5

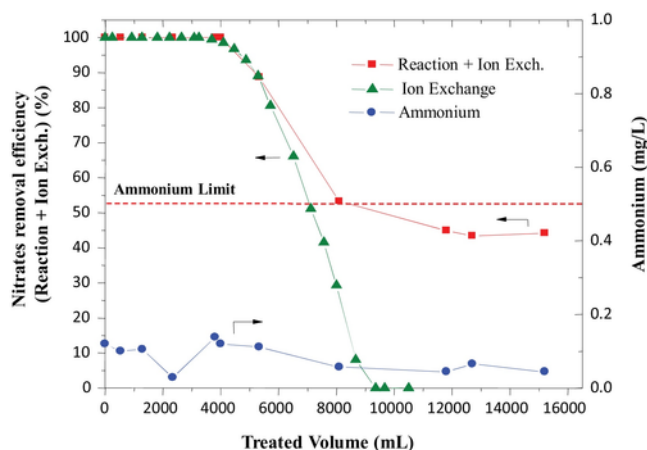


Fig. 6. Comparison of Ion Exchange and (Reaction + Ion Exchange) processes, without competing ions in the system. Nitrate initial concentration: 96.1 mg/L, H₂ flow rate: 0.3 mL/min (only in the RIE experiment), water flow rate: 2.6 mL/min.

Exchange) occurred. In the third zone, the nitrates elimination stabilized in 45%, and was due to the reduction.

The conversion due to chemical reaction increased from the 15.6% in the first zone to 45% in the third one. This is because in zone 1 at the beginning of the experiment, only a small fraction of the catalytic bed was occupied by nitrates, and the conversion occurred in this region, reaching an average value of 15.6%. As the fraction of the resin saturated with nitrates increased and reached the whole bed, the nitrates that enter the reactor can react with hydrogen on the metal sites all along the bed, thus increasing the conversion to 45%.

The ammonium concentration at the reactor outlet was below 0.2 mg/L during all the experiment. The first point shows a low ammonium concentration, because in this experiment the resin was washed with distilled water before starting the experiment, thus eliminating the ammonium ions that appeared in the system due to the decomposition of the functional groups of the resin, as shown in Fig. 5.

3.3. Reaction + ion exchange – regeneration (RIE-R). Without competing ions

In order to eliminate the nitrates adsorbed in the resin, new processes were developed, as described in Sections 2.2.1 and 2.2.2, and called Reaction + Ion Exchange – Regeneration (RIE-R) and Ion Exchange – Regeneration (IE-R) [34].

The Pd-Cu/WA30 catalyst was used to process 16 L of water. During the Reaction + Ion Exchange stage, the conversion was stabilized in 45% and the ammonium mean concentration was 0.25 mgNH₄⁺/L, as shown in the previous section. After this step, the water flow was stopped, maintaining a hydrogen flow of 0.5 mL/min during 63 h. Afterwards, a NaCl solution was fed in order to elute the nitrates adsorbed in the resin and that were not converted during the regeneration. It was found that all the nitrates were reduced during the regeneration step; thus, the resin could be used in a new cycle. This is a very important result, because the water obtained during the reaction had nitrates and ammonium concentrations well below the maximum limits recommended by the WHO. The regeneration mechanism is explained in Section 3.7. All the cycle was repeated two more times, in order to verify the stability of the catalyst. Results are shown in Fig. 7. It can be observed that there is a small decrease in the nitrates conversion obtained in the third zone in each cycle. This indicates that there was deactivation of the metal sites in which the nitrates were reduced. As above described, the Pd metal particles suffered sinterization during the reaction, and this may be the reason of

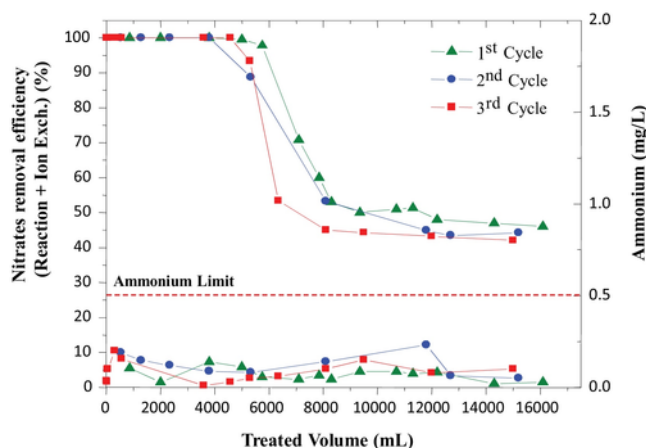


Fig. 7. Nitrates removal efficiency and ammonium concentration during the (Reaction + Ion Exchange) step during three consecutive cycles, without competing ions.

the small conversion decreased in successive cycles. The dispersion as determined by CO adsorption decreased from 30.8% in the fresh catalyst to 26% after the three reaction-regeneration cycles, representing 14% loss of dispersion. On the other hand, the conversion decreased from 47% to 42%, i.e. there was 11% loss of activity. There is a very good correlation between the loss of dispersion and activity loss. It is possible that a fraction of the exchange groups decomposed during the operation. However, the lower conversion obtained in zone 3 (once the resin was saturated with nitrates) was only due to a decrease in the activity of the metal function.

3.4. Reaction + ion exchange vs ion exchange. Effect of competing ions

Fig. 8 shows results obtained with the Pd-Cu/WA30 catalyst, using water doped with sulphates, bicarbonates, and chloride ions, which are the main anions present in natural water, under the conditions described in Section 2.2. The water flow rate was 2.76 mL/min and the hydrogen flow 1.2 mL/min. The exchange capacity was evaluated using the same conditions but without bubbling hydrogen.

The nitrates removal efficiency curves in both cases (Ion Exchange and Reaction + Ion Exchange) display the same zones as those described in Fig. 6. However, the volume of water treated obtaining 100% elimination of nitrates in the presence of competing ions, was

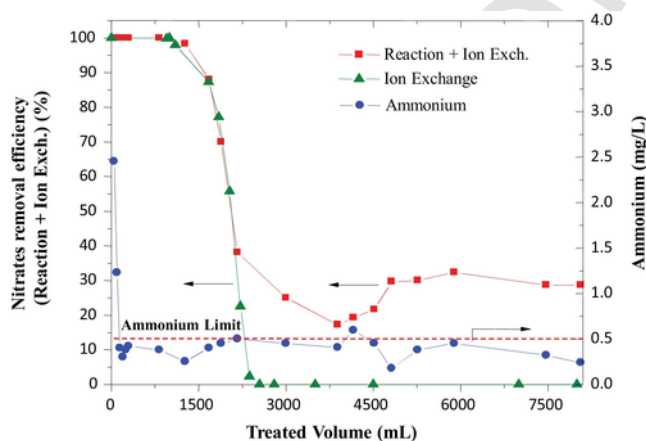


Fig. 8. Comparison of Ion Exchange and (Reaction + Ion Exchange) processes, with competing ions.

significantly lower. During the Ion Exchange, at the end of zone 1 the total amount of nitrates eliminated from the water stream was 13.7 mg $\text{NO}_3^-/\text{mL}_{\text{cat}}$. On the other hand, in the experiment Reaction + Ion Exchange, the amount of nitrates eliminated was 16.1 mg $\text{NO}_3^-/\text{mL}_{\text{cat}}$. These values are lower than those shown in Fig. 6 (46.74 mg $\text{NO}_3^-/\text{mL}_{\text{cat}}$ y 55.4 mg $\text{NO}_3^-/\text{mL}_{\text{cat}}$ respectively). Note that the volume of water that was treated in this case (without competing ions) was approximately 4 L (Fig. 6), while in the case of having the competing ions, only 1.5 L approximately was treated before the nitrates appeared at the reactor outlet. This is due to the fact that the competing ions (sulphates, bicarbonates and chloride) are also adsorbed in the resin, thus decreasing the fraction of nitrates eliminated from the water by ion-exchange. In addition, it was possible to calculate the percentage of elimination of nitrates by chemical reaction in zone 1 of Fig. 8, resulting to be 14.3%, value very similar to that obtained when no competing ions were present (15.2%).

The slope of the nitrates elimination curves in zone 2 (Fig. 8) are similar at the beginning, and then as the resins get saturated the slope of the curve that corresponds to the Ion Exchange process is higher than in the Reaction + Ion exchange, which is a similar behaviour to that previously shown in the case in which there were no competing ions. It can be observed in Fig. 8 that there is a minimum in the nitrates elimination at approximately 20%. Afterwards, the fraction of nitrates eliminated from the water stream stabilized at 30%. This might be due to the dynamic of the system, in which the pseudo-steady state was reached once the full catalytic bed was equilibrated with the actual ions concentrations present in the liquid phase. These concentrations changes since the nitrates reduction varies as the resin is gradually saturated with nitrates. The nitrates conversion stabilizes in 30% approximately, which is lower than the value obtained without competing ions (45%). This decrease in the conversion may be attributed to two factors: the lower pH obtained in the nitrates solution at the reactor inlet (pH = 5.3 in the case of having competing ions, and 3.9 without competing ions, Table 1), or to the adsorption of these ions on Pd, thus decreasing the number of available active sites.

Finally, in the presence of competing ions the selectivity to nitrogen is lower. Even though the nitrites were not detected, the ammonium formation was higher (compare Figs. 6 and 8) mainly due to the higher pH in the inlet water in the case of having competing ions.

It can be concluded that it is possible to catalytically remove nitrates from water using the Pd (2%)-Cu (0.5%)/WA30 catalyst in a fixed bed reactor, even in the presence of competing ions in the water, and with very high selectivity.

3.5. Reaction + ion exchange – regeneration (RIE-R). With competing ions

The experimental variables for this alternative are presented in Section 2.2.1. The water and hydrogen flow rates were 2.76 and 1.2 mL/min respectively. During the (Reaction + Ion Exchange), the conversion stabilized in 30%, as shown in Fig. 8, with an average value of ammonium concentration of 0.45 mg NH_4^+/L . After this operation, the catalytic bed was regenerated. The feed was stopped maintaining the hydrogen flow of 1 mL/min during 63 h. Then, a NaCl solution was used to elute the non-converted ions, being possible to determine that the nitrates were fully converted during the regeneration. Therefore, the presence of competing ions did not affect the regeneration step.

3.5.1. RIE-R process: regeneration optimization

The effect of the regeneration time on the effectiveness of the RIE-R process was studied. Water containing nitrates, bicarbonates,

sulphates and chlorides was flowed through the catalyst bed at 2.6 mL/min, maintaining a hydrogen flowrate of 3.5 mL/min. A total water volume of 2.5 L was processed, and afterwards the catalyst was regenerated using a hydrogen flowrate of 1 mL/min. The regeneration times used were 14, 28, 48, 55 and 63 h. The average ammonium concentration obtained in these five RIE-R experiments was 0.38 mg/L. It is important to emphasize that the same catalyst was used in this sequence of 5 reaction-regeneration cycles. Results are shown in Table 2. Increasing the regeneration time increases the fraction of nitrates eliminated from the resin, being necessary approximately 60 h to fully reduce the nitrates. However, in only 14 h, 80% of the nitrates retained in the resin at the end of the Reaction + Ion Exchange stage were reduced. These data makes it possible to optimize the whole process adjusting the regeneration time and the volume of water that can be treated during the reaction.

3.6. Ion exchange – regeneration (IER)

The conditions used in this process [34] are presented in Section 2.2.2. The Ion Exchange step processed 3.1 L of water containing the competing ions. Afterwards, the regeneration was carried out using 1 mL/min of hydrogen during 63 h. The fraction of nitrates reduced during this treatment was 36.7% of the nitrates present in the resin at the end of the Exchange step. This fraction was calculated as described in Section 2.3. This conversion was significantly lower than that obtained in the RIE-R process, in which in 63 h 100% of the nitrates were eliminated. A shorter regeneration time of 28 h was also used in another experiment, obtaining that only 19.2% of the nitrates present in the catalyst were eliminated. This value is also lower than the corresponding fraction obtained during the RIE-R process that was 86.5% (Table 2). This can be due to several factors. First, at the beginning of the regeneration in the RIE-R process, there is a profile of OH⁻ ions along the bed generated by the nitrates reduction during the (Reaction + Ion Exchange) step. As it will be discussed in Section 3.7, these ions have an important role during the resin regeneration. On the other hand, during the (Reaction + Ion Exchange) step, hydrogen is fed to the reactor during the whole cycle, thus contributing to maintain the metals fully reduced.

3.7. Regeneration mechanism

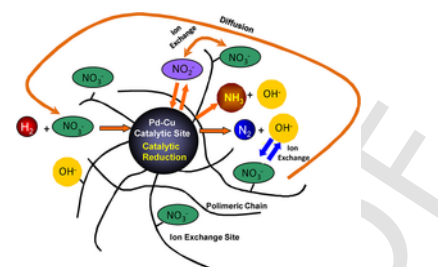
Scheme 1 shows the proposed regeneration mechanism. At the beginning of the regeneration, a high fraction of nitrates are present in the ion exchange sites in the resin, while a low fraction is in the liquid phase and chemisorbed on the Pd-Cu bimetallic sites. The nitrates ions adsorbed in the resin can not be directly reduced, since they are not in contact with the active sites of the catalyst. When the hydrogen is fed, the nitrates present in the liquid reacts on the Pd-Cu sites, forming OH⁻ ions during the reduction. These OH⁻ ions are then exchanged with the ions adsorbed in the resin, thus releasing nitrates that can be reduced on the metal sites.

The pH of the NaCl solution used in the nitrates elution at the end of the regeneration was strongly basic. Even when the bed was purged with distilled water after the regeneration, the pH of the NaCl solu-

Table 2

Percentage of nitrates eliminated as a function of regeneration time.

Regeneration Time (h)	% Nitrates Eliminated
14	80.0
28	86.5
48	92.3
55	96.8
63	100



Scheme 1. Catalyst regeneratin mechanism.

tion did not change. This demonstrates that the resin contains a high concentration of OH⁻ ions exchanged during the regeneration process. Nitrites, formed by nitrate reduction, may desorb from the active site and then exchange with an anion (e.g. nitrate) pre-adsorbed in the resin, or the nitrite may be re-adsorbed on an active site and be reduced to ammonium or nitrogen. Experimentally, it was found that nitrites were not present after the regeneration, what indicates that the main path for nitrites is a rapid reduction, before being readsorbed in the resin.

4. Conclusions

The process named (Reaction + Ion Exchange) – Regeneration (RIE-R) for the purification of water contaminated with nitrates using the Pd(2%)-Cu(0.5%)/WA30 catalyst showed excellent results, making it possible to eliminate 100% of the nitrates with a final ammonium concentration below 0.5 mg/L, which is the maximum limit allowed by the WHO. During the (Reaction + Ion Exchange) step, both the hydrogen flowrate and the pH gradient along the catalytic bed are fundamental variables that affect the nitrates conversion and the selectivity to nitrogen, independently if there are competing ions in the solution or not.

The regeneration time to transform 100% of the nitrates adsorbed in the resin was 63 h, although in 28 h, 86% of the nitrates can be reduced. This is very important, because makes it possible to scale-up the process.

The presence of competing ions does not significantly affect the regeneration step. The best conversion and selectivity results were obtained using CO₂ as acidifying agent, because it forms a buffer, thus regulating the pH along the bed and inside the pores.

The Pd is deposited in egg-shell geometry. It was determined that during the reaction the Pd sinters and migrates towards the external surface of the resin particle. This leads to an activity loss which is similar to the dispersion decrease.

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