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The use of Pd catalysts on carbon-based structured materials for the catalytic hydrogenation of bromates in different types of water.

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Keywords: bromate reduction, Pd-catalysts, catalytic hydrogenation, natural water, industrial wastewater.

Abstract

The aim of this work is to study the activity of new Pd catalysts, supported on two different nano structured carbon materials, for bromate catalytic hydrogenation. The influence of the support has been studied, obtaining the best results with a palladium catalyst supported on carbon nanofibers (CNF) grown in sintered metal fibers (SMF). The results have shown the importance of the catalyst support in order to minimize the mass-transfer limitations ensuring an efficient catalyst use. In this way the most active catalysts are those with a mesoporous structure containing high dispersed Pd nanoparticles. The activity of this catalyst for bromate reduction has been tested in different types of water, namely, distilled water, natural water and industrial wastewater. It has been shown that the catalyst activity depends on the water matrix and bromate reduction rate depends on the hydrogen partial pressure. The potential use of the catalyst has been studied in a continuous reactor. It has been observed that the catalyst is active without any important deactivation at least during 100 hours of reaction, but is necessary to avoid salt precipitation and plugging problems.

1. Introduction

The increased demand of water purity in both industrial and domestic use leads to a strict regulation of the water pollutants. In this way, the presence of undesirable and toxic by-products due to water disinfection has to be controlled. Bromate is an oxyhalid disinfection byproduct that is formed during the ozonation of drinking water from bromide-containing sources [1-4]. It can be also formed during the generation and use of hypochlorite solutions in drinking or wastewater treatment plants [1, 5]. The World Health Organization is regulating the bromate levels (provisional guideline value: 0.01 mg/L) in drinking water since the International Agency for Research on Cancer has classified bromate as a possibly carcinogenic substance [6]. This value has been established in USA, European Union and Japan as the maximum allowed in drinking water and for this reason, some water sources have been dumped because the unusually high levels of bromate [7, 8].

There are different techniques for bromate removal from water like ultraviolet irradiation, photocatalytic decomposition, arc discharge, coagulation, biological remediation, adsorption, chemical reduction, membrane processes or ion exchange [1, 5, 7, 9-11]. Nevertheless, these techniques present some limitations due to the necessary post-treatment of the effluent or to the high exploitation cost. Therefore, it is necessary to find an alternative technology. This alternative can be the reduction of bromates to bromides in an aqueous solution. This reduction can be done through a stoichiometric reaction with an active metal, as zerovalent iron [7, 12] or with Fe-Al layered double hydroxides [8] and by a catalytic reaction. In this way, Dung et al [13] proposed that $\text{RuO}_2/\text{TiO}_2$ particles can catalyze the reduction of bromates to bromine and to bromide while oxidizing the water to form oxygen. Mills et al [4] showed that the presence in water of an easily oxidable organic compound as methanol, ethanol or propanol enhances the rate of bromate reduction when using ruthenium

catalyst. The effect of Ru precursor and Ru loading on the catalytic activity of Ru catalysts supported on activated carbon was studied by Dong et al [14] and recently Thakur et al [15] prepared a very active Ru/CNF catalyst active for the bromate reduction in silicon-based structured microreactors.

Another option is the catalytic hydrogenation of bromates. This reaction has been broadly studied for the reductive transformation of a number of priority drinking water contaminants as nitrate, nitrite, chlorate, perchlorate, N-nitrosamines and a number of halogenated alkanes, alkenes and aromatics [16]. In these reactions usually monometallic and bimetallic Pd-based catalysts have been used, due to the hydrogen activation properties of Pd [16]. Considering the oxidative nature of bromate it is reasonable to hypothesize that the catalytic hydrogenation is also an effective method for the reductive removal of aqueous bromates, as it has been shown recently by Chen et al [17]. They compare under different reaction conditions, the activity for bromate reduction of Pd and Pt catalysts supported on different materials, showing that catalytic hydrogenation can be used as a potential treatment technique for bromate removal in drinking water. To the best of our knowledge, besides of this work there are not more papers studying the catalytic hydrogenation of bromates.

The objective of this work is to extend the study of this reaction to different types of water, but using new Pd catalysts supported on nano structured carbon materials, as activated carbon fibers and sintered metal fibers coated by carbon nanofibers. Carbon nanofibers and carbon nanotubes have recently gained much interest in a series of applications due to their unique properties [18, 19]. The catalytic activity of these materials has been studied in continuous and batch reactors using distilled water, natural water and industrial wastewater containing bromates.

2. Experimental

Activated Carbon Fibers (ACF) in the form of woven fabrics (AW1101, KoTHmex, Taiwan Carbon Technology Co.) were used as a catalyst support. Before metal deposition, ACF were boiled in 15% HNO₃ for 1 h, then rinsed with water and dried in air.

Other catalyst supports were synthesized on the base of Inconel sintered metal fibers (SMF), (Bekipor ST20AL3, with thickness of 0.49 mm, elementary fibre diameter - 8 μm). This material was used as a growth-media for carbon nanofibers (CNF) and the preparation details are described elsewhere [20]. The obtained 5% CNF/SMF composites were activated in a boiling 30% H₂O₂ during 1 h, treated ultrasonically in ethanol using a Bransonic ultrasonic cleaner, then rinsed with water and dried in air.

The Pd catalysts based on ACF and CNF/SMF were prepared by palladium deposition, either via adsorption on ACF from a Na₂PdCl₄ aqueous solution or by the incipient wetness impregnation of CNF/SMF by a Pd(CH₃COO)₂ solution in acetonitrile. After drying, the catalysts were reduced by H₂ at 300°C for 2 h.

The catalysts were tested in a continuous and in a batch system. The batch experiments were carried out at room temperature (23°C) and atmospheric pressure in a discontinuous stirred tank reactor of one liter volume. The reactor was equipped with a mechanical Teflon stirrer with a rotation rate of 900 rpm. The continuous reactions were carried out with a 5 ml/min flow of water containing bromates in a plug flow reactor (inner diameter – 1.5 cm, length 14.5 cm) operating as a conventional fixed bed reactor. The experiments were also made at room temperature and atmospheric pressure. Before reaction, the solution was bubbled with hydrogen during 1 h in order to pre-saturate the solution with hydrogen. During the reaction a continuous hydrogen flow of 250 cm³/min was flown through the reactor. Different types of water (distilled water, natural water and industrial wastewater) containing bromates were used for the experiments. The bromates reduction progress was

mainly followed by withdrawing small aliquots for ionometric measurements of bromide concentration. Nevertheless in the most interesting reactions (those made with natural and industrial water containing bromates) both bromates and bromides were measured. In these reactions we observed that the moles of reacted bromates were the same than the moles of formed bromides, indicating that the measurement of bromides is an adequate procedure to follow the progress of the reaction.

The metal loading of the synthesized catalysts was measured by atomic absorption spectroscopy using a Shimadzu AA-6650 spectrophotometer with an air–acetylene flame.

The specific surface areas (SSA) of the carbon based composites were measured by adsorption–desorption of saturated nitrogen at -196°C using a Sorptomatic 1990 instrument (Carlo Erba). The structured catalysts were cut into slices and placed in the reactor for measurement. The SSA was calculated employing the BET method. The Dollimore/Heal approach was applied to calculate the pore volume and size.

SEM analysis were carried out with a SEM EDX Hitachi S-3400 N microscope with variable pressure up to 270 Pa and with an analyzer EDX Röntec X Flash de Si(Li). Transmission electron microscopy (TEM) images were obtained using a JEOL 2010F electron microscope equipped with a field emission gun. For sample preparation, the coating retrieved from the catalyst was dispersed in ethanol by ultrasonication.

XPS spectra were recorded ex-situ, before and after reaction, with an ESCAPlus Omnicrom system equipped with an Al $K\alpha$ radiation source to excite the sample. Calibration of the instrument was done with Ag $3d_{5/2}$ line at 368.27eV. All measurements were performed under UHV, better than 10^{-10} Torr. Internal referencing of spectrometer energies was made using the dominating C 1s peak of the support at 284.6 eV and Al 2p, at 74.3eV. The program

used to fit the spectra was CASA XPS using a baseline Shirley. The ratio of reduced metal to total metal was calculated from XPS deconvolution.

3. Results and discussion

3.1 Characterization

The catalysts were characterized by different techniques before and after reaction. The specific surface area of ACF catalysts was $\sim 950 \text{ m}^2/\text{g}$ and the specific pore volume was equal to $0.58 \text{ cm}^3/\text{g}$. The ACF pore network is formed by short pores with a narrow pore size distribution with most of them having a diameter $< 2 \text{ nm}$. On the contrary, the specific surface area of SMF is negligible and it is equal to the geometrical outer surface area of their constituent metal filaments ($\text{SSA}_{\text{SMF}} \sim 0.5 \text{ m}^2/\text{g}$). A thin porous layer of CNF created on the fiber surface increases the SSA of the formed CNF/SMF composite and a 5 wt% CNF loading on SMF gives a SSA of $\sim 15 \text{ m}^2/\text{g}$. The average thickness of the CNF layer as measured by SEM was found to be $\sim 1.5 \mu\text{m}$. The diameter of an elementary carbon nanofiber was $\sim 60 \text{ nm}$. The calculated specific surface area per gram of CNF for the 5% CNF/SMF samples was $\sim 260 \text{ m}^2/\text{g}_{\text{CNF}}$ and the specific pore volume was equal to $0.62 \text{ cm}^3/\text{g}_{\text{CNF}}$. The hysteresis loop formed by CNF/SMF adsorption-desorption isotherms corresponds to the type IV behavior indicating that the material is mostly mesoporous. The pore size distribution was found bimodal with maxima at 20 and 85 nm [21].

Metal nanoparticles (NPs) on used catalysts were characterized *via* Transmission Electron Microscopy. STEM images of Pd^0 NPs supported on ACF and on CNF/SMF, after reaction, are shown in Figure 1. It can be seen that Pd^0 NPs are highly dispersed and homogeneously distributed over the ACF and CNF/SMF surface. The mean particle size was smaller for Pd/ACF than for Pd/CNF/SMF. Also, the particle size distribution was narrower for Pd/ACF

(between 1-3 nm) than for Pd/CNF/SMF (between 1-5 nm). These differences can be related to the different support surface morphology.

Figure 2a and 2b displays the X-ray photoelectronic profiles of survey and Pd 3d core level of the Pd catalysts supported on ACF and CNF/SMF as prepared and the later also after reaction with different types of water. The measurements were performed ex-situ, that is, the samples were exposed to atmospheric conditions before being introduced in the XPS chamber. The core level Pd 3d_{5/2} signal shows a contribution at 335.7-336.0 eV corresponding to Pd⁰ and another one at 336.8-337.7 eV corresponding to PdO [22]. The quantification of these signals is displayed in Table 1. The Pd/C ratio is one order of magnitude smaller for Pd/ACF than for Pd/CNF/SMF indicating that Pd is more superficial on the later while it is inside the micropores on the former. Since XPS probes the outermost surface, nanoparticles deep into the micropores are not detected. As it can be seen, in all the cases the Pd/C ratio of the Pd/CNF/SMF catalysts decreases after reaction, but the reason for this is not clear yet.

The fraction of reduced palladium is an indication of the tendency to reoxidation of the catalyst. The lower is this ratio the higher is the extent of metal reoxidation. The fraction of reduced palladium (Pd⁰) is substantially higher for the CNF/SMF catalyst than for the ACF catalyst. This is probably related to the more graphitic character of CNF/SMF that favors the delocalization of the π electrons on the graphene increasing the reducibility of the palladium nanoparticles. Nevertheless, it can be also attributed to the slightly smaller metal particle size of the Pd/ACF compared to the Pd/CNF/SMF that results in a higher electrodefficiency of the Pd/ACF, favoring the metal reoxidation on this catalyst. On the other hand, comparing the Pd⁰ fraction of the CNF/SMF catalyst, before and after reaction, it is observed that it slightly decreases after reaction. This suggests that some of the Pd⁰ sites have been additionally oxidized to Pd²⁺ under reaction conditions or that some electrowithdrawing species have been

deposited on the carbon during reaction favoring the metal reoxidation. Similar results were obtained in Pd-Sn catalysts supported on alumina used for the catalytic reduction of nitrates [23]. More significant is the shift of the core level Pd $3d_{5/2}$ signal (Figure 2b and Table 1) to higher binding energies, observed in the XPS spectrum of the Pd/CNF/SMF catalyst after reaction with industrial wastewater. This can be related with the deposition of some electropositive substances on the catalyst surface. In this way, the XPS spectra of the catalysts after reaction with natural and industrial water show two additional peaks at 348-351 eV (Figure 2b) corresponding to the $2p$ core level of Ca^{2+} . These peaks appear because the deposition of the calcium salts present in the water reaction on the catalyst surface.

3.2 Catalytic hydrogenation of bromates in a batch reactor

The activity of the (0,3 %wt) palladium catalysts supported on two types of nanostructured carbon materials is shown in figure 3. As it can be observed, the best results are obtained with the catalyst supported on CNF/SMF that is the catalyst that presents the highest reaction rate. Using this catalyst all bromates present in the water were reduced after 20 minutes of reaction. This gives an initial activity for the catalyst containing 0.3% Pd of $1.41 \text{ mM}_{\text{BrO}_3^-}/\text{g}_{\text{cat}}\cdot\text{h}$, that is a value similar to that obtained in [17], but in that case with a Pd catalyst containing 0.48% of Pd. If the activity of the Pd/CNF/SMF catalyst is normalized to the Pd content, it results in $470 \text{ mM}_{\text{BrO}_3^-}/\text{g}_{\text{Pd}}\cdot\text{h}$ with a TOF (reduction rate of bromate per mol of Pd) of 0.014 s^{-1} . On the other hand, for the catalyst supported on ACF a lower reaction rate was observed and it was not possible to remove completely the bromates of the liquid. The different reaction rate is probably related with the different porous structures of both materials. Microporous ACF based catalysts could have some mass transfer limitation within ACF micropores [21]. On the contrary, the CNF/SMF has a mesoporous structure and the products and reactants can easily diffuse from the catalyst surface to the bulk liquid. In

addition, in spite of the high palladium dispersion observed by STEM in both catalysts, Pd catalyst supported on CNF/SMF has a higher content of surface Pd⁰, as it was observed by XPS, favoring the hydrogen activation and as a consequence increasing the bromate reduction rate. This can be related with the presence of smaller metal clusters in the Pd/ACF that could be more susceptible to the (self)poisoning, deactivating the Pd/ACF catalyst.

The influence of the Pd content on the activity of the CNF/SMF catalysts was studied and the results obtained are presented in figure 4. As it can be seen, the carbon support (without palladium) removes some of the bromates present in the solution. This has been also observed by Dong et al. when using active carbon [14]. They showed that this support presents some capability to remove bromates in the same reaction at room temperature. The loading of 0.1% of Pd to the support results in a complete removal of bromates after 45 minutes of reaction. As it is expected, an additional increase of the palladium content (0.3%) produces an increase of the reaction rate, reducing all the bromates after 20 minutes of reaction. It should be pointed out that in both cases the same catalyst activity per mol of palladium was achieved. These results clearly indicate that metallic Pd provides the catalytic active sites which are fully used. In this way an increase in the Pd loading enhances the bromate hydrogenation because more reaction sites are available, being the role of the support to stabilize the reduced palladium active sites and to decrease the mass-transfer limitations. On the other hand a blank reaction without catalyst was made proving that the homogeneous reduction of bromates with hydrogen is not feasible at room temperature.

3.3 Catalytic hydrogenation of bromates in a continuous reactor

The activity of the 0.3%Pd/5%CNF/SMF catalyst was tested for the bromate hydrogenation reaction in a continuous system using a plug flow reactor. As it can be

observed in Figure 5, the catalyst activity is very stable in the continuous reactor, obtaining a bromate conversion of around 75-80% during the 45 hours of reaction, without any important deactivation of the catalyst. This can be explained by the stability of the Pd⁰ active sites on this support, as it was observed by XPS and STEM.

The influence of the hydrogen partial pressure, in the bromate reduction was studied in this system at room temperature. The results obtained are shown in Figure 6. As it can be seen, the conversion lineally decreases with the hydrogen partial pressure. We must consider that this is a three phase system and therefore hydrogen transport should be taken into account. Solubility of hydrogen in water at temperatures close to room temperature is in the Henry's region, and therefore the concentration of hydrogen in water phase is directly correlated to the hydrogen pressure applied on the system [24] and consequently the Henry coefficient of hydrogen solubility can be included into the kinetic constant of the reduction process. The direct relationship between the hydrogen partial pressure and the catalyst activity, indicates that the bromate reduction by catalytic hydrogenation over supported Pd catalysts is not only controlled by the adsorption of bromate in the catalyst surface, as it was suggested by Chen et al [17], but also by the hydrogen partial pressure.

In order to test the real possibilities of this catalyst for a commercial process, the activity of the Pd nanostructured catalyst for the bromate reduction was tested in a continuous reaction with natural water and with industrial wastewater containing both bromates. The water samples were supplied by VEOLIA and their compositions are reflected in Table 2. The results obtained with the natural water during 100 hours of reaction are shown in Figure 7. As it can be observed, the catalyst is active during almost 5 days of reaction, observing only a small deactivation during the experiment (from 75% conversion to 60%). Similar results were found [25, 26] in some papers studying an analogous reaction, i.e. the nitrate reduction. In those works, the slow deactivation of the catalyst was related with the deposition of different

salts present in natural water, on the catalyst surface that blocks the palladium active sites. The same mechanism could be responsible for the catalyst partial deactivation observed in this reaction. Nevertheless after 100 hours of reaction a 60% of bromate conversion is still obtained.

The results obtained with the industrial wastewater are shown in Figure 8. In this graph, the activity of the 0.3%Pd/5%CNF/SMF catalyst for the bromates hydrogenation in the industrial wastewater is shown together with the results obtained with natural water. As it can be seen, the catalyst is also active for the reduction of bromates in an industrial wastewater with a high alkalinity, conductivity and an important content of different species other than bromates (see Table 2). Nevertheless, since the beginning of the reaction, the bromate conversion obtained with this type of water is lower than that obtained with natural water, because the different initial bromate concentration and for the different composition of both types of water. Chen et al [17] have shown that the presence of other ions in the reaction media inhibits the bromate reduction, because they competitively adsorb on the active centers and this will be an important issue in the experiments made with the industrial water. Similar results have also been observed, when using water with a high conductivity, in different Pd catalysts used for the reduction of nitrates [25, 26]. Nevertheless, the main problem in this reaction was an operational problem, because due to the high calcium content of the water (1000 mg/L) and to the basic pH (pH=7.8 that did not change in the continuous reaction), important quantities of calcium salts (as determined by XPS) precipitated in different parts of the reactor and on the catalyst surface, plugging the system after seven hours of reaction. This can be avoided buffering the system at a pH of 6 with CO₂, as it is made in other reactions as the nitrate reduction reaction [27]. In addition, as it was shown in [17], the bromate reduction is pH-dependent and a decrease of the pH would lead to a higher reducibility of bromates and

to a higher catalytic activity. The results obtained in the bromate reduction when adding a mixture of H₂ and CO₂ in the reactor (pH of solution = 6) are shown in Figure 9. In these conditions, after achieving the steady state, there was not plugging of the reactor neither an important catalyst deactivation during the 80 hours of the experiment. Nevertheless, a lower conversion was obtained when using the gas mixture. As it was discussed above, this is due to the change of the hydrogen partial pressure. The decrease of the hydrogen partial pressure by a factor of two results in a decrease of the activity by the same factor. In this way to avoid the precipitation of calcium carbonate would be preferable, for instance, to add an acid solution than to add an acidic gas that decreases the hydrogen partial pressure.

Conclusions

Palladium catalysts supported on CNF/SMF have shown promising results in the removal of bromate from water via catalytic reduction using hydrogen as reductant. The results obtained show that this support minimizes the mass-transfer limitations, ensuring an efficient catalyst use. It has been observed that it is possible to reduce bromates contained in water with hydrogen using both batch and continuously operated mode, but bromate reduction depends on the hydrogen partial pressure. The catalyst stability was tested using distilled water, natural water and industrial wastewater containing bromates. It has been shown that it strongly depends on the type of water matrix. The best results were obtained with the distilled water containing bromates and the worst results were obtained for the industrial wastewater, with a high conductivity. Furthermore, it is necessary to avoid the precipitation of calcium salts in waters with a high alkalinity for an adequate performance. Taking all these precautions into consideration, the catalytic reduction of bromates is a feasible method for the reduction of bromates in order to comply with the environmental regulations.

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Caption to figures

Figure 1. STEM images of the Pd (0.3% wt) catalysts supported on (a) ACF and on (b) CNF/SMF, after reaction.

Figure 2. XPS (a) survey and (b) deconvolution of Pd 3d peaks of the, as prepared 0.3%Pd/ACF and 0.3%Pd/CNF/SMF catalysts and of the 0.3%Pd/CNF/SMF catalysts after reaction with different types of waters.

Figure 3. Catalytic hydrogenation of bromates in water using (\square) 0.3%Pd/ACF and (Δ) 0.3%Pd/CNF/SMF catalysts (discontinuous stirred tank reactor, distilled water with 50 ppm of bromates, 250 mL/min H₂, 600 mL of water, 1 g. of catalyst, room temperature).

Figure 4. Hydrogenation of bromates in water using (Δ) 0.3%Pd/5%CNF/SMF, (\oplus) 0.1%Pd/5%CNF/SMF, (\blacksquare) 5%CNF/SMF or (\ast) without catalyst (discontinuous stirred tank reactor, distilled water with 50 ppm of bromates, 250 mL/min H₂, 600 mL of water, 1 g. of catalyst, room temperature).

Figure 5. Catalytic hydrogenation of bromates in a continuous system (plug flow reactor, distilled water with 50 ppm of bromates, 250 mL/min H₂, 5 mL/min of water, 0.22 grams of 0.3%Pd/5%CNF/SMF, room temperature).

Figure 6. Influence of the hydrogen partial pressure in the catalytic reduction of bromates; (\diamond) H₂ partial pressure = 1 atm; (\square) H₂ partial pressure = 0.5 atm; (Δ) H₂ partial pressure = 0.25 atm (plug flow reactor, distilled water with 50 ppm of bromates, 5 mL/min of water, 250 mL/min of H₂+N₂ gas flow, room temperature, 0.22 grams of 0.3%Pd/5%CNF/SMF).

Figure 7. Catalytic hydrogenation of bromates in natural water (plug flow reactor, 5 mL/min of water, 250 mL/min H₂, 0.22 grams of 0.3%Pd/5%CNF/SMF, room temperature).

Figure 8. Catalytic hydrogenation of bromates in (□) industrial wastewater and in (◇) natural water (plug flow reactor, 5 mL/min of water, 250 mL/min H₂, 0.22 grams of 0.3%Pd/5%CNF/SMF, room temperature).

Figure 9. Catalytic hydrogenation of bromates in industrial wastewater (■) with a mixture of H₂ and CO₂ (250 mL/min H₂ + 250 mL/min CO₂) and (●) with H₂ (plug flow reactor, 5 mL/min of water, 250 mL/min H₂, 0.22 grams of 0.3%Pd/5%CNF/SMF, room temperature).

**The use of Pd catalysts on carbon-based structured materials for the catalytic
hydrogenation of bromates in different types of water.**

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Keywords: bromate reduction, Pd-catalysts, catalytic hydrogenation, natural water, industrial wastewater.

Abstract

The aim of this work is to study the activity of new Pd catalysts, supported on two different nano structured carbon materials, for bromate catalytic hydrogenation. The influence of the support has been studied, obtaining the best results with a palladium catalyst supported on carbon nanofibers (CNF) grown in sintered metal fibers (SMF). The results have shown the importance of the catalyst support in order to minimize the mass-transfer limitations ensuring an efficient catalyst use. In this way the most active catalysts are those with a mesoporous structure containing high dispersed Pd nanoparticles. The activity of this catalyst for bromate reduction has been tested in different types of water, namely, distilled water, natural water and industrial wastewater. It has been shown that the catalyst activity depends on the water matrix and bromate reduction rate depends on the hydrogen partial pressure. The potential use of the catalyst has been studied in a continuous reactor. It has been observed that the catalyst is active without any important deactivation at least during 100 hours of reaction, but is necessary to avoid salt precipitation and plugging problems.

1. Introduction

The increased demand of water purity in both industrial and domestic use leads to a strict regulation of the water pollutants. In this way, the presence of undesirable and toxic by-products due to water disinfection has to be controlled. Bromate is an oxyhalid disinfection byproduct that is formed during the ozonation of drinking water from bromide-containing sources [1-4]. It can be also formed during the generation and use of hypochlorite solutions in drinking or wastewater treatment plants [1, 5]. The World Health Organization is regulating the bromate levels (provisional guideline value: 0.01 mg/L) in drinking water since the International Agency for Research on Cancer has classified bromate as a possibly carcinogenic substance [6]. This value has been established in USA, European Union and Japan as the maximum allowed in drinking water and for this reason, some water sources have been dumped because the unusually high levels of bromate [7, 8].

There are different techniques for bromate removal from water like ultraviolet irradiation, photocatalytic decomposition, arc discharge, coagulation, biological remediation, adsorption, chemical reduction, membrane processes or ion exchange [1, 5, 7, 9-11]. Nevertheless, these techniques present some limitations due to the necessary post-treatment of the effluent or to the high exploitation cost. Therefore, it is necessary to find an alternative technology. This alternative can be the reduction of bromates to bromides in an aqueous solution. This reduction can be done through a stoichiometric reaction with an active metal, as zerovalent iron [7, 12] or with Fe-Al layered double hydroxides [8] and by a catalytic reaction. In this way, Gratzel and coworkers [13] proposed that $\text{RuO}_2/\text{TiO}_2$ particles can catalyze the reduction of bromates to bromine and to bromide while oxidizing the water to form oxygen. Mills et al [4] showed that the presence in water of an easily oxidable organic compound as methanol, ethanol or propanol enhances the rate of bromate reduction when

using ruthenium catalyst. The effect of Ru precursor and Ru loading on the catalytic activity of Ru catalysts supported on activated carbon was studied by Dong et al [14] and recently Seshan et al [15] prepared a very active Ru/CNF catalyst active for the bromate reduction in silicon-based structured microreactors.

Another option is the catalytic hydrogenation of bromates. This reaction has been broadly studied for the reductive transformation of a number of priority drinking water contaminants as nitrate, nitrite, chlorate, perchlorate, N-nitrosamines and a number of halogenated alkanes, alkenes and aromatics [16]. In these reactions usually monometallic and bimetallic Pd-based catalysts have been used, due to the hydrogen activation properties of Pd [16]. Considering the oxidative nature of bromate it is reasonable to hypothesize that the catalytic hydrogenation is also an effective method for the reductive removal of aqueous bromates, as it has been shown recently by Chen et al [17]. They compare under different reaction conditions, the activity for bromate reduction of Pd and Pt catalysts supported on different materials, showing that catalytic hydrogenation can be used as a potential treatment technique for bromate removal in drinking water. To the best of our knowledge, besides of this work there are not more papers studying the catalytic hydrogenation of bromates.

The objective of this work is to extend the study of this reaction to different types of water, but using new Pd catalysts supported on nano structured carbon materials, as activated carbon fibers and sintered metal fibers coated by carbon nanofibers. Carbon nanofibers and carbon nanotubes have recently gained much interest in a series of applications due to their unique properties [18, 19]. The catalytic activity of these materials has been studied in continuous and batch reactors using distilled water, natural water and industrial wastewater containing bromates.

2. Experimental

Activated Carbon Fibers (ACF) in the form of woven fabrics (AW1101, KoTHmex, Taiwan Carbon Technology Co.) were used as a catalyst support. Before metal deposition, ACF were boiled in 15% HNO₃ for 1 h, then rinsed with water and dried in air.

Other catalyst supports were synthesized on the base of Inconel sintered metal fibers (SMF), (Bekipor ST20AL3, with thickness of 0.49 mm, elementary fibre diameter - 8 μm). This material was used as a growth-media for carbon nanofibers (CNF) and the preparation details are described elsewhere [20]. The obtained 5% CNF/SMF composites were activated in a boiling 30% H₂O₂ during 1 h, treated ultrasonically in ethanol using a Bransonic ultrasonic cleaner, then rinsed with water and dried in air.

The Pd catalysts based on ACF and CNF/SMF were prepared by palladium deposition, either via adsorption on ACF from a Na₂PdCl₄ aqueous solution or by the incipient wetness impregnation of CNF/SMF by a Pd(CH₃COO)₂ solution in acetonitrile. After drying, the catalysts were reduced by H₂ at 300°C for 2 h.

The catalysts were tested in a continuous and in a batch system. The batch experiments were carried out in a discontinuous stirred tank reactor of one liter volume. The reactor was equipped with a mechanical Teflon stirrer with a rotation rate of 900 rpm. The continuous reactions were carried out with a 5 ml/min flow of water containing bromates in a plug flow reactor (inner diameter – 1.5 cm, length 14.5 cm) operating as a conventional fixed bed reactor. The experiments were made at room temperature and atmospheric pressure. Before reaction, the solution was bubbled with hydrogen during 1 h in order to pre-saturate the solution with hydrogen. During the reaction a continuous hydrogen flow of 250 cm³/min was flown through the solution. Different types of water containing bromates were used for the experiments. The bromates reduction progress was followed by withdrawing small aliquots for ionometric measurements of bromide concentration.

The metal loading of the synthesized catalysts was measured by atomic absorption spectroscopy using a Shimadzu AA-6650 spectrophotometer with an air–acetylene flame.

The specific surface areas (SSA) of the carbon based composites were measured by adsorption–desorption of saturated nitrogen at -196°C using a Sorptomatic 1990 instrument (Carlo Erba). The structured catalysts were cut into slices and placed in the reactor for measurement. The SSA was calculated employing the BET method. The Dollimore/Heal approach was applied to calculate the pore volume and size.

SEM analysis were carried out with a SEM EDX Hitachi S-3400 N microscope with variable pressure up to 270 Pa and with an analyzer EDX Röntec X Flash de Si(Li). Transmission electron microscopy (TEM) images were obtained using a JEOL 2010F electron microscope equipped with a field emission gun. For sample preparation, the coating retrieved from the catalyst was dispersed in ethanol by ultrasonication.

XPS spectra were recorded with an ESCAPlus Omnicrom system equipped with an Al $K\alpha$ radiation source to excite the sample. Calibration of the instrument was done with Ag $3d_{5/2}$ line at 368.27eV. All measurements were performed under UHV, better than 10^{-10} Torr. Internal referencing of spectrometer energies was made using the dominating C 1s peak of the support at 284.6 eV and Al 2p, at 74.3eV. The program used to fit the spectra was CASA XPS using a baseline Shirley. The ratio of reduced metal to total metal was calculated from XPS deconvolution.

3. Results and discussion

3.1 Characterization

The catalysts were characterized by different techniques before and after reaction. The specific surface area of ACF catalysts was $\sim 950\text{ m}^2/\text{g}$ and the specific pore volume was equal

to $0.58 \text{ cm}^3/\text{g}$. The ACF pore network is formed by short pores with a narrow pore size distribution with most of them having a diameter $<2 \text{ nm}$. On the contrary, the specific surface area of SMF is negligible and it is equal to the geometrical outer surface area of their constituent metal filaments ($\text{SSA}_{\text{SMF}} \sim 0.5 \text{ m}^2/\text{g}$). A thin porous layer of CNF created on the fiber surface increases the SSA of the formed CNF/SMF composite and a 5 wt% CNF loading on SMF gives a SSA of $\sim 15 \text{ m}^2/\text{g}$. The average thickness of the CNF layer as measured by SEM was found to be $\sim 1.5 \mu\text{m}$. The diameter of an elementary carbon nanofiber was $\sim 60 \text{ nm}$. The calculated specific surface area per gram of CNF for the 5% CNF/SMF samples was $\sim 260 \text{ m}^2/\text{g}_{\text{CNF}}$ and the specific pore volume was equal to $0.62 \text{ cm}^3/\text{g}_{\text{CNF}}$. The hysteresis loop formed by CNF/SMF adsorption-desorption isotherms corresponds to the type IV behavior indicating that the material is mostly mesoporous. The pore size distribution was found bimodal with maxima at 20 and 85 nm [21].

Metal nanoparticles (NPs) on used catalysts were characterized *via* Transmission Electron Microscopy. STEM images of Pd^0 NPs supported on ACF and on CNF/SMF, after reaction, are shown in Figure 1. It can be seen that Pd^0 NPs are highly dispersed and homogeneously distributed over the ACF and CNF/SMF surface. The mean particle size was smaller for Pd/ACF than for Pd/CNF/SMF. Also, the particle size distribution was narrower for Pd/ACF (between 1-3 nm) than for Pd/CNF/SMF (between 1-5 nm). These differences can be related to the different support surface morphology.

Figure 2a and 2b displays the X-ray photoelectronic profiles of survey and Pd 3d core level of the Pd catalysts supported on ACF and CNF/SMF as prepared and the later also after reaction with different types of water. The core level Pd $3d_{5/2}$ signal shows a contribution at 335.7-336.0 eV corresponding to Pd^0 and another one at 336.8-337.7 eV corresponding to PdO [22]. The quantification of these signals is displayed in Table 1. The Pd/C ratio is one

order of magnitude smaller for Pd/ACF than for Pd/CNF/SMF indicating that Pd is more superficial on the later while it is inside the micropores on the former. Since XPS probes the outermost surface, nanoparticles deep into the micropores are not detected. As it can be seen, in all the cases the Pd/C ratio of the Pd/CNF/SMF catalysts decreases after reaction, but the reason for this is not clear yet.

The fraction of reduced palladium (Pd^0) is substantially higher for the CNF/SMF catalyst than for the ACF catalyst. This is probably related to the more graphitic character of CNF/SMF that favors the delocalization of the π electrons on the graphene increasing the reducibility of the palladium nanoparticles. On the other hand, comparing the Pd^0 fraction of the CNF/SMF catalyst, before and after reaction, it is observed that it slightly decreases after reaction. This suggests that some of the Pd^0 sites are oxidized to Pd^{2+} under reaction conditions. However, the fraction of Pd^0 that gets oxidized is not very significant and similar results were obtained in Pd-Sn catalysts supported on alumina used for the catalytic reduction of nitrates [23]. More significant is the shift of the core level Pd $3d_{5/2}$ signal (Figure 2b and Table 1) to higher binding energies, observed in the XPS spectrum of the Pd/CNF/SMF catalyst after reaction with industrial wastewater. This can be related with the deposition of some electronegative substances on the catalyst surface. In this way, the XPS spectra of the catalysts after reaction with natural and industrial water show two additional peaks at 348-351 eV (Figure 2b) corresponding to the $2p$ core level of Ca^{2+} . These peaks appear because the deposition of the calcium salts present in the water reaction on the catalyst surface.

3.2 Catalytic hydrogenation of bromates in a batch reactor

The activity of the palladium catalysts supported on two types of nanostructured carbon materials is shown in figure 3. As it can be observed, the best results are obtained with the catalyst supported on CNF/SMF that is the catalyst that presents the highest reaction rate.

Using this catalyst all bromates present in the water were reduced after 20 minutes of reaction, while for the catalyst supported on ACF a lower reaction rate was observed and it was not possible to remove completely the bromates of the liquid. This is probably related with the different porous structures of both materials. Microporous ACF based catalysts could have some mass transfer limitation within ACF micropores [21]. On the contrary, the CNF/SMF has a mesoporous structure and the products and reactants can easily diffuse from the catalyst surface to the bulk liquid. In addition, in spite of the high palladium dispersion observed by STEM in both catalysts, Pd catalyst supported on CNF/SMF has a higher content of surface Pd⁰, as it was observed by XPS, favoring the hydrogen activation and as a consequence increasing the bromate reduction rate.

The influence of the Pd content on the activity of the CNF/SMF catalysts was studied and the results obtained are presented in figure 4. As it can be seen, the carbon support (without palladium) removes some of the bromates present in the solution, probably by an adsorption process. The loading of 0.1% of Pd to the support results in a complete removal of bromates after 45 minutes of reaction. As it is expected, an additional increase of the palladium content (0.3%) produces an increase of the reaction rate, reducing all the bromates after 20 minutes of reaction. It should be pointed out that in both cases the same catalyst activity per mol of palladium was achieved. These results clearly indicate that metallic Pd provides the catalytic active sites which are fully used. In this way an increase in the Pd loading enhances the bromate hydrogenation because more reaction sites are available, being the role of the support to stabilize the reduced palladium active sites and to decrease the mass-transfer limitations. On the other hand a blank reaction without catalyst was made proving that the homogeneous reduction of bromates with hydrogen is not feasible at room temperature.

3.3 Catalytic hydrogenation of bromates in a continuous reactor

The activity of the 0.3%Pd/5%CNF/SMF catalyst was tested for the bromate hydrogenation reaction in a continuous system using a plug flow reactor. As it can be observed in Figure 5, the catalyst activity is very stable in the continuous reactor, obtaining a bromate conversion of around 75-80% during the 45 hours of reaction, without any important deactivation of the catalyst. This can be explained by the stability of the Pd⁰ active sites on this support, as it was observed by XPS and STEM.

The influence of the hydrogen partial pressure in the bromate reduction was studied in this system. The results obtained are shown in Figure 6. As it can be seen, the conversion decreases in the same ratio as the hydrogen partial pressure. The direct relationship between the hydrogen partial pressure and the catalyst activity, indicates that the bromate reduction by catalytic hydrogenation over supported Pd catalysts is not only controlled by the adsorption of bromate in the catalyst surface, as it was suggested by Chen et al [17], but also by the hydrogen partial pressure.

In order to test the real possibilities of this catalyst for a commercial process, the activity of the Pd nanostructured catalyst for the bromate reduction was tested in a continuous reaction with natural water and with industrial wastewater containing both bromates. The water samples were supplied by VEOLIA and its composition is reflected in Table 2. The results obtained with the natural water during 100 hours of reaction are shown in Figure 7. As it can be observed, the catalyst is active during almost 5 days of reaction, observing only a small deactivation during the experiment (from 75% conversion to 60%). Similar results were found [24, 25] in some papers studying an analogous reaction, i.e. the nitrate reduction. In those works, the slow deactivation of the catalyst was related with the deposition of different salts present in natural water, on the catalyst surface that blocks the palladium active sites.

The same mechanism could be responsible for the catalyst partial deactivation observed in this reaction. Nevertheless after 100 hours of reaction a 60% of bromate conversion is still obtained.

The results obtained with the industrial wastewater are shown in Figure 8. In this graph, the activity of the 0.3%Pd/5%CNF/SMF catalyst for the bromates hydrogenation using this water is compared with the results obtained with natural water. As it can be seen, the catalyst is also active for the reduction of bromates in an industrial wastewater with a high alkalinity, conductivity and an important content of different species other than bromates (see Table 2). Nevertheless, since the beginning of the reaction, the bromate conversion obtained with this type of water is lower than that obtained with natural water, probably because the different ions present in the media competitively adsorb on the active centers. Similar results have been observed, when using water with a high conductivity, in different Pd catalysts used for the reduction of nitrates [24, 25]. Nevertheless, the main problem in this reaction was an operational problem, because due to the high calcium content of the water and to the basic pH, important quantities of calcium salts (as determined by XPS) precipitated in different parts of the reactor and on the catalyst surface, plugging the system after seven hours of reaction. This can be avoided buffering the system at a pH of 6 with CO₂, as it is made in other reactions as the nitrate reduction reaction [26]. The results obtained in the bromate reduction when adding a mixture of H₂ and CO₂ in the reactor (pH of solution = 6) are shown in Figure 9. In these conditions, after achieving the steady state, there was not plugging of the reactor neither an important catalyst deactivation during the 80 hours of the experiment. Nevertheless, a lower conversion was obtained when using the gas mixture. As it was discussed above, this is due to the change of the hydrogen partial pressure. The decrease of the hydrogen partial pressure by a factor of two results in a decrease of the activity by the

same factor. In this way to avoid the precipitation of calcium carbonate would be preferable, for instance, to add an acid solution than to add an acidic gas that decreases the hydrogen partial pressure.

Conclusions

Palladium catalysts supported on CNF/SMF have shown promising results in the removal of bromate from water via catalytic reduction using hydrogen as reductant. The results obtained show that this support minimizes the mass-transfer limitations, ensuring an efficient catalyst use. It has been observed that it is possible to reduce bromates contained in water with hydrogen using both batch and continuously operated mode, but bromate reduction depends on the hydrogen partial pressure. The catalyst stability was tested using distilled water, natural water and industrial wastewater containing bromates. It has been shown that it strongly depends on the type of water matrix. The best results are obtained with the distilled water containing bromates and the worst results are obtained for the industrial wastewater, with a high conductivity. Furthermore, it is necessary to avoid the precipitation of calcium salts in waters with a high alkalinity for an adequate performance. Taking all these precautions into consideration, the catalytic reduction of bromates is a feasible method for the reduction of bromates in order to comply with the environmental regulations.

Acknowledgements

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Caption to figures

Figure 1. STEM images of the Pd catalysts supported on (a) ACF and on (b) CNF/SMF, after reaction.

Figure 2. XPS (a) survey and (b) deconvolution of Pd 3d peaks of the, as prepared Pd/ACF and Pd/CNF/SMF catalysts and of the Pd/CNF/SMF catalysts after reaction with different types of waters.

Figure 3. Catalytic hydrogenation of bromates in water using (□) Pd/ACF and (Δ) Pd/CNF/SMF catalysts (discontinuous stirred tank reactor, distilled water with 50 ppm of bromates, 250 mL/min H₂, 600 mL of water, 1 g. of catalyst).

Figure 4. Hydrogenation of bromates in water using (Δ) 0.3%Pd/5%CNF/SMF, (⊕) 0.1%Pd/5%CNF/SMF, (▪) 5%CNF/SMF or (✱) without catalyst (discontinuous stirred tank reactor, distilled water with 50 ppm of bromates, 250 mL/min H₂, 600 mL of water, 1 g. of catalyst).

Figure 5. Catalytic hydrogenation of bromates in a continuous system (plug flow reactor, distilled water with 50 ppm of bromates, 250 mL/min H₂, 5 mL/min of water, 0.22 grams of 0.3%Pd/5%CNF/SMF).

Figure 6. Influence of the hydrogen partial pressure in the catalytic reduction of bromates; (◇) H₂ partial pressure = 1; (□) H₂ partial pressure = 0.5; (Δ) H₂ partial pressure = 0.25 (plug flow reactor, distilled water with 50 ppm of bromates, 5 mL/min of water, 250 mL/min of H₂+N₂ gas flow, 0.22 grams of 0.3%Pd/5%CNF/SMF).

Figure 7. Catalytic hydrogenation of bromates in natural water (plug flow reactor, 5 mL/min of water, 250 mL/min H₂, 0.22 grams of 0.3%Pd/5%CNF/SMF).

Figure 8. Catalytic hydrogenation of bromates in (□) industrial wastewater and in (◇) natural water (plug flow reactor, 5 mL/min of water, 250 mL/min H₂, 0.22 grams of 0.3%Pd/5%CNF/SMF).

Figure 9. Catalytic hydrogenation of bromates in industrial wastewater (■) with a mixture of H₂ and CO₂ (250 mL/min H₂ + 250 mL/min CO₂) and (●) with H₂ (plug flow reactor, 5 mL/min of water, 250 mL/min H₂, 0.22 grams of 0.3%Pd/5%CNF/SMF).

Table 1. Surface atomic Pd/C ratio and XPS spectra deconvolution results of studied samples

catalyst	Pd/C atomic ratio	Pd ⁰ position eV	Pd ²⁺ position eV	Fraction of Pd ⁰ %
Pd/ACF as prepared	0,21	335,8	337,0	53,0
Pd/CNF/SMF as prepared	3,41	335,7	336,8	82,6
Pd/CNF/SMF used with distilled water	1,01	335,8	337,0	69,9
Pd/CNF/SMF used with natural water	0,87	335,7	336,8	76,5
Pd/CNF/SMF used with industrial wastewater	1,43	336,0	337,7	69,2

Table 2 Composition of the water supplied by VEOLIA

	Natural water	Industrial wastewater	Unit
pH	7.5-8	7.5-8	
BrO_3^-	60	300	$\mu\text{g/L}$
Conductivity at 25°C	500-600	2000-5000	$\mu\text{S/cm}$
Total alkalinity	8	108	°F
Total Organic Carbon	0.5	15-40	mg/L
NH_4^+	<0.01	0.2-0.4	mg/L
Ca^{2+}	20-120	1000	mg/L
Mg^{2+}	8	130	mg/L
CO_2	20	48	mg/L
SO_4^{2-}	70	2000	mg/L
Cl^-	24	80	mg/L
HCO_3^-	180-200	1300	mg/L

Figure 1

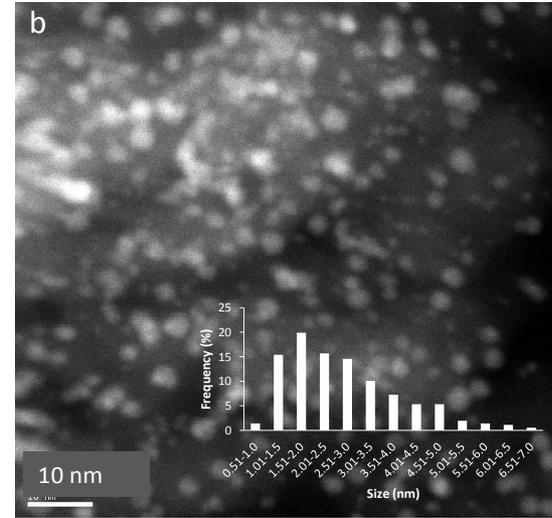
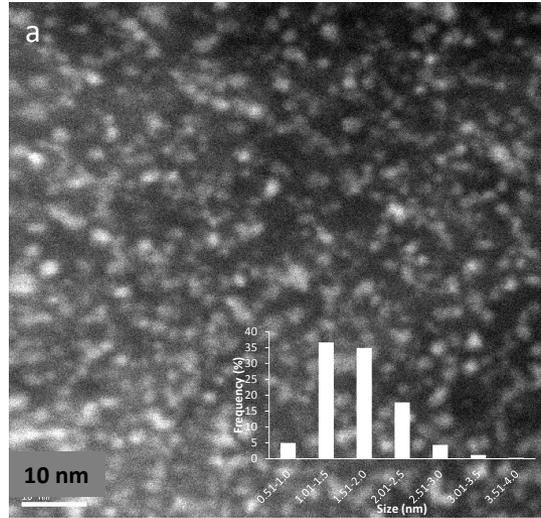


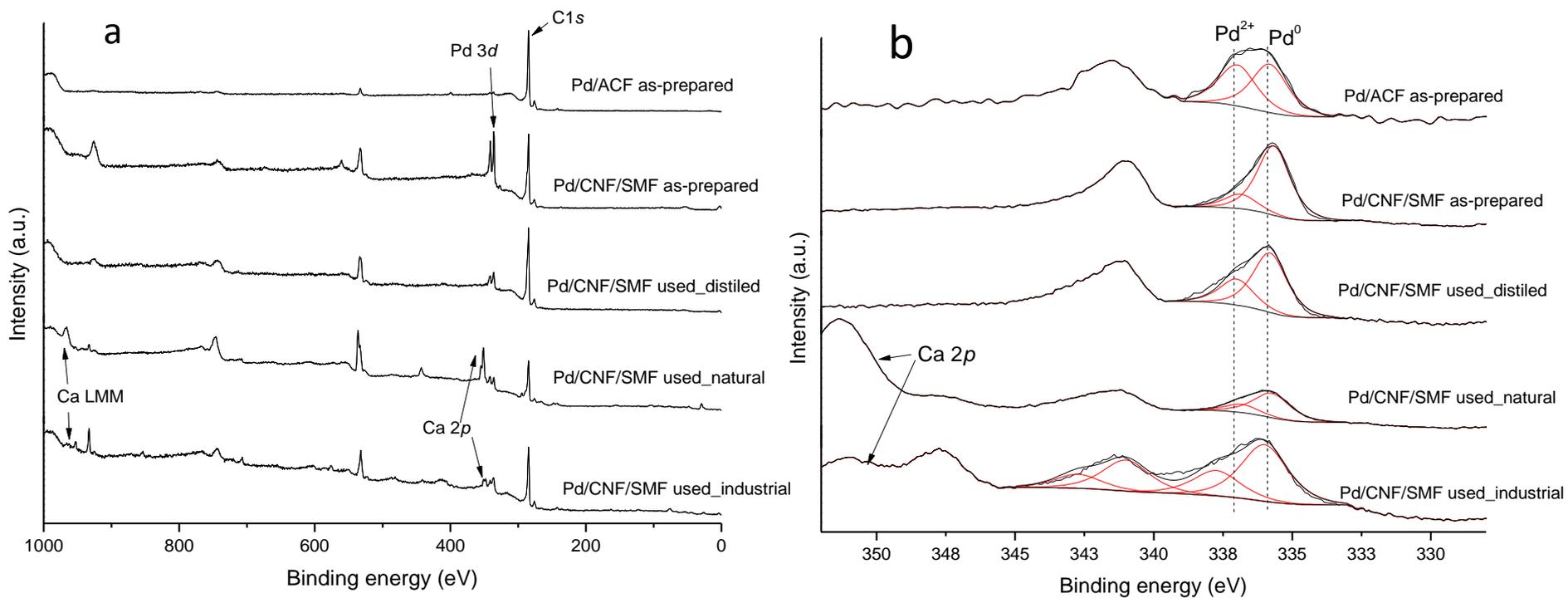
Figure 2

Figure 3

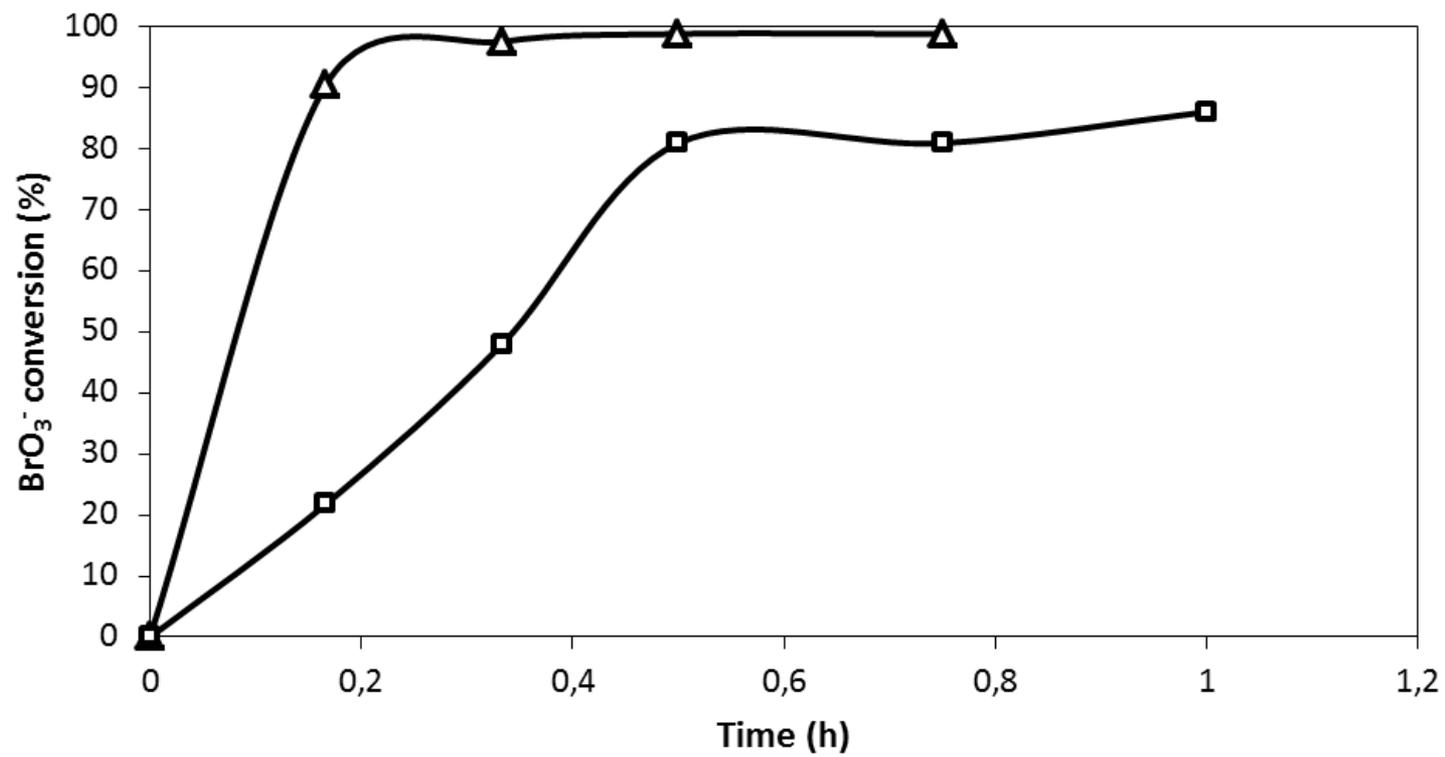


Figure 4

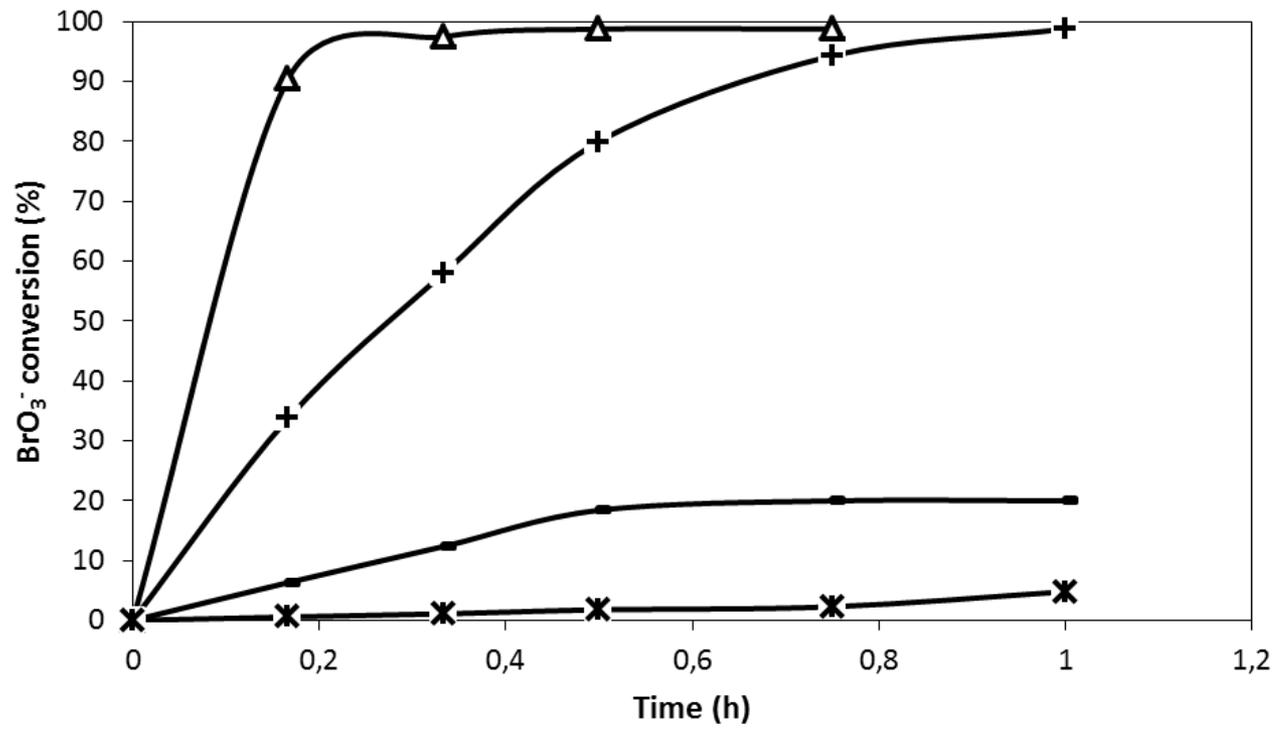


Figure 5

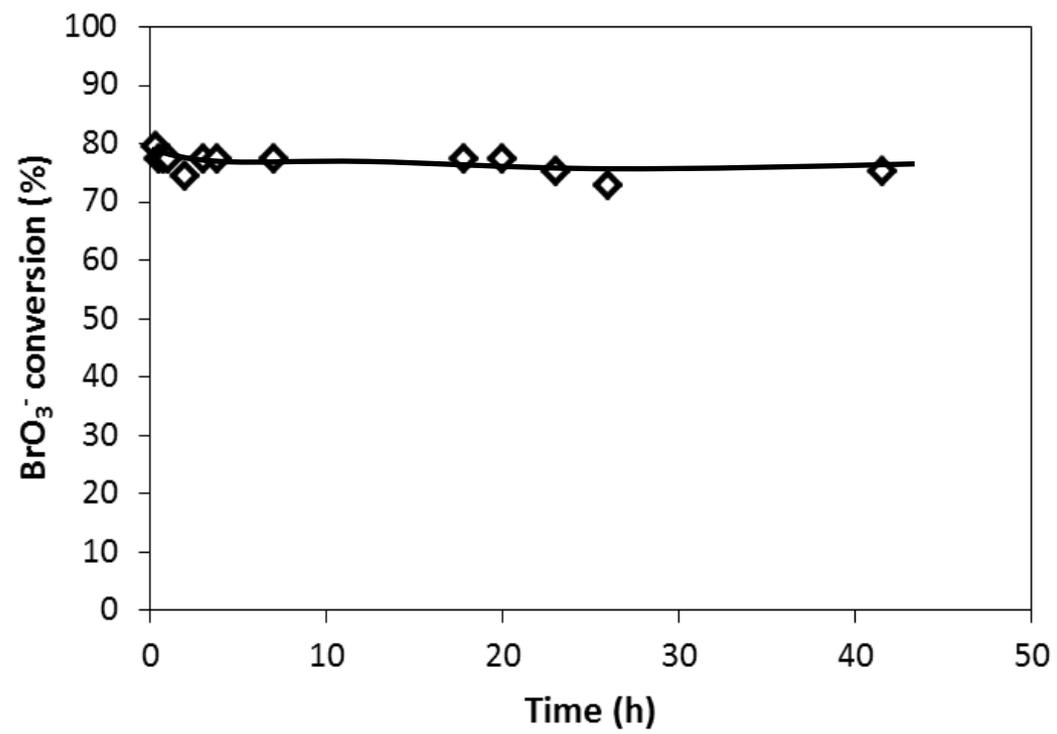


Figure 6

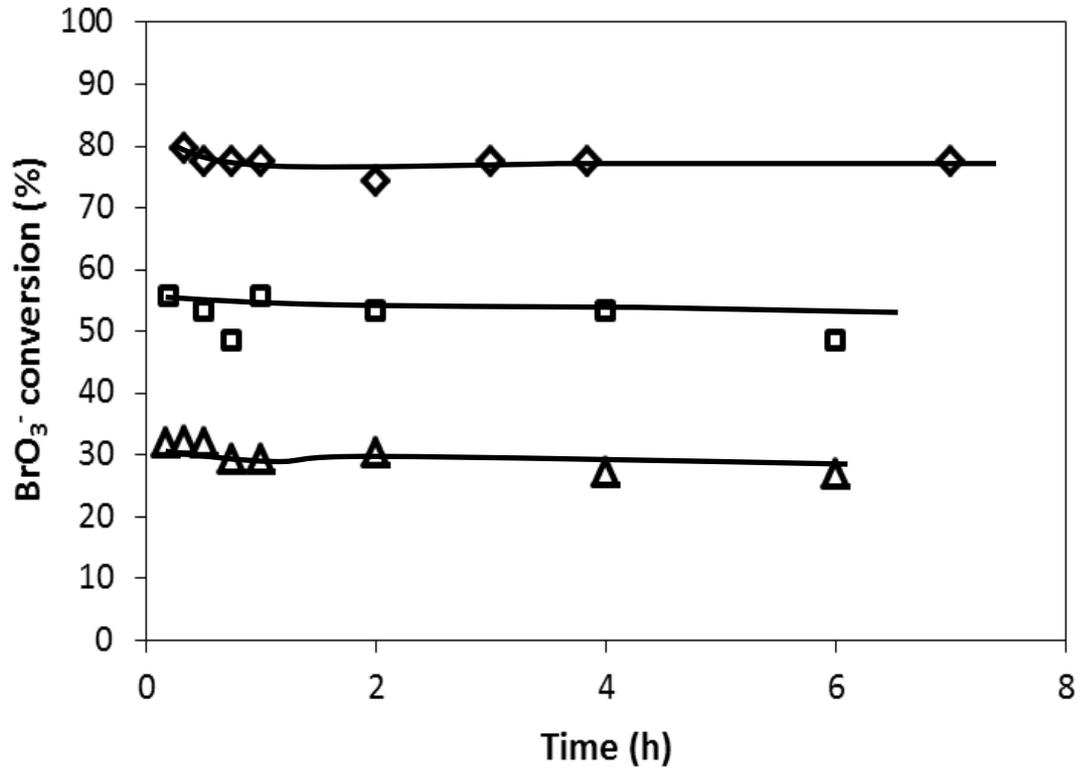


Figure 7

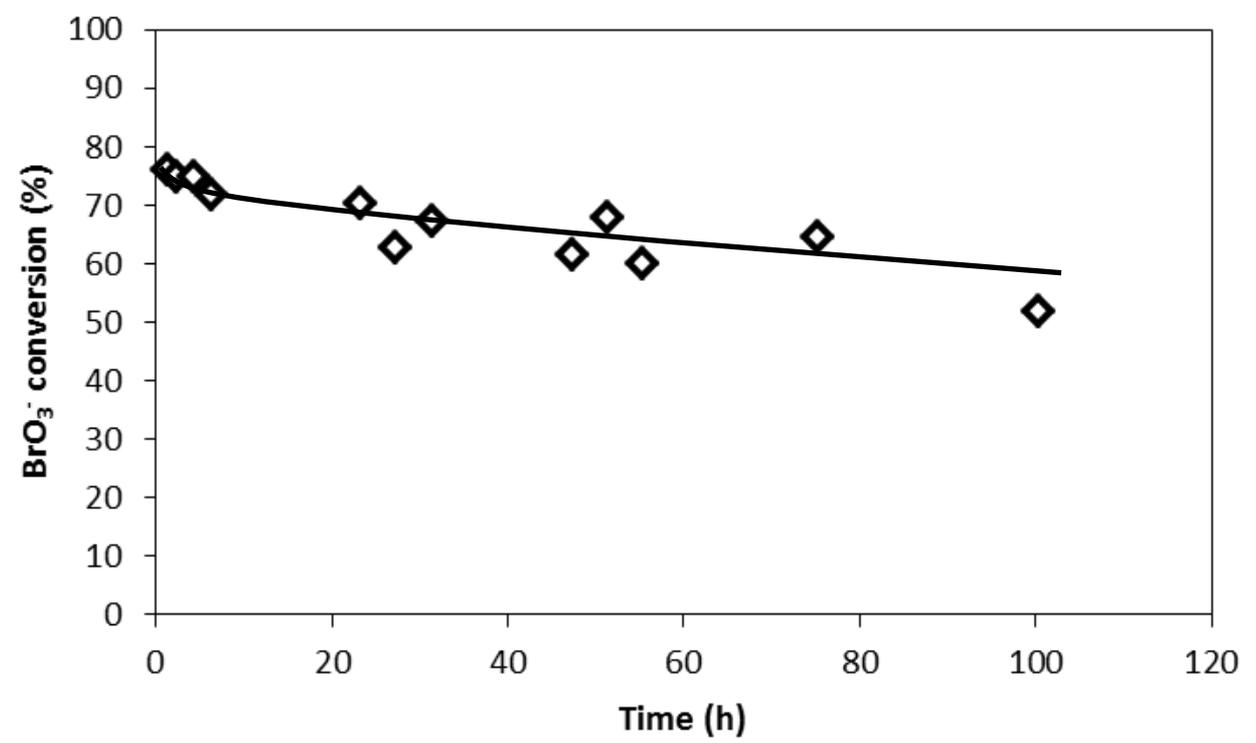


Figure 8

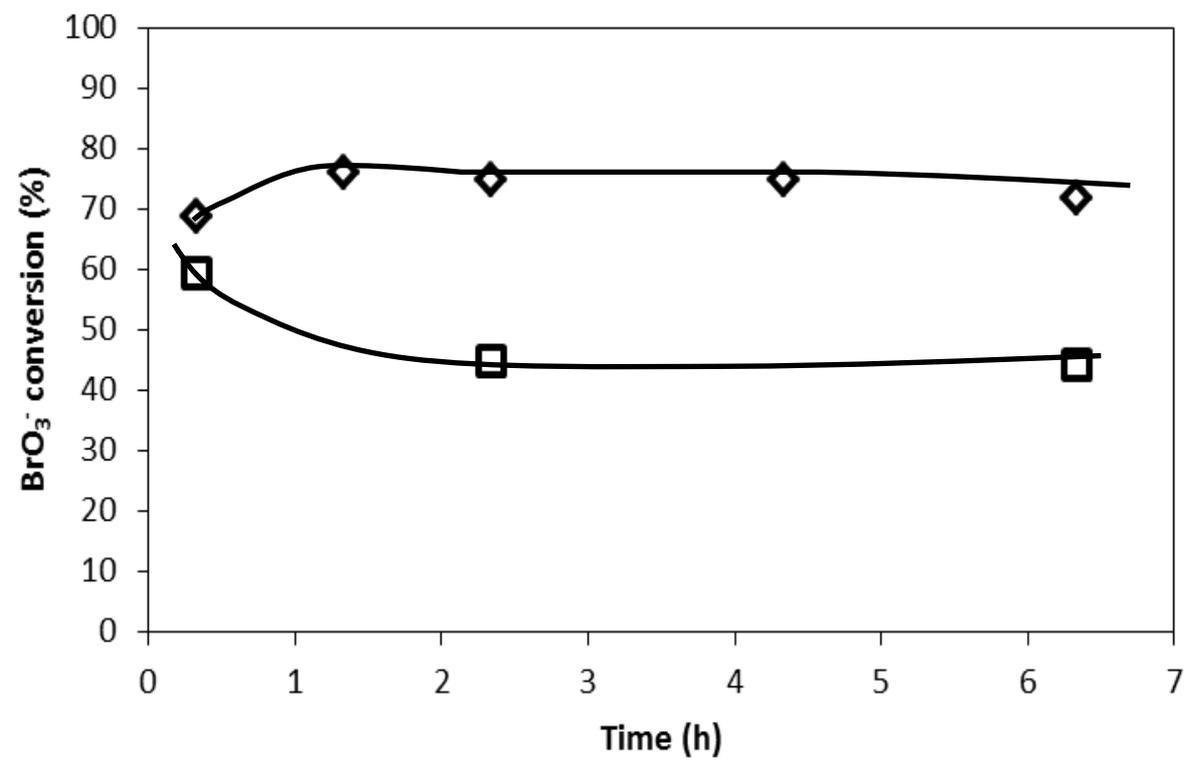
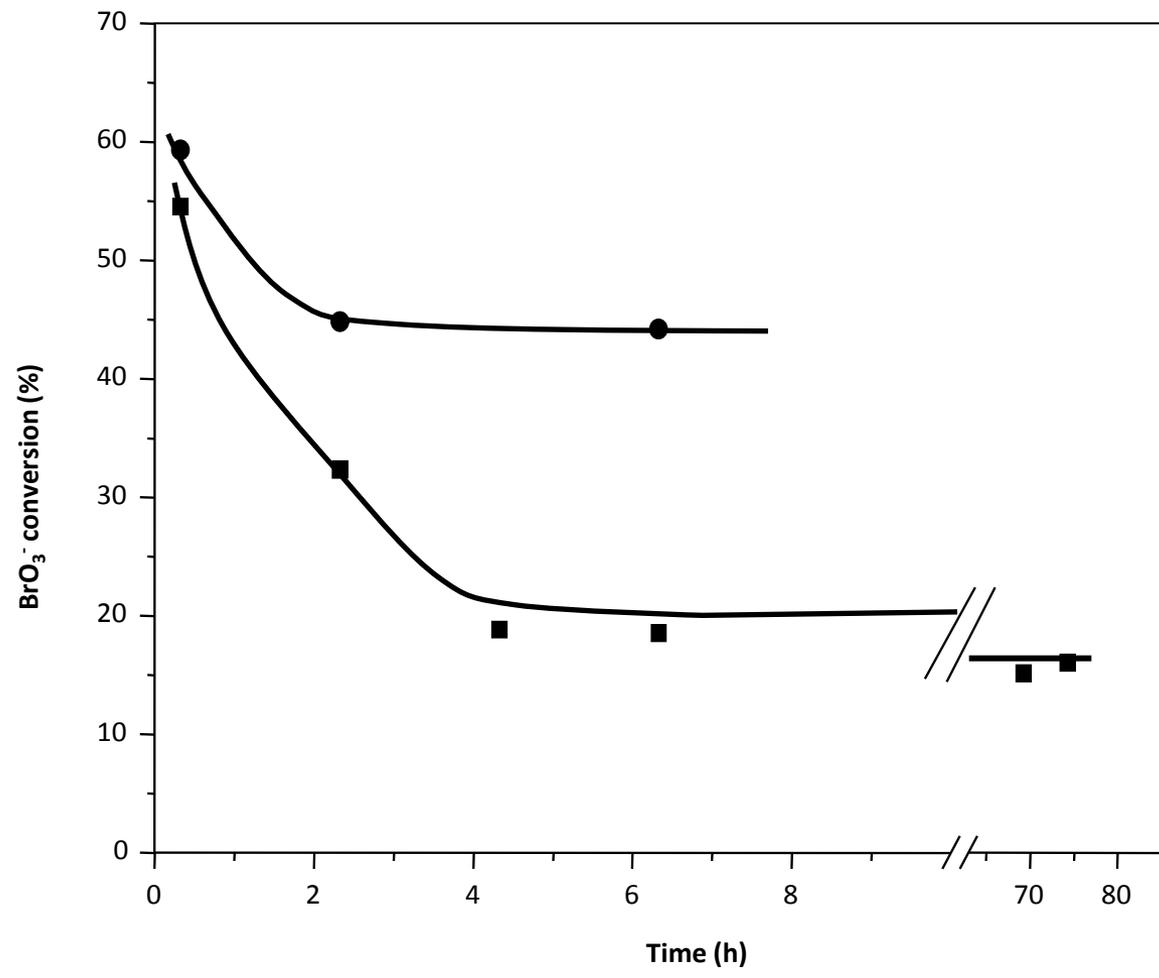
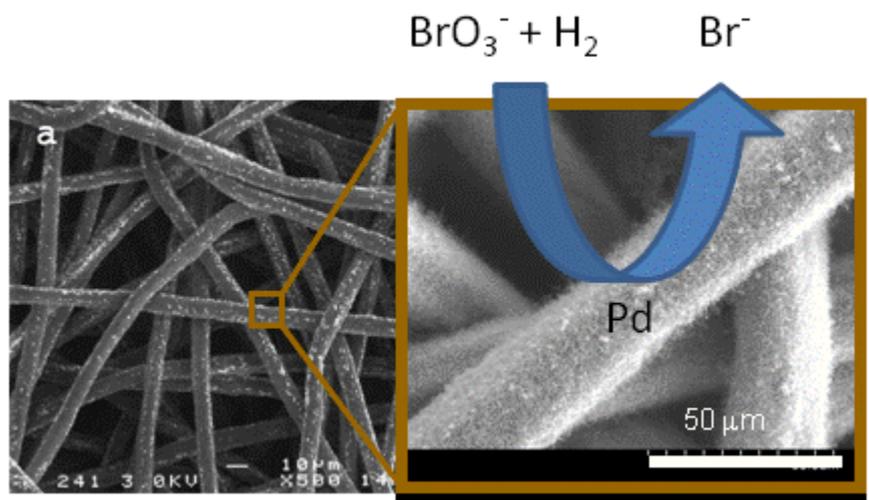


Figure 9





*Highlights (for review)

- Pd/carbon-based materials show high catalytic activity for the bromates removal.
- Bromates conversion is favored with mesoporous supports.
- Catalysts are active in a continuous system with natural and industrial wastewater.
- Bromates conversion decreases in the same ratio as the H₂ partial pressure.