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Catalytic removal of pharmaceutical compounds in water medium under an H_2 stream over various metal-supported catalysts: A promising process

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ABSTRACT

To date, very few prescriptive studies have been reported in the literature concerning the catalytic removal of pharmaceutical substances in wastewater using H_2 in the presence of O_2 for the *in situ* formation of H_2O_2, while the mechanism of the reaction has not been studied in detail yet. Hydrogen peroxide is a potent oxidizing agent used extensively in catalytic wet air oxidation (CWAO) applications and can be used for the elimination of pharmaceuticals from waste water. In the present work, an attempt has been made to elucidate the actual effects of the *in situ* production of hydrogen peroxide on the CWAO of pharmaceuticals. Therefore, the effects of the nature of the active phase (Pd, Pt, and Rh), as well as the feed gas composition have been examined toward the reaction at hand. The results showed that 1% Pd/Al_2O_3 and 1% Rh/Al_2O_3 are the most effective catalysts for the elimination of paracetamol from the reaction medium using hydrogen-rich streams, having a conversion of up to 70% in 2 h. A maximum conversion of paracetamol of 90% was obtained in just 30 min of reaction over 1 wt.% Rh/Al_2O_3, when using pure hydrogen in the feed. Total organic carbon measurements performed over the latter catalyst showed that practically no organic carbon is removed from the liquid phase, indicating the conversion of paracetamol to a different organic (probably aromatic) compound, through hydrogenation. Toxicity tests that followed showed a dramatic decrease in the toxicity of the products solution, indicating that paracetamol hydrogenation might be a promising method for the elimination of its toxicity.

Keywords: Reduction; Pharmaceuticals; Catalytic removal; Hydrogen peroxide; Xenobiotics

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1. Introduction

In the last decades, the consumption of pharmaceutical substances increased exponentially, with the environment to be, especially, burdened from their rejection [1,2]. Human and veterinary drugs are released to the environment mainly as a result of manufacturing processes, improper disposal or metabolic excretion. Several studies have been reported that prove the existence of pharmaceuticals in aquatic ecosystems. More specifically, residues of antibiotics, which constitute a significant percentage of the pharmaceuticals consumed worldwide, were found in surface waters [3], groundwaters [4], seawaters [5], drinking water [6], municipal wastewater treatment plants effluents [7], and hospital wastewaters [8]. Based on the literature [9–13], the amount of residues (ng/L to low μg/L) that remains even after wastewater treatment is still able to induce toxic effects. This is due to the fact that pharmaceuticals are extensively used around the world both for humans and for animals, and are thus introduced into the environment continuously, which means they are bioaccumulated. Their continuous introduction into the environment makes them pseudopersistent, even though pharmaceuticals have short environmental half-lives [9]. Moreover, some pharmaceuticals are highly polar and non-volatile, which means that they cannot escape from the aquatic matrix [9].

Pharmaceutical residues were also detected in soil for several months after the fertilization of the soil with manure or sludge. Moreover, these residues were also detected in vegetables and cereals [14,15].

Consequently, the removal of pharmaceutical substances from industrial effluents is of paramount importance, since industry constitutes a significant polluter of the environment.

Advanced oxidation processes (AOPs) are extensively used for the treatment of wastewaters from industries, such as pulp and paper, dyeing, and petrochemical, which contain harmful and refractory organic pollutants. The use of catalysts in AOPs has several advantages including increasing the reaction rates, allowing the use of more compact reactors, reducing the reaction time, and improving the efficiency. However, heterogeneous catalysis has additional advantages over the homogeneous catalysis, the main one being that the additional step in the process chain that concerns the recovery of the catalyst is not necessary.

An alternative method is the catalytic wet air oxidation (CWAO) [16,17], which reduces the severity of reaction conditions compared with wet air oxidation and more easily decomposes even refractory substances. Nobel metals such as Ru, Rh, Rd, Pd, and Pt are used extensively, since they show higher catalytic activity and higher resistance to metal leaching than base metal oxide catalysts [17]. These noble metals are usually supported on γ-Al_2O_3, TiO_2, CeO_2, ZrO_2, and carbon materials with less than 5% metal loading. Strong oxidizing agents like ozone, hydrogen peroxide, and ultraviolet (UV) radiation which involve the generation of hydroxyl radical ($^{\cdot}OH$) with high oxidative power can also be used in CWAO to further reduce the severity of reaction conditions. Methods involving ozone and UV radiation due to the specialized equipment needed are too expensive to be used widely [18]. Moreover, ozonation has mass transfer limitations which are the limiting step of the process when the ozone consumption rate per unit of volume is high, reducing the efficiency and increasing the operating costs [19]. In addition to that it was reported [20,21] that ozonation achieves only low rates of mineralization and does not change or even increases ecotoxicity, indicating that the metabolites produced are more toxic than the parent compounds.

Alternatively, hydrogen peroxide can be used as the source of the $^{\cdot}OH$ radicals due to its low cost. In addition, using hydrogen, in excess of oxygen/air, in the presence of a catalyst can lead to the *in situ* production of hydrogen peroxide, which further reduces the cost of operation.

Only very few research studies have been reported in the literature [22,23], concerning the heterogeneous CWAO in excess of oxygen (air) and in the presence of hydrogen, while the reaction's mechanism has not been studied yet. The scope of the present research is to develop a suitable, innovative catalytic system with high reactivity toward the elimination of pharmaceutical substances using air/hydrogen mixtures. For the first time, the reactions of the *in situ* production of hydrogen peroxide and the catalytic wet oxidation of pharmaceuticals were studied simultaneously, so as to find the best catalytic system for the elimination of pharmaceuticals from aqueous medium. According to the limited literature [22,23], the introduction of small amount of hydrogen gas into air feed stream leads to an appreciable increase of the wet oxidation activity of the catalyst, reducing the operation costs significantly. Other advantages of the proposed catalytic system are the low cost of installation and maintenance, the conversion of pharmaceutical compounds to innocuous compounds, such as carbon dioxide and water, and absence of bacterial contamination of the effluent and the environment. Additionally, this methodology can be used for the degradation of a wide spectrum of organic compounds in aqueous solutions since the method is non-selective. In the case however that the

pharmaceutical compounds are not converted to innocuous compounds, the toxicity of the reaction products needs to be assessed, in order to evaluate the applicability of the method toward a sustainable environment.

In the present paper, the first promising results derived from the study of the conversion of paracetamol by the use of different reaction mixtures (%vol H_2 in air) over various monometallic 1 wt.% M (M = Pd, Pt, and Rh) catalysts supported on γ-Al_2O_3 spheres are presented. In addition, toxicity and total organic carbon (TOC) of the solution were tested before and after the reaction (95 vol.% H_2/5 vol.% air and 5 vol.% H_2/95 vol.% air). Acute toxicity tests can provide preliminary information on the toxic nature of a substance for which no other toxicological information is available.

2. Experimental

2.1. Catalyst preparation

Three monometallic catalysts (Pt, Pd, and Rh) supported on γ-alumina spheres were prepared and examined toward the oxidation of pharmaceuticals under a hydrogen/oxygen stream.

Coated γ-alumina spheres with 1 wt.% metal oxide (M_xO_y) loading were prepared by immersing commercial alumina spheres (d = 1.8 mm, Sasol, 604,130) in the solution containing the desired amount of metal oxide precursor. The solution was then heated until evaporation at 60˚C. The spheres were then dried at 100˚C, followed by calcination at 500˚C for 2 h.

The deposition of the metallic phase was performed by the incipient wetness method. Cl_6H_2Pt (00669, Fluka), $Pd(NO_3)_2$ (380040, Aldrich), and Rh $(NO_3)_2$ (309206, Aldrich) were used as precursors for Pt, Pd, and Rh, respectively. After metal impregnation, catalysts were calcined in air at 500˚C for 2 h.

2.2. Apparatus

The use of a special flow apparatus that is suitable for three-phase catalytic experiments (solid–liquid–gas) was necessary for the implementation of the catalytic studies in this work [24]. Catalytic experiments were conducted in a custom-made autoclave CSTR reactor (Autoclave Engineers, USA, and PIF Eng&Tech., Spain) equipped with a Mahoney–Robinson catalyst basket (200 mL). Moreover, the catalyst basket, the reactor's inlet and outlets were especially designed to maximize the contact area between the three phases and to minimize possible external mass transfer phenomena. All the catalytic experiments in this work were performed in a batch mode. The solid phase was stationary, whereas the liquid- (known concentration of paracetamol solution dissolved in water) and the gas-phase oxidizing medium (hydrogen/oxygen gas mixture) were under continuous flow at about 1.3 atm total pressure and 25˚C.

2.3. Reaction conditions process

All experiments were performed in a batch mode using the apparatus described above. The volume of the liquid was 180 mL, the initial concentration of paracetamol was 10 mg/L, the mass of the catalyst was 4.0 g, the gas feed stream composition was varied (0–5% H_2 in 100–95% O_2 and 0–5% O_2 in 100–95% H_2), and stirrer's rotation speed was 400 rpm. The paracetamol solution was prepared by dissolving an appropriate amount of paracetamol in deionized water. A 10 mg/mL concentration of paracetamol was used, although much greater than the concentration of pharmaceuticals in water matrices in the environment (ng/mL), since concentration in the order of mg/L is easier to be handled and measured using a simple and robust method, such as the UV/vis spectrophotometry. Moreover, using concentrations in the order of mg/L, we were able to illustrate the proof of concept of this work. Lower concentrations in the order of ng/L which are met in the water matrices of the environment will be studied at a later stage using more sophisticated equipment, such as a LC/MS-MS. Nevertheless, it should be noted that effluents from pharmaceutical industries have higher concentration of pharmaceutical substances, in the order of mg/L.

Prior to each catalytic reaction, catalysts were *in situ* calcined in air at 500˚C for 1 h, followed by reduction with pure H_2 at 300˚C for 1 h. The start-up procedure was completed by introducing 180 mL of the paracetamol solution in the reactor tank which was kept at 25˚C and under He flow (100 mL/min) to achieve a constant pressure of 1.3 atm.

2.4. Quantitative analysis

The initial paracetamol solution (time = 0) as well as samples at 30, 60, and 120 min after the reaction were analyzed using a Thermo Scientific Evolution 300 UV/vis spectrophotometer between 220 and 600 nm, to investigate the possibility of the formation of a derivative that absorbs in either the UV or the visible region of the spectrum. The concentration of paracetamol in the water solution at different time intervals was determined at 243 nm, which corresponds to the maximum absorption for paracetamol.

TOC was also measured in each of the samples (at 0, 30, 60, and 120 min after the reaction), using a OI Analytical Aurora Model 1030 TOC/TON analyzer with a 0.1–30,000 ppm detection range of organic carbon and a precision of 0.22 ppb.

The assessment of the toxicity was done using *Vibrio fischeri*, as described elsewhere [25]. Briefly described, the bacteria (NRRL B-11177) were tested to obtain percentile bioluminescence inhibition during a 15 min exposure. The Microtox® assay was performed in accordance to the operational procedures from Azur Environmental Ltd. Lyophilized bacteria (approx. one million in one preparation) were reconstituted by adding a reconstitution solution, and then, the suspensions were sequentially diluted and tested at 15°C. Light transmission was recorded by a luminometer (Microtox® Model 500 Analyzer, UK). All samples were adjusted at pH 8 and 2% salinity.

3. Results and discussion

The remarkable effect of the presence of hydrogen in the reaction's feed stream toward the conversion of paracetamol is reported for first time in a batch mode system. The conversion of paracetamol was studied over three monometallic catalysts, 1 wt. in % Pd/γ-Al_2O_3 (a), 1 wt.% Pt/γ-Al_2O_3 (b), and 1 wt.% Rh/γ-Al_2O_3 (c) using different reducing feed gas composition. Fig. 1 compares the different conversion profiles of paracetamol obtained over the examined catalysts, at different hydrogen concentrations in the gas feed. As shown in Fig. 1(a), a slight increase in the conversion of paracetamol is obtained over the 1 wt.% Pd/γ-Al_2O_3 catalyst, when increasing the concentration of hydrogen from 0 to 5% vol., whereas a dramatic decrease is observed at hydrogen concentrations higher than 5% vol. (Fig. 1(a)). A completely different behavior is observed in the case of 1 wt.% Pt/γ-Al_2O_3 (Fig. 1(b)), where the conversion of paracetamol does not seem to be affected by the concentration of hydrogen in the feed (in the range from 0 to 5% vol. H_2). On the other hand, a very interesting behavior was observed in the case of the 1 wt.% Rh/γ-Al_2O_3 catalyst (Fig. 1(c)), where the conversion of paracetamol was found to dramatically increase when increasing the concentration of H_2, in the 5–100 vol.% range. A practically complete conversion of paracetamol is obtained at H_2 concentrations higher than 95%.

A comparison of the three catalysts, when hydrogen concentrations in the 0–5 vol.% range are used, clearly shows that both 1 wt.% Pd/γ-Al_2O_3 and 1 wt.% Rh/γ-Al_2O_3 show significantly higher paracetamol conversions (up to 30% more) as compared with 1 wt.% Pt/γ-Al_2O_3. The small but significant increase observed in the cases of Pd/Al_2O_3 and Rh/Al_2O_3 is probably due to the *in situ* production of hydrogen peroxide (a source of •OH radicals) that facilitated the rapid oxidation of paracetamol. It appears that

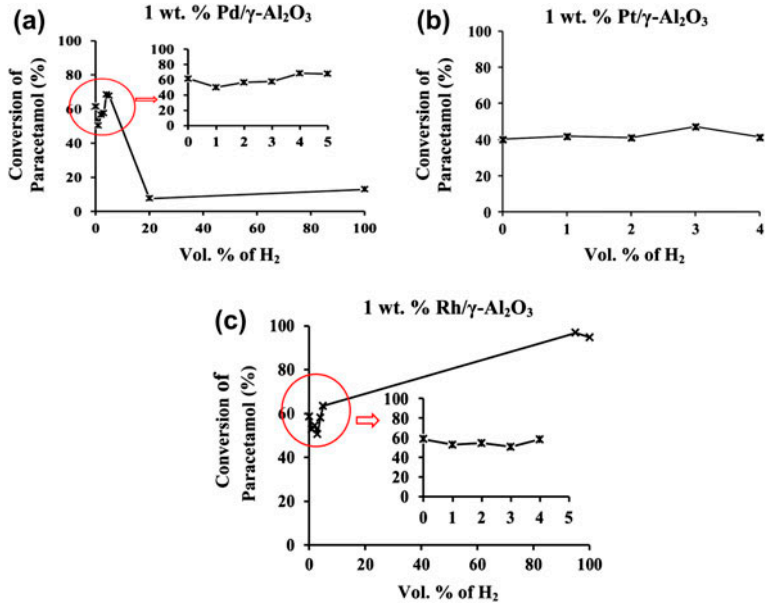

Fig. 1. Conversion of paracetamol as a function of H_2 concentration over monometalic 1 wt.% Pd (a), 1 wt.% Pt (b), and 1 wt.% Rh (c) catalysts supported on γ-Al_2O_3 spheres. Reaction conditions: [paracetamol] = 10 mg/L; W_{cat} = 4 g (dp = 1.8 mm); T = 25°C; P = 1.3 atm.

Pt/Al_2O_3 does not favor the *in situ* production of hydrogen peroxide, a fact that is consistent with the literature, whereas Pd-containing catalysts are commercially used for the direct formation of hydrogen peroxide from H_2 and O_2 [26,27].

The comparative results presented in Fig. 1 indicate that the conversion of paracetamol is clearly affected by the nature of the active phase of the catalyst. Consequently, 1% wt. Rh/Al_2O_3 is clearly the most efficient catalyst for the conversion of paracetamol, particularly at high concentration of H_2 in the gas stream. Therefore, the catalytic performance of 1 wt.% Rh/γ-Al_2O_3 catalyst was examined further and in detail, at different reaction times. Fig. 2 presents the paracetamol conversion profile obtained over 1 wt.% Rh/γ-Al_2O_3 catalyst, when 95 vol.% H_2 in air, pure H_2, and pure air are used in the feed gas. As shown in Fig. 2, the conversion of paracetamol at high H_2 concentrations was remarkably higher than the one obtained in the case when pure air was used in the gas feed. More specifically, the conversion of paracetamol when 95% H_2 and pure H_2 were used exceeded the value of 95%, in both cases, in just 30 min of continuous reaction, at which point a steady state is observed. On the contrary, a maximum conversion of 50% is obtained in the case when pure air is used in the feed. When pure hydrogen is used, paracetamol can be completely converted and thus eliminated from the liquid medium. Consequently, one can claim that the use of 1% wt. Rh/Al_2O_3 and high concentrations of H_2 in the gas stream can be considered as a promising method for the elimination of high concentrations of paracetamol in water media. The latter result indicates that this process might be also suitable for the elimination of other xenobiotic substances from water media, through the reduction instead of oxidation of the xenobiotic substance.

To investigate in detail its effectiveness, the latter reaction was further examined over the 1 wt.% Rh/γ-Al_2O_3 catalyst using different paracetamol concentrations and at two different gas feed compositions (95% H_2/5% O_2 and 95% O_2/5% H_2) (Fig. 3). As shown in Fig. 3, when 5 vol.% H_2/95 vol.% air was used in the gas feed stream, reaction's conversion is significantly decreased with the increase of paracetamol concentration, indicating a negative reaction order for paracetamol. This could be due to the saturation of the surface sites of the active phase (Rh), or even the support, which is possible at high concentrations of paracetamol (above 10 mg/L). In such a case, the adsorption of hydrogen will be hindered, leading to a decrease in the overall conversion of paracetamol. On the contrary, in the case where 95 vol.% H_2/5 vol.% air is used in the feed, the conversion of paracetamol remained at high levels (nearly 100%) and irrespective to the increase in concentration of paracetamol, indicating that the catalytic sites (possibly different than those where excess oxygen was used) are not saturated when increasing the concentration of the pollutant. Therefore, paracetamol continues to be converted and eliminated even at concentrations as high as 500 ppm.

The toxicity of the product solution was studied before and after the reaction for both gas stream compositions used (95 vol.% H_2/5 vol.% air and 5 vol.% H_2/95 vol.% air) and for a range of paracetamol concentrations (Fig. 4). As shown in Fig. 4 the initial toxicity of the solution increases when the concentration of paracetamol in the solution is increased, a result which is expected. When 95% vol. H_2/5% vol. O_2 is used in the gas stream (Fig. 4(a)) the toxicity decreases to negligible levels after the catalytic reaction, indicating that paracetamol is eliminated from the

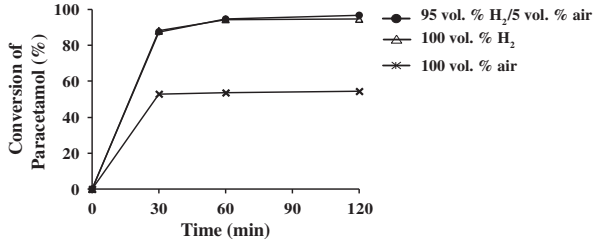

Fig. 2. Conversion of paracetamol as a function of time over 1 wt.% Rh/γ-Al_2O_3, using of different gas feed stream composition. Reaction conditions: Gas feed stream composition = 95 vol.% H_2/5 vol.% air, 100 vol.% H_2, and 100 vol.% air; $[paracetamol]^o = 10$ mg/L; $W_{cat} = 4$ g (dp = 1.8 mm); $T = 25$°C; $P = 1.3$ atm.

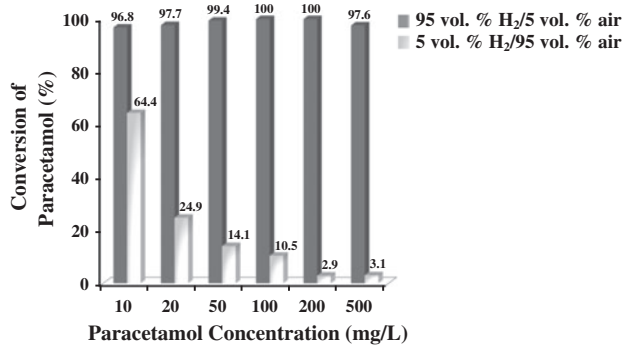

Fig. 3. Conversion of paracetamol (%) as a function of paracetamol concentration (mg/L) over 1 wt.% Rh/γ-Al_2O_3, at different gas feed stream composition. Reaction conditions: Gas feed stream composition = 95 vol.% H_2/5 vol.% air or 5 vol.% H_2/95 vol.% air; $W_{cat} = 4$ g (dp = 1.8 mm); $T = 25$°C; $P = 1.3$ atm.

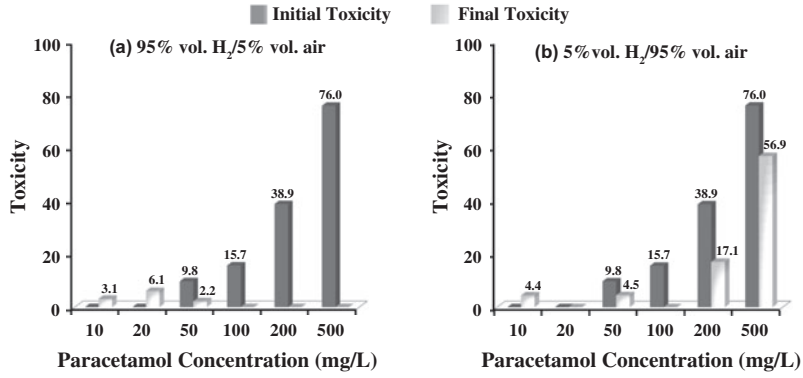

Fig. 4. Toxicity of the reaction and product solution (before and after the reaction) as a function of paracetamol concentration (mg/L) over 1 wt.% $Rh/\gamma\text{-}Al_2O_3$, using different gas feed stream composition. Reaction conditions: Gas feed stream composition = 95 vol.% H_2/5 vol.% air (a) and 5 vol.% H_2/95 vol.% air (b); W_{cat} = 4 g (dp = 1.8 mm); T = 25 °C; P = 1.3 atm.

water solution. This is extremely promising since it is shown that paracetamol can be eliminated even in the presence of high concentrations of the pollutant. On the contrary, when 5 vol.% H_2/95 vol.% was used in the gas feed stream (Fig. 4(b)), the toxicity of the solution decreased but remained at high levels, for paracetamol concentrations above 200 ppm.

The TOC of the solution was studied before and after reaction, when using 95 vol.% H_2/5 vol.% air (Fig. 5(a)) and 5 vol.% H_2/95 vol.% air (Fig. 5(b)) in the feed, for a range of paracetamol concentrations (10–500 mg/L). As shown in Fig. 5, similar results were obtained for any reaction mixture and all different concentrations of the pollutant. TOC values do not decrease considerably after reaction for both gas feed streams. The latter results in combination to the very mild reaction conditions (T ~25 °C, P ~1 bar), used in the present work, indicate that the benzyl ring of paracetamol might not be affected by the catalytic reaction and probably the total number of organic carbons in the paracetamol structure remain unchanged. Consequently, the only possible sites for paracetamol reduction are the hydroxyl and the enolic sites of paracetamol. Fig. 6 illustrates the functional groups in the structure of paracetamol that most probably are affected by the aforementioned catalytic reaction. The fact however that for both gas feed streams, the toxicity of the liquid phase decreases after reaction, indicates that paracetamol is converted to a less toxic substance, which is extremely encouraging for the catalytic process studied in the present work. Further, more detailed experiments are currently in progress in order to examine the exact nature of the actual products of the reaction at hand. Moreover, catalysts with other metal loadings and support oxides (TiO_2, CeO_2, and Fe_2O_3) will be tested. In addition, several other

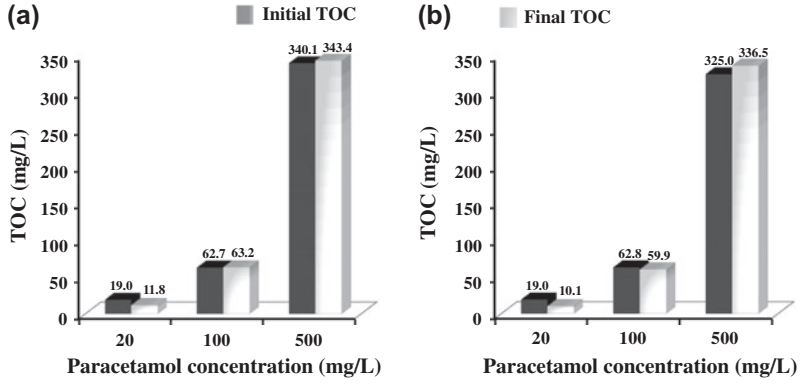

Fig. 5. TOC (mg/L) of the reaction and product solution (before and after the reaction) as a function of paracetamol concentration (mg/L) over 1 wt.% $Rh/\gamma\text{-}Al_2O_3$ catalyst, using different gas feed stream composition. Reaction conditions: Gas feed stream composition = 95 vol.% H_2/5 vol.% air (a) and 5 vol.% H_2/95 vol.% air (b); W_{cat} = 4 g (dp = 1.8 mm); T = 25 °C; P = 1.3 atm.

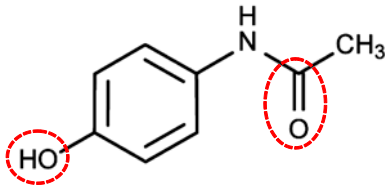

Fig. 6. Structural representation of the functional groups of paracetamol those are most probably affected by catalytic hydrogenation at room temperature.

pharmaceutical substances are going to be tested, in order to investigate the applicability and selectivity of the method.

4. Conclusions

Based on the results of the present research work, CWAO using excess of H_2 appears to be a very promising technique for the complete removal of paracetamol and maybe for other pharmaceutical residues found in water or wastewater, especially when using monometallic Rh catalysts supported on γ-Al_2O_3 spheres. The 1 wt.% Rh/γ-Al_2O_3 catalyst completely converts paracetamol in 30 min of reaction, minimizing the cost of the process. In addition, TOC and ecotoxicity analyses indicated that paracetamol is converted to a less-toxic derivative with probably the same number of organic carbons in its structure. Based on the results of the present work, it can be said that catalytic hydrogenation might be a promising method for the elimination of the toxicity of aqueous effluents containing paracetamol and maybe other pharmaceutical residues.

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