Catalytic Elimination of the Ecotoxicity of Pharmaceutical Compounds in Water Media under a H_2 stream over Various Metal Supported Catalysts: A Promising Process

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Abstract: In the present work an attempt is being made for a development of a suitable catalytic system for the elimination of the ecotoxicity of pharmaceutical substances using hydrogen/oxygen mixtures in the feed. Hydrogen in an excess of oxygen in the presence of a suitable catalyst produces hydrogen peroxide that is a potent oxidizing agent that is used extensively in the Catalytic Wet Air Oxidation (CWAO) for the elimination of ecotoxicity of pharmaceuticals from waste water.To date, very few such prescriptivestudies have been reported in the literatureconcerning the catalytic removal of pharmaceutical substances in wastewater using H_2in the presence of O_2 for the *in situ* formation of H_2O_2, while the mechanism of the reaction have not been studied yet. In the present work an attempt has been made, to elucidate the actual effects of the *in situ* production of hydrogen peroxide on the catalytic wet air oxidation of pharmaceuticals. Therefore, the effects of the chemical composition of the support, the nature of the active phase (Pd, Pt, Rh, Cu, Mo, Ni, Fe), as well as the reaction conditions (feed gas composition) have been examined towards the reaction at hand. The results show that 1% Pt/Al_2O_3 and 1%Rh/Al_2O_3 are the most effective catalysts for the elimination of Paracetamol from the reaction medium using the reaction at hand. In addition, it was found that when increasing the % concentration of H_2 to 95% and 100% (in air), the conversion of Paracetamol increases to 90% in just 30 minutes, when using the 1% Rh/Al_2O_3 catalyst. Total Organic Carbon (TOC) measurements indicated that pharmaceutical compounds are not mineralized (converted to inorganic carbon), but they are converted to a different, non-toxic compound. In order to investigate the applicability of this catalytic method several pharmaceutical substances were used i.e.,Amoxicillin, Diclofenac Sodium, Tetracycline HCl and Ibuprofen. Conversions higher than 80% were obtained for all pharmaceutical substances except Ibuprofen, a result which is extremely encouraging for the applicability of this method.

Keywords:oxidation; pharmaceuticals; catalytic removal; hydrogen peroxide.

1. INTRODUCTION

In the last decades, the consumption of pharmaceutical substances increased exponentially, with the environment to be especially burdened from their rejection. 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 (Constanzo et al, 2005), groundwaters (Sacher et al., 2001), sea waters (Xu et al., 2007), drinking water (Watkinson et al., 2009), WWTP effluents (McArdell et al., 2003) and hospital wastewaters (Brown et al., 2006). Based on the literature (Hernando et al., 2006, Hernando et al., 2004, Makris & Snyder, 2010, Ollers et al., 2001, Stackelberg et al., 2004), the amount of residues (ng/L to low μg/L) that remainseven 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 (Hernando et al., 2006). Moreover, some pharmaceuticals are highly polar and nonvolatile, which means that they cannot escape from the aquatic matrix (Hernando et al., 2006).

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 (Migliore et al., 2003, Kumar et al., 2005). Consequently, the removal of pharmaceutical substances from industrial effluents is of paramound 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, 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, improving the efficiency. However, heterogeneous catalysis has additional advantages over the homogeneous catalysis, the main one being that an additional step in the end of the process is not necessary for the recovery of the catalyst.

An alternative method is the catalytic wet air oxidation (CWAO) (Fatta-Kassinos et al., 2011, Khetan SK et al., 2007), which reduces the severity of reaction conditions compared to Wet Air Oxidation (WAO) and more easily decomposes even refractory substances. Heterogeneous catalysts are advantageous compared to homogeneous catalysts since they do not require an additional separation step to recover the metal ions from the effluent, which increases the operation costs. Strong oxidizing agents like ozone, hydrogen peroxide and UV radiation which involve the generation of hydroxyl radical (˙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 (Cunningham VI, 2008). 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 (Babic et al., 2007). In addition to that, it was reported (Nikolaou et al., 2007, Kummerer et al., 2009), 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 radicals ·OH source 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 to the literature (Kim et al., 2003, Lee at al., 2004) concerning the heterogeneous CWAO in excess of oxygen (air) and in the presence of hydrogen, while the mechanism of the reaction have not been studied yet. The scope of the present research is to develop a suitable, innovative catalytic system, which will show high reactivity and selectivity towards the CWAO of pharmaceutical substances in excess of oxygen and in the presence of hydrogen. For the first time ever the reactions of the *in situ* production of hydrogen peroxide and the catalytic wet oxidation of pharmaceuticals will be studied simultaneously, so as to find the best catalytic system for the oxidation of pharmaceuticals in water medium. In the present work an attempt has been made, to elucidate the actual effects of the *in situ* production of hydrogen peroxide on the catalytic wet air oxidation of pharmaceuticals. According to the limited literature(Kim et al., 2003, Lee at al., 2004) 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, making the operation costs significantly lower. Other advantages of the proposed catalytic system are the low cost of installation and maintenance, the transformation of pharmaceutical compounds to innocuous compounds, such as carbon dioxide and water, absence of bacterial contamination of the effluent and the environment, and can be used for the degradation of a wide spectrum of organic compounds in aqueous solutions since the method is nonselective. 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 towards 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 mixture (% vol H_2 in air) over various monometallic 1 wt. % M (M=Pd, Pt, Rh, Ni, Cu, Fe and Mo) catalysts supported on γ-Al_2O_3 spheres are presented. In addition, toxicity and total organic carbon of the solution were tested before and after the reaction (95 vol. % H_2/5 vol. % air and 5 vol. % H_2/95vol. % air). Acute toxicity tests can provide preliminary information on the toxic nature of a substance for which no other toxicological information is available.

Different pharmaceutical substances were used to assess the applicability of the method. Other pharmaceutical substances that were used include Amoxicillin Trihydrate, TetracyclineHCl, Ibuprofen and Diclofenac Sodium. All the pharmaceutical substances used with the 1 wt. % Rh/γ-Al_2O_3 catalyst under gas feed stream of 95% vol. H_2/5% vol. O_2 showed remarkable conversion except for Ibuprofen that had no conversion.

2. EXPERIMENTAL

2.1 Catalyst preparation

In the present work seven monometallic catalysts (Pt, Pd, Rh, Mo, Ni, Fe and Cu) supported on γ-alumina spheres, were prepared and examined towards 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 ^oC. The spheres were then dried at 100^oC and then calcined at 500^oC for 2 hours.

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 for 2 hours.

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[22]. Catalytic experiments were conducted in a custom-made autoclave CSTR reactor (Autoclave Engineers, U.S.A., and PIFEng&Tech., Spain) equipped with a Mahoney-Robinson catalyst basket (200ml). 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^{o}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 10mg/L, the mass of the catalyst was 4.0g, 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), stirrer's rotation speed was 400 rpm. The paracetamol solution was prepared by dissolving an appropriate amount of paracetamol in deionized water. A 10mg/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 are easier to be handled and measured using a simple and robust method, such as the UV/visspectophotometry. 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 in a later stage using more sophisticated equipment, such as a LC/MS-MS. Nevertheless, effluents from pharmaceutical industries have higher concentration of pharmaceutical substances, in the order of mg/L.

Prior to each catalytic reaction, the catalyst was calcined in air at 500 ^{o}C for 1h, followed by reduction of the catalytic active phase with pure H_2 at 300^{o}C for 1h. The start up procedure was completed by introducing 180 ml of the paracetamol solution in the reactor tank which was kept at 25^{o}C and under He flow (100ml/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/visspectrophotometer between 220 – 600 nm in order to investigate the possibility of the formation of a derivative that absorbs in either the ultraviolet or the visible region of the spectrum. The concentration of paracetamol in the water solution at the different time intervals was determined at 243 nm, which is the maximum wavelength for paracetamol.

Total Organic Carbon (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 1030with a 100 ppb-30,000 ppm of Organic Carbon and a precision of 2 ppb.

The assessment of the toxicity was done using *Vibrio fischeri*, as described elsewhere[23]. 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 with 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. The light transmissions were recorded by a luminometer (Microtox® Model 500 Analyzer, UK). All samples were adjusted at pH 8 and 2 % salinity.

3. RESULTS AND DISCUSSION

3.1 Catalytic Studies

The remarkable effect of the presence of hydrogen in the reaction's feed stream in the presence of a catalyst towards the conversion of paracetamol with oxygen was reported for first time in a batch mode system. The conversion of paracetamol was studied first over three monometallic catalysts, 1 wt. in % Pd/γ-Al_2O_3 (a) and 1 wt. % Pt/γ-Al_2O_3 (b) and 1 wt. % Rh/γ-Al_2O_3 (c)using different reducing feed gas composition. An additional four monometallic catalysts 1 wt. in % Cu/γ-Al_2O_3, 1 wt. in % Fe/γ-Al_2O_3, 1 wt. in % Mo/γ-Al_2O_3, 1 wt. in % Ni/γ-Al_2O_3were tested using the 95% H_2/5% vol. air to determine the best catalyst for the elimination of the ecotoxicity of Paracetamol. In Figure 1, the different conversion profiles obtained with paracetamol are compared using the examined catalysts and different Hydrogen concentrations. As shown in Figure 1a, no remarkable change in the conversion of Paracetamol was observed over 1 wt. % Pd/γ-Al_2O_3, whereas an almost complete (>96 vol. % H_2)conversion of Paracetamol occurs in the case of the 1 wt. % Rh/γ-Al_2O_3 catalyst (Figure 1c). In addition to that, the catalysts1 wt. % Pd/γ-Al_2O_3 and 1 wt. % Rh/γ-Al_2O_3 show higher paracetamol conversion (up to 30% more) than when using the 1 wt. % Pt/γ-Al_2O_3catalyst at low H_2 concentrations (≤5 vol. % H_2). The latter result is probably due to the in situ production of hydrogen peroxide, which is a source of ·OH radicals. It appears that

Pt/Al_2O_3 does not favor the *in situ*production of Hydrogen Peroxide, which is consistent with the literature, where Pd containing catalysts are used for the direct formation of hydrogen peroxide from H_2 and O_2(Lunsford 2003, Landon et al., 2003).

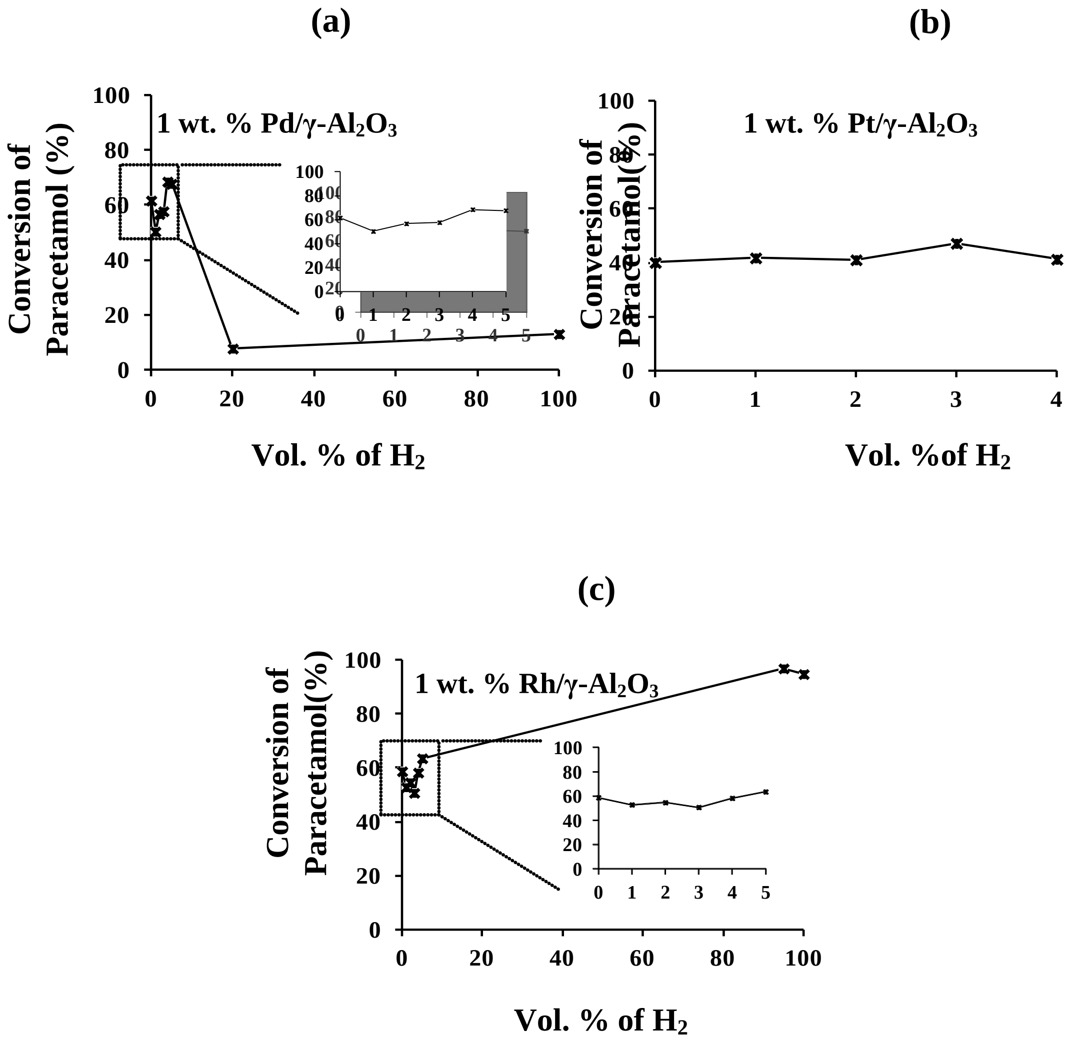

Figure 1. Conversion of Paracetamol as a function of H_2 concentration over monometalic 1 wt. % Pd (a), 1 wt % Pt (b), 1 wt % Rh (c) catalysts supported on γ-Al_2O_3 spheres. Reaction conditions: $[Paracetamol]^o$= 10 mg/L; W_{cat}= 4 g (dp=1.8mm); T= 25 ^{o}C; P= 1.2 atm.

The comparative results presented in Figure 1 indicate that the conversion of paracetamol is clearly affected by the active phase of the catalyst, especially when Rh was used. Consequently, 1% wt Rh/Al_2O_3 catalyst 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, using different feed gas compositions. Figure 2 presents the paracetamol conversion profile obtained during 2h of reaction over 1 wt % Rh/γ-Al_2O_3 catalyst, when 95 vol.% H_2 in air, pure H_2 and pure O_2 are used in the feed gas. As shown in Figure 2, the conversion of paracetamol at high H_2 concentrations was remarkably higher than when pure O_2 was used in the gas feed. More specifically, the conversion of Paracetamol when 95% H_2 and pure H_2 was used was above 95% in both cases, in just 30 minutes after the reaction, at which point it reached steady state. At 120 min after the reaction started, Paracetamol is completely converted and thus eliminated from the medium. Consequently, the use of high concentrations of H_2 in the gas stream using 1% wt. Rh/Al_2O_3 as a catalyst effectively eliminates Paracetamol from the water medium. The latter result clearly indicates that this process is extremely promising in elimination of the ecotoxicity of xenobiotic substances from water medium, due to reduction instead of oxidation of the substance.

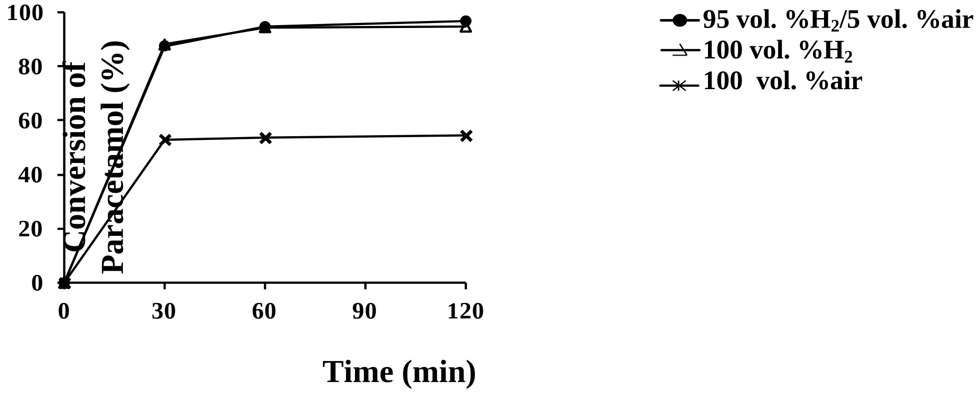

Figure 2. Conversion of Paracetamol as a function of time over 1 wt % Rh/γ-Al_2O_3 by the use of different gas feed stream composition. Reaction conditions: Gas Feed Stream Composition= 95 vol. % H_2/5 vol. % air, 100 vol. % H_2, 100 vol. % air; [Paracetamol]^o= 10 mg/L; W_{cat}= 4 g (dp=1.8mm); T= 25 °C; P= 1.2 atm.

Moreover, to investigate the effectiveness of the reactions studied in this work, different Paracetamol concentrations were prepared and tested over the1 wt. % Rh/γ-Al_2O_3 catalyst using2 different gas feed concentrations (95% H_2/5% O_2 and 95% O_2/5% H_2) (Figure 3). As shown in Figure 3, the conversion of Paracetamol is greatly reduced with the increase of paracetamol concentration when 5 vol. % H_2/95 vol. % air was used in the gas feed stream. This indicates that the reaction at hand is saturated above 10 mg/L, since paracetamol is no longer converted and eliminated from the reaction solution at concentration above 10 mg/L. In contrast to the above-mentioned results, in the case of95 vol. % H_2/5 vol. % air reaction the conversion of Paracetamol remained at high levels (nearly 100%) regardless of the increase in concentration, indicating that the reaction mixture is not saturated with an increase in concentration of the pollutant. Therefore, the pollutant continues to be converted and eliminated even at concentrations of 500 ppm.

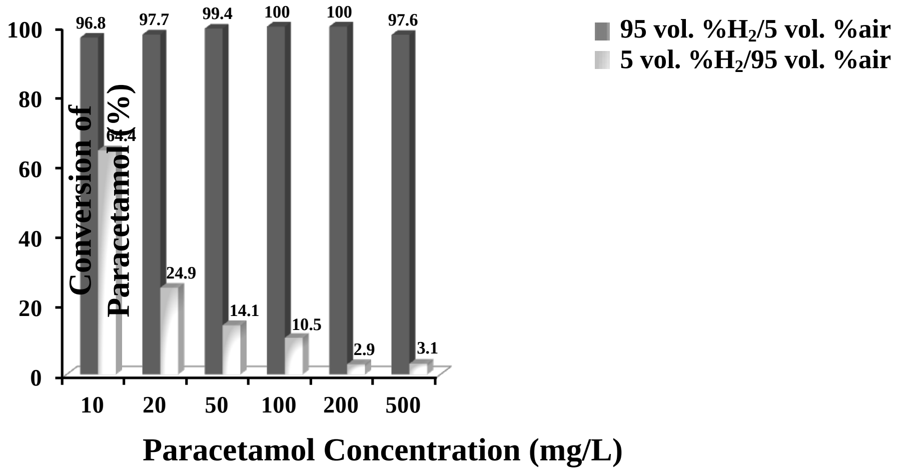

Figure 3. Conversion of Paracetamol (%) as a function of Paracetamol concentration (mg/L) over 1 wt. % Rh/γ-Al_2O_3 by the use of different gas feed stream composition. Reaction conditions: Gas Feed Stream Composition= 95 vol. % H_2/5 vol. % air and 5 vol. % H_2/95vol. % air;W_{cat}= 4 g (dp=1.8mm); T= 25 ^oC; P= 1.2 atm.

The toxicity of the solution was studied before and after the reaction for the 2 different gas stream compositions used above (95 vol. % H_2/5 vol. % air and 5 vol. % H_2/95vol. % air)fora range of paracetamolconcentrations (Figure 4). As shown in figure 4 the initial toxicity of the solution increases when the concentration of paracetamol in the solution increases, which is expected. When 95% vol. H_2/5% vol. O_2 is used in the gas stream the toxicity decreases to negligible levels after the catalytic reaction, indicating that paracetamol is eliminated from the water solution. This is extremely promising since it is shown that paracetamol is eliminated even in high concentrations of the pollutant. On the contrary, when 5 vol. % H_2/95vol. % was used in the gas feed stream (Figure 4b), the toxicity of the solution was kept at high levels for Paracetamol concentrations above 200 ppm, even though it decreases even at 500 ppm. This means that the catalytic reaction using 5 vol. % H_2/95vol. % air in the gas feed stream can be used effectively for Paracetamol concentrations of up to 100 ppm.

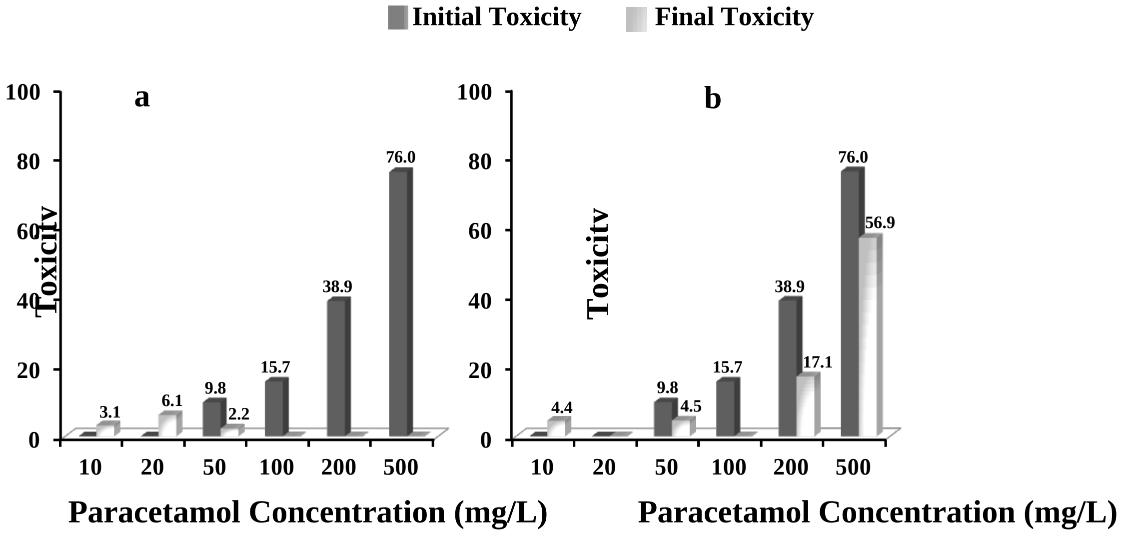

Figure 4. Toxicity of the solution (before and after the reaction) as a function of Paracetamol concentration (mg/L) over 1 wt. % Rh/γ-Al_2O_3 by the use of different gas feed stream composition. Reaction conditions: Gas Feed Stream Composition= 95 vol. % H_2/5 vol. % air (a) and 5 vol. % H_2/95vol. % air (b);W_{cat}= 4 g (dp=1.8mm); T= 25 ^oC; P= 1.2 atm.

The total organic carbon (TOC) of the solution was studied before and after 95 vol. % H_2/5 vol. % air (Figure 5a) and 5 vol. % H_2/95vol. % air (Figure 5b) reactions for a range of paracetamolconcentrations (10-500 mg/L). As shown in Figures 5a and 5b, similar results were obtained for any reaction mixture and for different concentrations. Figure 5 shows that the TOC values do not decrease considerably after the reaction takes places for both gas feed streams. This indicates that the benzyl ring of paracetamol is not affected by the catalytic reaction and the total number of organic carbons in the paracetamol structure is unchanged. Figure 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, toxicity decreases after the reaction takes place, indicates thatparacetamol is converted to a less toxic substance, which is extremely encouraging for the current catalytic procedures studied in this work.

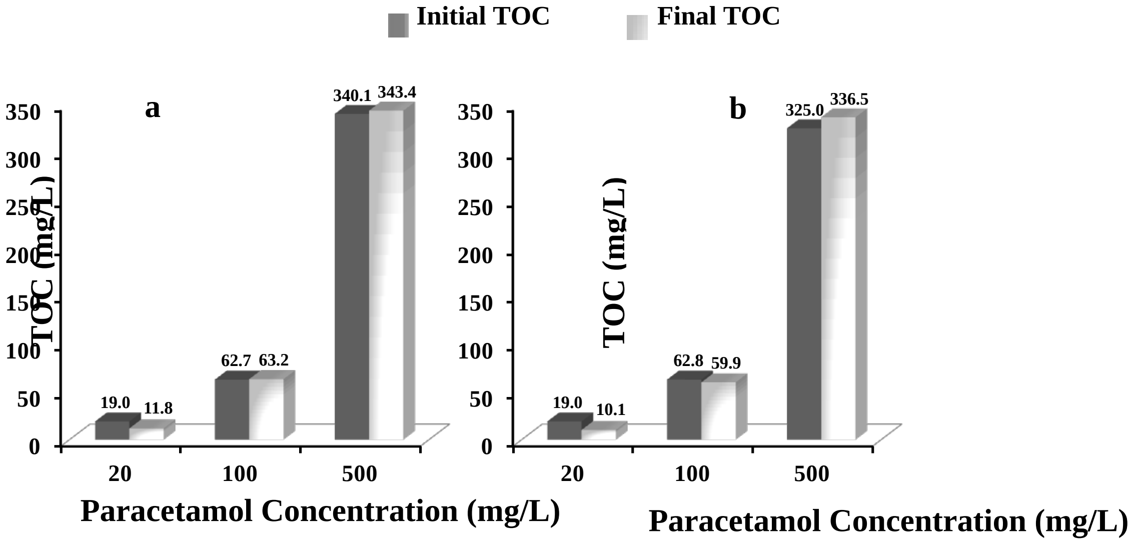

Figure 5. Total Organic Carbon (mg/L) of the solution (before and after the reaction) as a function of Paracetamol concentration (mg/L) over 1 wt. % Rh/γ-Al_2O_3 catalyst by the use of different gas feed stream composition. Reaction conditions: Gas Feed Stream Composition= 95 vol. % H_2/5 vol. % air (a) and 5 vol. % H_2/95vol. % air (b);W_{cat}= 4 g (dp=1.8mm); T= 25 ^{o}C; P= 1.2 atm.

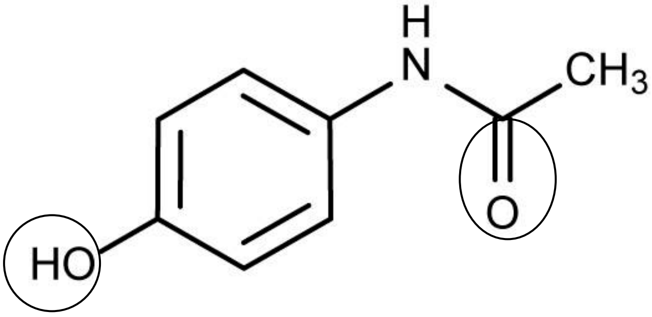

Figure 6. Structure of Paracetamol indicating the functional groups in the structure of paracetamol that most probably are affected by the catalytic reaction at hand.

In order to find the best catalyst to be used for this catalytic procedure, catalysts with different metal precursors were prepared and tested. The following catalysts were prepared and tested using the gas feed stream composition of 95 vol. % H_2/5 vol. % air: 1 wt. in % Cu/γ-Al_2O_3 (d), 1 wt. in % Mo/γ-Al_2O_3 (e), 1 wt. in % Fe/γ-Al_2O_3 (f) and 1 wt. in % Ni/γ-Al_2O_3 (g).

The % conversion of paracetamol using all the catalysts prepared and tested in this work are presented in Table 1.

Table 1: Conversion of Paracetamol using the different catalysts under gas stream feed of 95 vol. % H_2/5 vol. % air

Catalyst	% Conversion of Paracetamol
1 wt. in % Pt/γ-Al_2O_3	41.3 %
1 wt. in % Pd/γ-Al_2O_3	13.4%
1 wt. in % Rh/γ-Al_2O_3	96.8%
1 wt. in % Ni/γ-Al_2O_3	1.4%
1 wt. in % Mo/γ-Al_2O_3	0%
1 wt. in % Cu/γ-Al_2O_3	23.4%
1 wt. in % Fe/γ-Al_2O_3	0%

Comparing the results obtained with all the catalysts used it is concluded that the most efficient catalysts for the elimination of the ecotoxicity of Paracetamolunder a gas feed stream of 95 vol. % H_2/5 vol. % air is the 1 wt. in % Rh/γ-Al_2O_3 catalyst.

In order to assess the applicability of the method further, different pharmaceutical substances were used diluted in water in suitable concentrations to allow for UV/vis measurement before and after the catalytic process. The catalyst 1% Rh on Al_2O_3 spheres was used under a gas feed stream of 95 vol. % H_2/5 vol. % air.For this purpose, Amoxicillin Trihydrate, Diclofenac Sodium, TetracyclineHCl and Ibuprofen were used. All pharmaceutical substances except Ibuprofen were converted satisfactorily. Table 2 illustrates the conversion of each of the pharmaceutical substances used.

Table 2: Conversion of the different pharmaceutical substances used under a gas feed stream of 95 vol. % H_2/5 vol. % air using the 1 wt. in % Rh/γ-Al_2O_3 catalyst.

Pharmaceutical Substance	% Conversion

Paracetamol	96.8 %
Ibuprofen	8.9%
Diclofenac Sodium	85.6%
Tetracycline HCl	61.5%
Amoxicillin Trihydrate	57%

4. CONCLUSIONS

Based on the results of the present research work, catalytic wet air oxidation using excess of H_2 appears a very promising technique for the complete elimination of the ecotoxicity of pharmaceutical residues from wastewater such as paracetamol, especially when using monometallic Rh catalyst supported on γ-Al_2O_3 spheres. The later catalyst completely eliminatesparacetamol in 30 min of reaction, minimizing the cost of the process. In addition, TOC and toxicity analysis indicate that 1 wt. % Rh/γ-Al_2O_3converts paracetamol into less toxic derivatives with the same number of organic carbons in its structure. The method was also tested with Amoxicillin Trihydrate, Ibuprofen, Tetracycline and Diclofenac Sodium and found to convert the initial pharmaceutical substance with a minimum conversion of 80 % except for Ibuprofen that had very low conversion. Moreover several catalysts with different metals were used and it was concluded that the 1 wt. in % Rh/γ-Al_2O_3 catalyst is the most suitable catalyst for this catalytic system.

Future experiments will be conducted for further investigation and optimization of the method. Therefore, catalysts with other metal loadings and support oxides (TiO_2, CeO_2 and Fe_2O_3) will be tested. The mechanism of the reaction at hand will also be investigated using TPD and TPSR.

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