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February 5th, 2014

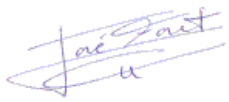
Editor-in-Chief
Journal of Applied Catalysis B: Environmental

Dear Xenophon E. Verykios,

With this cover letter, we will submit the revised manuscript (APCATB-D-13-01690) entitled, "Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol" for publication in the journal of Applied Catalysis B: Environmental. We would like to thank you and the reviewers for the careful and constructive reviews. We do appreciate the comments and suggestions made by the reviewers and we do think that they contributed to improve the quality of the manuscript. Based on the comments and suggestions from the reviewers, we have revised the manuscript. Please find attached our responses to the questions and suggestions given by the reviewers. Each comment of the reviewers is listed in italic style followed by our responses.

Looking forward to hearing from you,

Best regards,



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Tarragona, November 11th, 2013

Editor-in-Chief
Journal of Applied Catalysis B: Environmental

Dear Sir,

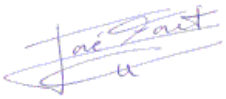
We are pleased to submit our manuscript entitled "Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol" for consideration towards the journal of Applied Catalysis B: Environmental.

The paper shows the preparation, characterization and activity test zero-valent iron supported catalysts on modified activated carbon support with different nitrogen containing precursors. The results from the different characterization techniques demonstrate that the nitrogen-containing groups are successfully introduced into the carbon surface via all the precursors used. The tests of the different modified carbons as adsorbents/catalysts indicated that the adsorption capacity and the efficiency in phenol oxidation are governed by the specific surface area and functional groups present. The modified carbons supported iron catalysts revealed significantly enhanced phenol removal efficiency, reaching over 85% conversion after 3 h. We believe that these findings will be of great interest to researchers working on heterogeneous catalysis for water treatment and your journal is the perfect platform for sharing these results with the international research community.

Finally, we confirm that this manuscript has not been previously published elsewhere and is not under consideration by another journal. All authors have approved the manuscript and agree with submission to this special issue of Applied Catalysis B: Environmental.

Looking forward to hearing from you,

Best regards,



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Our answers to reviewers' comments

First of all, we would like to thank the reviewers for reading the paper critically. We do appreciate the comments and suggestions made by the reviewers and we do think that they contributed to improve the quality of the manuscript. Listed below are our responses to the questions and suggestions given by the reviewers. Each comment of the reviewers is listed in italic style followed by our responses.

Reviewer #1:

Thank you very much for your constructive comments and suggestions to our manuscript submission. We have incorporated all your feedbacks into our revised manuscript. We do think that they have resulted in improving the quality of the manuscript. The following summarizes how we responded to your comments and suggestions. Each comment is listed in italic style and followed by our responses.

Page 12

Results and discussion:

The subchapter 3.1 is not needed. This information is in the experimental part.

The reviewer is right and we have removed the paragraph in the subchapter 3.1 from the manuscript.

Page 13

Why impregnation with iron did not result in any property changes?

In previous works, we observed that for small amounts of metals supported on activated carbon the textural properties of the catalysts remained practically unchanged compared to the unloaded carbon. In the preparation of the ZVI catalysts, we have used 3% (wt %) of iron, and therefore we can realistically assume that the textural properties of the supported metal catalysts are not significantly different from those of the activated carbon. In fact, it can be observed in Table 3 that the textural properties of the ZVI supported on the original AC are similar to the unloaded carbon. This information was included in section 3.1.1 of the manuscript.

Nitrogen containing carbons are known of having oxidizing properties and the authors should use this and support from the literature for their discussion.

We have included some references which have used nitrogen containing carbons as catalyst and catalyst support (refer introduction section paragraph 5).

The authors should try to clarify about the role of iron

ZVI acts as a heterogeneous catalyst for the degradation of phenol in aqueous solution by effectively decomposing hydrogen peroxide and generating hydroxyl radical, which reacts at high rate with phenol and its intermediates. This information was included in section 3.2.2.2 of the manuscript.

Reviewer #2:

We thank you very much for your careful analysis and thoughtful comments and suggestions. We have carefully taken them into consideration in preparing the revised

manuscript. We do think that your comments and suggestions contributed to the improvement of the quality of the manuscript. Below are our responses to your comments and suggestions. Each comment of the reviewer is listed in italic style followed by our responses.

Abstract

The interesting stability of the catalyst should be emphasized in the Abstract Section.

We have emphasized the stability of the catalyst in the Abstract section based on the comment made by the reviewer. We have added the last sentence of the paragraph to the previous Abstract.

1. *Page 3, lines 3-6: "Fenton process (Fe^{2+}/H_2O_2) belongs to catalytic wet peroxide oxidation (CWPO) technologies and operates under relatively mild operating conditions (room temperature and atmospheric pressure) using hydrogen peroxide as oxidant and iron as a catalyst". This can be a quite controversial statement. Fenton was developed before CWPO. The latter is an adaptation of Fenton process to overcome some process drawbacks. In fact, a wide number of researchers consider CWPO as a different AOP than Fenton, both using H_2O_2 as oxidant but, in the former, in presence of a heterogeneous catalyst and, in the latter, using a salt of Fe^{2+} (S. Perathoner, G. Centi, Top. Catal. 33 (2005) 207- 224). In both treatments, temperatures above 100 ºC have been reported.*

We agree with the suggestion and in order to avoid the controversy we re-wrote the sentence in the previous manuscript as: “Fenton process mainly operates under relatively mild operating conditions using hydrogen peroxide as oxidant and iron as a catalyst”.

2. *Page 3, lines 17-21: “On the other hand, the catalytic activity of AC is far from well understood. Besides the direct relationship with the physical properties (surface area, pore volume, etc.) of activated carbon [15], the surface chemistry can play an important role [16-18]. Moreover, it has been reported [19] that the mineral content (in particular Fe content) of AC is a key to display catalytic activities.” The recent work of Dominguez et al., (2013, Carbon, 76-83) should be referred, and in general an update of the references is highly recommended. In this work, thanks to the use of cyclic voltammetry, the effects of physicochemical characteristics of carbon materials on the rate of hydrogen peroxide decomposition were elucidated. The results indicate that the most important factor in the catalytic activity was the content of metals, in particular iron, this was followed by the specific surface area and finally the content of surface oxygen groups.*

We have included (in the introduction of the manuscript) the proposed reference and the main findings of the work about the importance of the presence of metals, in particular iron, on the catalytic activity.

3. *Page 4, line 2: Why does the attachment of a N-functional group ligand help the oxidative power for the H_2O_2?, An explanation should be given, more considering*

that opposite results were found in the CWPO experiments since the BET area is reduced in presence of these groups.

We revised the whole paragraph with the justification of why the attachment of N-functional groups helps to increase the catalytic activity of the system. (Refer paragraph 5 in the introduction section).

4. *Page 4, line 3-4: "However, care should be given to the load of iron or ligand to be incorporated on the AC". Why?, This statement should be better explain.*

We decided to remove this sentence to avoid ambiguity. In fact, we did not compare different iron or ligand loads in the current study.

5. *In my opinion, the approach of the study should be better introduced in the Introduction Section **(a)**. The oxidation and activation steps before N-functionalization are not expected at all. A good explanation about the use of thionyl chloride should be given before the Section 2.2.3**(b)**. Can the activate carbons contain Cl on their surface?, can Cl affect the AC activity?, Shouldn´t Cl be measured?**(c).** According to this paragraph in pag 15: "…it is important to have high density of oxygenated groups on the surface of carbon before functionalization with the N containing compounds. The N-containing groups (EDA, urea and melamine) strongly interact with carboxylic acids, anhydrides and lactones [24, 34].." why is the thionyl chloride activation required then?**(d)***

Several sentences were included in the manuscript:

(a) We revised the last paragraph of the introduction section and added a sentence stating about the oxidation and activation steps before N-functionalization.

(b) An explanation about the role of thionyl chloride is given in the first sentence of the paragraph in section 2.2.2. “Thionyl chloride was used as a linking agent on the surface of AC for the attachment of N-functional groups.”

(c) We didn’t quantify the amount of Cl on the modified AC. However, selected modified activated carbons were characterized using scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS) and surface characterization confirmed that the activated carbon treated with thionyl chloride (AC2) contains small amount of Cl, but after the treatment with N-containing precursors the amount is minimized and become negligible. In addition, the ZVI catalyst was calcined and reduced at 400ºC and at this temperature all the Cl that still remained in the carbon surface was released.

(d) The thionyl chloride activation is required just for a comparison purpose, in order to see whether AC1 (oxidized with HNO_3) or AC2 (activated by $SOCl_2$) can be functionalized more efficiently with the N-functional groups on the surface. As we discussed in section 2.2.3, in the direct method, using AC1, the N-functional groups condense with the carboxyl group on the surface, while in the case of AC2 the N-functional groups are anchored on the surface via a linkage agent ($SOCl_2$). In both approaches the N-functional groups were successfully attached with a similar amount of N-content, except melamine.

Based on the reviewer's comment, we added a sentence in the last paragraph of section 3.1.3.1 as: "…whereas, in the case of AC2, the N-functional groups were better introduced on the carbon surface via $SOCl_2$ linkage".

6. *Why was the ultrasonic mixing used for the Fe catalyst preparation by impregnation? , can it be expected differences from mechanical mixing?*

In previous works carried out in the research group, we observed that metal supported catalysts present higher dispersions when ultrasonic mixing is used, although it is not a critical factor.

7. *Page 12: "These oxygen containing groups possibly block the entry of N_2 inside the small pores [30] or the carbon structure of activated carbon is partially destroyed and some micropores are vanished by treatment with HNO_3 [24]. " According to the results given in Table 3, I do not understand this comment. AC1 have the same Vmicro as AC0, but the Smeso diminishes, therefore, one can deduce that HNO_3 treatment apparently affects the mesostructure but no the microstructure, do you agree?*

We agree with the comments and we re-wrote the previous sentence as: "In spite of having similar micropore volumes, AC0 and AC1 present different mesopore areas, suggesting that the mesostructure of activated carbon was partially destroyed after treatment with HNO_3". (Refer section 3.1.1)

8. *Melamine also affects the mesostructure according to the Smeso values.*

This observation is included in section 3.1.1.

9. Explanation about the textural properties of the urea-supports is missed, why?

We have included explanation about the textural properties of the urea-supports in section 3.1.1 line 312-314 of the manuscript.

10. Why do N-containing surface groups promote the adsorption of phenol?

The presence of N-containing groups on the surface, increases the electronic density, and therefore the basicity of samples (see pH_{PZC} in Table 4), which generally favors adsorption of aromatic compounds. We included the reason and two recent references in section 3.2.1, paragraph 5.

11. By using 150 mg/L of initial phenol concentration and a mass phenol/catalyst ratio of 0.15 the results obtained in the CWPO with modified activated carbons is expected (C.M. Dominguez et al., 2013, Appl. Catal. B Environ. Page 663-670). I guess that in spite of the disappearance of phenol by adsorption, H_2O_2 was completed consumed. Some comments should be given on this respect.

We did not measure the H_2O_2 concentration. Nevertheless, we included some comments in the second paragraph of section 3.2.2.1. "According to Dominguez et al [49], as the initial phenol concentration and the phenol/catalyst ratio used in the present work are relatively low, a large fraction of active sites on the carbon surface is available for hydrogen peroxide decomposition into hydroxyl radicals, which may be consumed by

non-effective reactions. This probably explains the poor performance of activated carbon in CWPO compared to adsorption."

12. *From the graphical abstract, it is not possible to deduce the application of the prepared Fe-catalysts in CWPO process.*

Changed as requested.

Reviewer #3:

First of all, we would like to thank the reviewer for his /her time in critically reviewing the manuscript and for his/her valuable suggestions for the improvement of the manuscript. We are so grateful and very much appreciate that. We have carefully taken them into consideration in preparing our response. We do hope that we properly address the main doubts and comments of the reviewer in this report and in the revised manuscript. Below are our responses to comments and suggestions of the reviewer. Each comment of the reviewer is listed in italic style followed by our responses.

Minor revision

Graphical abstract

I think it is a good presentation of the prepared AC materials, but the activation with thionyl chloride and subsequent nitrogen-containing AC2 and iron-containing nitrogen modified AC2 materials should be also included.

Changed as requested. As it was suggested by other reviewer, we also included the application of the prepared Fe-catalysts in the CWPO process.

Introduction:

It is not clearly justified what are the benefits of incorporating nitrogen containing groups into the carbon surface. Are these functional groups especially active as supports in wet peroxide oxidation or wet air oxidation? Are these functional groups especially interesting for the anchoring of iron species? These issues should be mentioned including also the state of the art for both of them.

It is right that the benefit of incorporating nitrogen containing groups into the carbon surface is not explicitly stated or discussed in the introduction of the previous manuscript. Some text was added to the 5th paragraph of the introduction section, in order to justify the interest of N-containing groups on carbon surface.

Major revision

Result and discussion

Textural properties.

In order to make a better discussion of the catalytic performance of Fe-AC materials, textural properties of all nitrogen-containing activated carbons after iron impregnation should be included. As it is discussed in the paper for nitrogen-containing activated carbons, the textural properties had a crucial role in the adsorption of phenol. I consider that this information is crucial for the evaluation of its catalytic performance. On the other hand, I also recommend giving Smicro instead of Vmicro.

In previous works, we observed that for small amounts of metals supported on activated carbon the textural properties of the catalysts remained practically unchanged compared

to the unloaded carbon. In the preparation of the ZVI catalysts we have used 3% (wt%) of iron, and therefore we can reasonably assume that the textural properties of the supported metal catalysts are not significantly different from those of the activated carbon. In fact, it can be observed in Table 3 that the textural properties of the ZVI supported on the original AC are similar to the unloaded carbon. This information was included in section 3.1.1 of the manuscript.

On the other hand, we prefer to maintain Vmicro, since this parameter gives more information about the microporosity of the activated carbons than Smicro.

CWPO experiments with iron supported nitrogen-containing ACs.

In my opinion the characterization of all nitrogen-containing activated carbons after iron impregnations is crucial for a deeper discussion of results and better interpretation of the catalytic behavior of each Fe-AC material. The study of the adsorption and CWPO of nitrogen-containing activated carbons as supports for phenol removal was very rigorous and well-detailed according to the presented characterization data. Unfortunately, these materials showed a negligible catalytic performance in the operation conditions of CWPO that they were tested. In terms of adsorption is undoubtedly that the different strategies of incorporating nitrogen functional groups drastically affect their adsorption properties. However, I consider that the most important objective of this work is the evaluation of ZVI supported on nitrogen-containing activated carbons for CWPO of phenol, and this issue was briefly discussed in the last point 6.3.2.2 of CWPO experiments for iron supported catalysts. As characterization data of Fe-AC are not presented (at least textural properties should be given), the discussion is very general, and in some cases, hypothesis are given to support the results. It was only mentioned that impregnation does not change

significantly the textural properties of the original AC material (AC0), but the resultant nitrogen-functionalized ACs could suffer some changes in its textural properties or even in the elemental composition due to the thermal reduction treatment that it is needed for the generation of ZVI. By this reason, textural properties of the materials after impregnation should be included. This information also allowed elucidating the influence of the different nitrogen functional groups on the effective dispersion of iron and its catalytic activity in CWPO. This point is also vaguely discussed in the manuscript.

As explained previously, the textural properties of the ZVI catalysts supported on the activated carbon are not significantly different from the unloaded carbon, and therefore we included in the manuscript only the textural properties of one of the ZVI catalysts to illustrate this fact. All the nitrogen-functionalized ACs were heat treated at 450ºC after the functionalization and were characterized only after this step. After the impregnation with iron, the samples were reduced at even lower temperature (400ºC). Thus, significant changes both in textural properties and elemental composition are neither expected not probable.

ZVI acts as a heterogeneous catalyst for the degradation of phenol in aqueous solution by effectively decomposing hydrogen peroxide and generating hydroxyl radicals, which react with phenol and its intermediates. This information was included in section 3.2.2.2.

Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol

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Abstract

Zero-valent iron supported catalysts were prepared through modifying an activated carbon (AC) support with different nitrogen containing precursors; (ethylenediamine, urea and melamine) and impregnating it with 3 wt% of iron. The supports were characterized by N_2 adsorption at -196 ºC, elemental analysis (EA), the pH at the point of zero charge (pH_{PZC}) and temperature programmed desorption (TPD). The iron catalysts were also characterized by temperature programmed reduction (TPR). Subsequently, the catalysts were tested in the adsorption and wet peroxidation of phenol. The results from the different characterization techniques demonstrate that the nitrogen-containing groups are successfully introduced into the carbon surface via all

the precursors used. The tests of the different modified carbons as adsorbents/catalysts indicated that the adsorption capacity and the efficiency in phenol oxidation are governed by the specific surface area and functional groups present. Both surface chemistry and textural properties of carbons are influenced by the nitrogen source and the type of oxygen functionalities preexisting on the surface. The modified carbons supported iron catalysts revealed significantly enhanced phenol removal efficiency, reaching over 85% conversion after 3 h, and showed interesting catalytic stability.

Keywords: Phenol; Activated carbon; Surface chemistry; Catalytic wet peroxide oxidation

1. Introduction

The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of wastewaters [1]. Besides, due to the increasing complexity and toxicity of organic pollutants in industrial wastewaters and the more increasingly strict environmental regulations, the toxicity nature must be reduced. Phenol is among the most common water pollutants [2, 3] because it is presented in the effluent of numerous industrial processes such as oil refineries, petrochemical and pharmaceutical industries [4, 5]. This draws the attention of policymakers and scientists to take the necessary measures by studying alternative technologies, such as Advanced Oxidation Processes (AOPs).

AOPs are technologies based on the action of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds towards by-products and eventually inert end products [6, 7]. Among others, hydrogen peroxide, ozone or

oxygen/air can be used as oxidizing agents, the processes being called wet peroxide oxidation (WPO), ozonation and wet air oxidation (WAO), respectively [8-10]. Fenton process mainly operates under relatively mild operating conditions using hydrogen peroxide as oxidant and iron as a catalyst [11].

Fenton process achieves good results so far. However, its application is mainly dependent on the narrow operational pH range, the loss of reagent activity and the need for a subsequent separation step to remove the homogeneous catalyst from the effluent, which significantly increases the cost of the operation [12]. Therefore, taking into consideration the aforementioned inconveniences of Fenton system, a strategy is proposed to prepare a heterogeneous catalyst containing both the catalytic metal (iron) and N-functional groups on the surface of activated carbon (AC).

On one hand, it is well known that AC is widely used as a good adsorbent and supporting material due to its excellent properties in mechanical strength and porous structures [13, 14]. On the other hand, the catalytic activity of AC is far from well understood. Besides the direct relationship with the physical properties (surface area, pore volume, etc.) of activated carbon [15], the surface chemistry can play an important role [16-18]. According to the recent work of Dominguez et al. [19], the effects of physicochemical characteristics of carbon materials on the rate of hydrogen peroxide decomposition were explained using cyclic voltammetry, and the main results indicated that the most important factor in the catalytic activity was the content of metals, in particular iron, this was followed by the specific surface area and finally the content of surface oxygen groups.

In addition, the presence of a chelating agent in homogeneous Fenton has demonstrated to enhance the oxidation capacity [20], either by powering the oxidation potential or keeping the iron in solution at higher pH, although the addition of a new

compound in solution is clearly an inconvenience [21]. Although, some interest has been showed in using nitrogen-containing carbon materials as metal catalyst supports [22], to the best of our knowledge, there are no data about their application in the catalytic wet peroxide oxidation (CWPO) process, but there are some recent studies on catalytic wet air oxidation (CWAO). Aminated activated carbon as a catalyst in the CWAO of cooking wastewater has been studied by Chen et al. [23]. The COD removal in CWAO of organic compounds by nitrogen containing AC was higher than that of the untreated AC and suggested that nitrogen-containing functional groups contributed to the enhanced activities of ACs. A similar study was reported by Ayusheev et al. [24], focusing on the effect of nitrogen content in N-doped carbon nanofibers (N-CNFs) on the catalytic activity of Ru/N-CNFs in the wet air oxidation of phenol. Ru-containing catalysts and nitrogen in N-CNFs was found to be responsible for both the increased activity and stability of the catalysts. Moreover, this study illustrates that the increase in catalytic activity is related with several factors: (1) introducing a heteroatom into carbon materials changes the acid-base properties of the support surface; (2) it makes possible to control the size of the supported metal particles; (3) using a support of higher conductivity leads to enhanced chemical reactivity for electron transfer process in a catalytic system.

Therefore, the main objective of this work is to prepare surface modified activated carbon materials (for utilisation as supports/catalysts) using different N-containing groups, i.e. ethylenediamine (EDA), urea or melamine. Prior to introducing the N-functional groups on the AC surface, the activated carbon was oxidized by HNO_3 and/or subsequently activated by thionyl chloride treatment. Later, iron impregnated and then their performances where evaluated on phenol adsorption and wet peroxide oxidation.

2. Experimental

2.1. Materials

Activated carbon Norit ROX 0.8 was used as starting material for further treatments. Phenol (99%) and sodium chloride (99%) were purchased from Panreac. Nitric acid (≥65%), hydrochloric acid (>37%), hydrogen peroxide (30%wt), urea (98%), sodium hydroxide (≥97%) and iron nitrate nonahydrate (>98%) were purchased from Sigma-Aldrich. Ethylenediamine (>99%) was obtained from Merck. Thionyl chloride (>99%), melamine (≥99%) and toluene (>99%) were purchased from Fluka. The main physico-chemical properties of these N-containing compounds are presented in Table 1. All chemicals were used as received without further purification. Deionised water was used throughout the work.

2.2. Modification of activated carbon supports and catalyst preparation

Prior to use, the Norit ROX 0.8 activated carbon was crushed and granules of 25 – 50 mesh size (0.3 – 0.7 mm) were separated and used as starting material (Sample AC0). Activated carbons were modified using a combination of surface modification protocols described below, in order to obtain supports having N-containing surface groups. Iron was then supported on these modified activated carbons by incipient wetness impregnation.

2.2.1. Oxidation with nitric acid in liquid phase

The starting activated carbon (sample AC0) was oxidized with HNO_3 using a 125 mL Soxhlet extraction apparatus containing 9 g of activated carbon, connected to a boiling flask and to a condenser. A volume of 250 mL of 6 M HNO_3 was introduced into a 500 mL Pyrex round-bottom flask and heated to boiling temperature with a heating mantle. The reflux was stopped after 3 h. The oxidized activated carbon was extensively washed with distilled water to neutral pH and then dried in an oven at 110 ºC for 24 h (sample AC1) [18].

2.2.2. Activation with thionyl chloride

Thionyl chloride was used as a linking agent on the surface of AC for the attachment of N-functional groups [25]. About 12 g of the oxidized activated carbon (AC1) was subsequently activated with 40 mL of 5% solution of thionyl chloride in toluene for 5 h at 70 ºC. The carbon was then rinsed at least two times with toluene, and then purified by Soxhlet extraction with toluene for 2 h, and dried in an oven at 110 ºC for 24 h (sample AC2) [26-28].

2.2.3. Functionalization with ethylenediamine, urea and melamine

Samples AC1 and AC2 were the starting materials for functionalization with N-containing compounds. The functionalization of activated carbons with EDA, urea or melamine can be conducted directly (using sample AC1) or indirectly (using sample AC2). In the direct method, amine groups of these compounds condense with carboxyl groups on AC to generate surface amide groups. In the indirect method, they are anchored on the surface via a linkage agent thionyl chloride ($SOCl_2$). In this case, first

151 the linking agent reacts with a carboxylic group of the surface to convert the surface
152 carboxylic groups into acyl chloride functionalities [25]; and in the second stage, the
153 amine groups of EDA/urea/melamine condense with anchored chlorine atoms [29].
154
155 *Ethylenediamine*: 2 g of AC1 (or AC2) were refluxed with 100 mL solution of EDA in
156 toluene (1 M) for 24 h. The amine grafted samples were washed in toluene under
157 sonication for 10 min and then were purified in a Soxhlet extraction unit for 2 h to
158 remove unattached or free EDA from activated carbon. The resulting activated carbons
159 were dried in an oven at 110 ºC for 24 h (samples AC1_EDA and AC2_EDA).
160
161 *Urea*: 2 g of AC1 (or AC2) were added into 100 mL of an aqueous urea solution (1 M),
162 and stirred at room temperature for 24 h. Then, the material was filtered and dried in the
163 oven. The sample treated with urea was carbonized under N_2 flow (100 cm^3 min^{-1}) at 10
164 ºC min^{-1} up to 450 ºC and held at this temperature for 50 min (samples AC1_Urea and
165 AC2_Urea)
166
167 *Melamine*: 2 g of AC1 (or AC2) were mixed with a melamine suspension (1.3 g of
168 melamine in 100 mL of 80% ethanol) and stirred at 70 ºC for 5 h. Then the mixture was
169 boiled to evaporate the solvent and the slurry was dried at 110 ºC for 24 h. The sample
170 impregnated with melamine was carbonized under N_2 flow (100 cm^3 min^{-1}) at 10 ºC
171 min^{-1} up to 450 ºC and held at this temperature for 50 min [30, 31]. After this treatment
172 the samples are labeled as AC1_Melamine and AC2_Melamine, respectively.
173
174 *2.2.4. Preparation of catalysts*
175

The active metal was supported on the original (AC0) and in all the modified activated carbons by incipient wetness impregnation of an aqueous solution of iron(III) nitrate nonahydrate. The impregnation was always conducted under vacuum and ultrasonic mixing. The precursor solutions with calculated concentration were added drop wise using a peristaltic pump and the slurry was left at room temperature under ultrasonic mixing for 90 min. After impregnation, the samples were dried at 110 ºC for 24 h and calcined under a nitrogen flow at 400 ºC for 1 h, then finally reduced at 400 ºC in hydrogen flow for 3 h (sample ZVI/support). The content of metal was maintained constant at 3 wt%. The reduction temperature for the iron catalysts was determined by temperature programmed reduction (TPR). The treatment methods for the activated carbon used in this work are summarized in Table 2.

2.3. Characterization of supports and catalysts

The supports were characterized by N_2 adsorption at -196 ºC, temperature programmed desorption (TPD), elemental analysis and determination of the pH at the point of zero charge (pH_{PZC}). The catalysts were also characterized by temperature programmed reduction (TPR).

2.3.1. Textural characterization

The textural characterization of all the materials was checked in order to evaluate if there had been significant textural changes after the modification of surface chemistry. This characterization was based on the N_2 adsorption isotherms, determined at -196 ºC with a Quanthachrome NOVA 4200e multi-station instrument. Prior to the measurements, the samples were outgassed at 120 ºC for 5 h under vacuum. The

specific surface area of the mesopores (S_{meso}) and the micropore volume (V_{micro}) were calculated by the t-method. Moreover, the surface area (S_{BET}) of the samples was calculated by the B.E.T. method.

2.3.2. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) analysis allows finding the most appropriate reduction temperature of the metal and to evaluate the effect of modified activated carbons on the reducibility. TPR profiles were obtained with a fully automated AMI-200 (Altamira Instruments). The catalyst (0.15 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 600 ºC under a flow of 5% (v/v) H_2 in Ar at 30 cm^3 min^{-1}. The H_2 consumption was monitored by a thermal conductivity detector (TCD). The temperature range where reduction occurs could be indicated directly from the H_2 consumption peaks.

2.3.3. Surface chemistry characterization

The surface chemistry of the starting and modified activated carbons was characterized by temperature-programmed desorption (TPD) [18]. The TPD spectra of CO and CO_2 were obtained with a fully automated AMI-300 (Altamira instruments). The carbon sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 1100 ºC under a constant flow rate of He at 25 cm^3 min^{-1} (STP). The amounts of CO (m/z = 28) and CO_2 (m/z = 44) released from the carbon samples were monitored with a mass spectrometer (Dymaxion, Ametek). CO and CO_2 were calibrated at the end of each analysis.

The pH at the point of zero charge (pH_{PZC}) was determined by mixing 0.05 g of each sample with 20 mL of 0.01 M NaCl solution with pH values adjusted between 2 and 11, by adding 0.1 M HCl or 0.1 M NaOH solutions. The final pH was measured after 48 h of shaking at room temperature. Blank experiments (without addition of carbon) were also performed for each pH and the values measured after 48 h are considered as the initial pH, in order to avoid the variation of pH caused by the effect of CO_2 present in head space. The pH_{PZC} value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH [32].

Carbon, hydrogen, nitrogen and oxygen (by difference) contents were determined using a Carlo Erba EA 1108 Elemental Analyzer. Prior to the analysis, water adsorbed on the surface of the supports was removed by drying at 110 ºC in the oven overnight.

2.4. Adsorption and Catalytic tests

Both adsorption and CWPO experiments were carried out in a magnetically stirred tank (batch reactor). The reactor was filled with 100 mL of a phenol aqueous solution (150 mg/L) and heated by immersion in a water bath at controlled temperature.

The solution pH was adjusted to a value of 3.0 using H_2SO_4 solution (1 M). When the desired temperature was reached (30 ºC), a calculated volume of H_2O_2 (0.25 mL) was added into the system after catalyst addition (100 mg), in order to reach a H_2O_2 concentration of 750 mg/L in the CWPO runs (the theoretical stoichiometric amount needed to completely mineralize phenol); at this moment the reaction was assumed to start. The CWPO oxidation runs were carried out both using the activated

carbons (without iron) and iron supported carbon as catalysts, in order to evaluate the ability of the supports alone to decompose H_2O_2, and subsequently to promote phenol oxidation. This may give an idea to discriminate between a potential catalytic surface chemistry and the catalytic activity owing to the presence of iron.

In addition, pure adsorption runs were performed in order to assess the contribution of adsorption to the removal of phenol. The experiments were carried out in the same conditions, but without H_2O_2 addition.

Selected experiments were performed in triplicate and the relative error of the experimental results was below ±4%.

2.5. Analytical methods

Both in pure adsorption and in CWPO, liquid samples were periodically withdrawn from the reactor. Then, each sample was filtered with a syringe filter of 0.20 µm nylon (Teknokroma, ref._TR-200101) and placed in a glass vial (Agilent) for immediate analysis.

The determination of phenol concentration was performed by High Performance Liquid Chromatograph (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm from Agilent Technologies). The analyses were carried out with a mobile phase (flow rate 1 mL/min) of a 40/60% mixture of methanol and ultrapure water (Milli-Q water). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL.

Total Organic Carbon (TOC) was also determined at the end of the experiments

277 in a TC Multi Analyzer 2100 N/C equipment from Analytic Jena with a non-diffractive
278 IR detector.

279 Fe leached to the reaction media was determined by using Atomic Absorption
280 Spectroscopy (AAS) at 249 nm.

281 The main parameters used to compare the results in the discussion section are
282 the removal of phenol (X_{PhOH}) and TOC abatement (X_{TOC}), which are respectively
283 defined as:

284 $$X_{PhOH}(\%) = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \quad (2)$$

285 where $[PhOH]_0$ is the initial phenol concentration and $[PhOH]_t$ is the concentration at
286 time t, and

287 $$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \quad (3)$$

288 where TOC_0 is the initial TOC concentration and TOC_t is the concentration at time t.

289

290 **3. Results and discussion**

291

292 *3.1. Characterization of activated carbons and catalysts*

293 *3.1.1. Textural properties*

294 BET surface area (S_{BET}), mesopore surface area (S_{meso}) and micropore volume
295 (V_{micro}) of the original AC, modified AC and one iron supported catalyst are
296 summarized in Table 3. The results revealed that the original AC (AC0) is highly
297 microporous and has high BET surface area, 984 m^2/g. In the case of acid-treated (AC1)
298 and HNO_3 plus $SOCl_2$-treated (AC2) activated carbons, the BET surface area decreased
299 following the treatments by 13% and 35%, respectively. The slight change in the
300 surface area of AC1 can be explained by the abundant presence of oxygen-containing

groups on the surface of the activated carbon, which are introduced by the HNO_3 treatment. In spite of having similar micropore volumes, AC0 and AC1 present different mesopore areas, suggesting that the mesostructure of activated carbon was partially destroyed after treatment with HNO_3. In the case of AC2, which is treated with HNO_3 and $SOCl_2$, the reduction in the surface area can be explained by the introduction of both oxygen and sulfur-containing groups. Such sulfur moieties (sulfones, sulfides, sulfoxides, and sulfur atoms) may lead to active sites occlusion inside the pores and on the surface of AC, as reported by Khayoon et al. [33]. Treatments with EDA and melamine lead to a drastic reduction of the surface area. This may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of N_2 molecules to the micropores. However, an appreciable increase of surface area and pore volume can be noticed only for urea treated samples (compared to AC1 and AC2). In general, the textural properties of carbons are highly influenced by the nitrogen containing precursor; specially, for the AC2_Melamine sample, for which the micropore volume decreased up to nearly zero and also affects the mesostructure according to the S_{meso} value. On the other hand, the impregnation of iron did not substantially change the textural properties of the original carbon material due to the small load of iron (3 wt%) used, which is in agreement with the previous literature [34].

3.1.2. TPR

TPR profiles of iron catalyst on the different supports are shown in Fig. 1. For comparison purpose, the TPR analyses of selected modified activated carbons were also performed and no additional peaks were observed. As it can be seen from Fig. 1, the position, width and intensity of the peaks mainly depend on the nature of the support. The major reduction peak is at a temperature around 400 ºC for original (AC0) and

oxidized AC (AC1). The second peak observed at temperature above 550 ºC in AC0 profile could be related to iron oxide which is strongly interacting with the support. In general, the reduction peak for samples treated with N-containing compounds is shifted to the right irrespective of the starting material (AC1 or AC2). The reduction temperature depends on the degree of interaction between the active species and the support. For all samples treated with N-containing compounds using either AC1 or AC2 as a starting material, the iron reduction peaks shift to higher temperatures. Exceptions are the samples treated with urea, which present a reduction peak at lower temperature.

3.1.3. Surface chemistry characterization

3.1.3.1. TPD and pH_{PZC}

TPD analyses were carried out to evaluate the surface chemistry of the different AC supports. The nature of the groups can be assessed by the decomposition temperature and the type of gas released. CO and CO_2 are released by thermal decomposition of oxygen containing groups on the surface of carbon materials at different temperatures [18]. The TPD profiles of the original and modified activated carbons are depicted in Fig. 2. From the TPD profiles, it is possible to identify and quantify the amounts of the oxygenated groups of each sample. CO_2 peaks result from carboxylic acids at low temperatures (150 – 450 ºC), or lactones at higher temperatures (600 – 800 ºC); carboxylic anhydrides originate both CO and CO_2 (400 – 650 ºC); groups such as phenols (600 – 800 ºC) and carbonyls/quinones (750 – 1000 ºC) originate CO peaks [35].

It can be seen that the nitric acid treatment (AC1) increase the amount of oxygenated surface groups, which is evidenced by the increase of CO_2 (Fig. 2a) and CO

(Fig. 2b) released. The samples treated with EDA originate CO peaks at lower temperatures (200-400 ºC) than the others.

The total amounts of CO and CO_2 released from the AC materials were calculated from the corresponding TPD spectra. This information as well as the point of zero charge of the samples with different surface chemistries are shown in Table 4.

As expected, AC1 has a low pH_{PZC} and the highest amount of CO and CO_2, due to the introduction of oxygen-containing surface groups having acidic properties, mainly carboxylic acids. After thionyl chloride treatment (sample AC2), the carboxyl groups were mostly converted into acid chloride groups, resulting a decrease of the amount of CO and CO_2, but this material (AC2) still has acidic properties with the corresponding pH_{PZC} value similar to that of sample AC1. With the exception of AC2_EDA, all materials obtained after the treatment with N-containing precursors using sample AC1 or AC2 as starting materials have approximately neutral or slightly basic properties. This can be explained by the presence of nitrogen groups having basic properties.

In general, the TPD profile shows that it is important to have high density of oxygenated groups on the surface of carbon before functionalization with the N-containing compounds. The N-containing groups (EDA, urea and melamine) strongly interact with carboxylic acids, anhydrides and lactones [28, 36]. Whereas, in the case of AC2, the N-functional groups were effectively introduced on the carbon surface via $SOCl_2$ linkage.

3.1.3.2. Elemental analysis

The carbon, hydrogen, nitrogen and oxygen contents obtained by elemental analysis are summarized in Table 5. Considering the treatment carried out, it was

expected that AC2 and AC2-based samples may contain some sulphur, which is summed with the oxygen content as oxygen determined by difference.

The original AC contains a small amount (about 1%) of nitrogen. Significant amounts of nitrogen were introduced on the surface after treatment with N-containing compounds. The highest amount of nitrogen incorporated into the structure was obtained when melamine was the source of nitrogen, as its molecule contains up to six nitrogen atoms.

Thus, the differences in the amounts of nitrogen may be related to the content of nitrogen in the precursors (67% in melamine; 47% in urea and EDA) and the promoting effect of surface acidity, enhanced by oxidation/activation of $SOCl_2$ on the retention of N-containing organic bases [31,37]. On the other hand, the EDA treated samples contain a relatively high content of hydrogen compared to others; this is probably due to the higher content of hydrogen found in the compound. It is interesting to note that in the urea and EDA treated samples similar total contents of nitrogen are found regardless the pretreatment applied, either using oxidized (AC1) or activated with thionyl chloride (AC2). However, in the case of melamine treated samples, the nitrogen content is higher when the AC2 sample is the starting material in comparison to the inactivated (only oxidized) sample AC1.

3.2. Catalytic activity

Although it is difficult to compare the performance of catalysts having different textural properties and surface chemistries, we performed some tests using the activated carbons as adsorbents or catalysts and the iron supported on modified AC as catalysts for the removal of phenol in solution.

The phenol removal on the original and modified activated carbons was studied as a function of time under the following conditions: 100 mL of solution having 150 mg/L of phenol, adsorbent/catalyst amount = 1 g/L, initial pH of the solution = 3.0, T = 30 ºC, atmospheric pressure and stoichiometric amount of H_2O_2.

3.2.1. Adsorption experiments

Adsorption experiments were carried out to evaluate the effect of textural and surface properties of the original and modified activated carbons on phenol removal by adsorption. The results of phenol removal in adsorption runs performed with the original and modified activated carbons are compiled in Fig. 3.

Even though the difference is not big compared to the original AC, it is clear that urea treated samples (AC1_Urea and AC2_Urea) improve the adsorption capacity of the original AC (AC0). These samples (AC0, AC1_Urea and AC2_Urea) present similar surface areas and pore volumes, their difference being mainly related with their surface chemistry. All the other materials showed lower adsorption capacities compared to the original AC. These adsorption results confirm that the textural properties of the carbon materials have a primary role in adsorption of phenol, irrespective of surface chemistry, but closely following the available surface area.

In the adsorption of aromatic compounds in liquid phase on activated carbons, there are mainly two types of interactions: (1) electrostatic and (2) dispersive [38]. The first mechanism is involved when the adsorbate is dissociated under the experimental conditions. For example, if solution pH > pH_{PZC}, then the carbon surface is negatively charged, the opposite occurs when the solution pH < pH_{PZC} as described elsewhere [39]. In the case of the second mechanism, the existence of π-π dispersion interactions is commonly accepted [38, 40]. Taking this in consideration, at pH of 3.0, phenol

(pK_a=9.89) is found in solution predominantly in the molecular form and only the dispersive interactions are most probably involved in its adsorption on the carbon surface [41, 42].

Among the materials tested, the best performance was obtained with AC2_Urea, reaching 67% of phenol removal after 3 h. The BET surface area of this adsorbent is slightly lower and the pH_{PZC} is higher compared to the original AC. The EDA treated samples show moderate adsorption performance having moderate surface area and pH_{PZC}. However, the melamine treated samples show a poor adsorption performance due to the drastic decrease of surface area, though having a higher pH_{PZC} compared to AC1 and AC2 (pH_{PZC} of 2.5).

The presence of N-containing groups on the surface, increases the electronic density, and therefore the basicity of samples (see pH_{PZC} in Table 4), which generally favors adsorption of aromatic compounds. Recently, ammonia-modified activated carbon was prepared for the adsorption of 2,4-dichlorophenol (2,4-DCP), which enhances the adsorption capacity in comparison with the parent activated carbon [43]. This was explained due to the basic surface functional groups created by nitrogen-incorporation. Similar results also presented by Yang et al [44] for phenol adsorption using aminated activated carbon.

Moreover, the analysis of the results shows that there is a correlation between the phenol removal efficiency by adsorption and the S_{BET} of the tested activated carbons. The correlation is shown in Fig. 4. The figure clearly shows that the phenol removal efficiency increases linearly with the S_{BET}, irrespective of the surface chemistry. This indicates that the surface area of activated carbons is the principal responsible for the phenol adsorption capacity. Fierro and co-workers [45] also

observed that the amount of adsorbed phenol in microporous activated carbons increases linearly with the increase in micropore volume.

As mentioned above, the textural and chemical properties of the tested samples are different. So, an additional study is needed to take conclusions about the effect of textural properties and surface functionalities. For this purpose, the apparent rate constants for the first-order (k_1) and second-order (k_2) adsorption models were determined for all samples tested. The constants of the two models are listed in Table 6. The ratio between k_1 or k_2 and S_{BET} is presented in the same table. Even though, both the first-order and the second-order model fit the experimental data quite well with R^2 values close to unity, the second-order model was suitable for the adsorption of lower molecular weight adsorbates on smaller adsorbent particles as reported by Wu et al. [46] and therefore the corresponding kinetic constants are used in the following discussion.

It is reported that phenol adsorption is dependent on both the surface area and the presence of surface groups [45, 47]. In order to evaluate the influence of the nitrogen content, the second-order apparent rate constants (k_2) are normalized by the specific surface area (S_{BET}). It can be observed in Fig. 5 that high normalized adsorption rate constants correspond to samples with high amounts of N-containing surface groups (see Table 5).

3.2.2. CWPO experiments

3.2.2.1. Modified activated carbons as catalysts

In order to evaluate the ability of the modified activated carbons to act as catalysts (without any supported metal) in the CWPO of phenol, runs were performed under the same conditions as the adsorption tests but now adding H_2O_2. The corresponding phenol removal curves are shown in Fig. 6.

Phenol removal by CWPO in the presence of modified activated carbons as catalysts was similar or slightly higher than those obtained by adsorption. However, the results of phenol removal by adsorption (Fig. 3) and CWPO (Fig. 6) lead to the conclusion that these modified carbon materials are not particularly active for CWPO of phenol. For instance, the phenol removal at 60 min for AC1_Urea is 43% without H_2O_2 and 42% in the presence of H_2O_2, or 65% and 64%, respectively, at 180 min, which suggests that both cases are governed by adsorption. So, the removal of phenol is mainly due to pure adsorption. Similar conclusion was obtained in a previous work for some dyes [48]. According to Dominguez et al [49], as the initial phenol concentration and the phenol/catalyst ratio used in the present work are relatively low, a large fraction of active sites on the carbon surface is available for hydrogen peroxide decomposition into hydroxyl radicals, which may be consumed by non-effective reactions. This probably explains the poor performance of activated carbon in CWPO compared to adsorption.

3.2.2.2. Iron supported catalysts

In order to study the influence of surface chemical characteristics of the support on the activity of iron catalysts in phenol oxidation, a set of runs were performed in CWPO for different ZVI supported catalysts. Fig. 7 shows the evolution of phenol removal in the presence of the iron catalyst supported on different supports. ZVI/AC2_Melamine and ZVI/AC2_EDA show a good and similar performance, reaching above 80% phenol conversion after 60 min. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of ZVI (i.e AC2_Melamine and AC2_EDA) shows low removal efficiency below 15 % after 60 min.

498 It must be strongly noted that the presence of ZVI on N-containing catalysts
499 yields a better phenol removal, reaching values over 85% after 3 h. Here, ZVI acts as a
500 heterogeneous catalyst for the degradation of phenol in aqueous solution by effectively
501 decomposing hydrogen peroxide and generating hydroxyl radical, which reacts at high
502 rate with phenol and its intermediates [50]. These results revealed that there is a direct
503 and positive relation between the catalytic activity and the nitrogen content of the
504 materials. Therefore, the activity of iron supported catalysts based on N-containing AC
505 in CWPO of phenol is enhanced when compared to that of the untreated ones. It is thus
506 observed that the presence of nitrogen groups on the surface of activated carbon, in
507 addition to iron, clearly increases the phenol removal. This synergy can be probably
508 assigned to the ability of retaining the iron ions close to the carbon surface due to the
509 complexing properties of these N-containing groups.
510 Similar trends were observed for TOC removal at the end of adsorption and
511 oxidation tests. Fig. 8 shows that the EDA and melamine treated AC present lower TOC
512 removal performance in the adsorption or oxidation tests when these materials were
513 used as adsorbents or catalysts, respectively. However, the ZVI supported catalysts on
514 the EDA and melamine treated supports also promote the TOC removal. The main
515 reason for this can be explained by the synergetic effect of the presence of nitrogen
516 group and iron on the surface of activated carbon, promoting oxidation instead of
517 adsorption. In this case, the access of H_2O_2 to the iron on the carbon surface could be
518 easier than for the other samples and accelerates the hydroxyl radical generation for
519 deep oxidation of phenol, as observed in Fig. 7. However, additional studies are still
520 required to reveal the exact origin of these effects.
521 Leaching tests were performed in order to evaluate the stability and contribution
522 of homogeneous reaction for each catalyst after 120 and 180 min of reaction. Leaching

of iron corresponds to values below 0.01% of the metal initially present in almost all catalysts; also limited values of 0.03 to 0.04% were measured in the case of AC1 and AC2 supported catalysts. This fact can be related with the pH_{PZC} of the support. In fact, AC1 and AC2 present the lowest pH_{PZC} and a relatively high iron leaching. In conclusion, the contribution of homogeneous system is quite negligible, as the amount of leached iron is quite low.

Since the stability of a catalyst is one important aspect in the general evaluation of its performance, the most efficient catalysts of this study (ZVI/AC2_Melamine and ZVI/AC2_EDA) were reused three times in consecutive CWPO reactions (Fig. 9). A slight loss of catalyst activity is observed with both catalysts from the 1st to the 2nd run, but the activity being practically maintained from the 2nd to the 3rd run, and the actual removal of phenol is around 80%. The decrease in the removal of phenol observed from the first to the second run may be due to the lower adsorption capacity of the used catalyst and/or the slight loss of the catalyst during the recovery process. In fact, at the end of the experiment, a fraction of organic compounds will remain adsorbed onto the catalyst under the employed operating conditions. These compounds can be either phenol or intermediates formed during the oxidation reaction, as discussed elsewhere [51]. In any case, both catalysts (ZVI/AC2_Melamine and ZVI/AC2_EDA) still present a good efficiency under consecutive runs.

4. Conclusions

Activated carbons with different N-containing precursors were modified, characterized and tested as adsorbents or catalysts for adsorption and peroxide oxidation

of phenol. Besides, these modified carbons were also impregnated with iron and used as catalysts for CWPO.

Treatments with EDA and melamine lead to a drastic surface area reduction. This may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of N_2 molecules to the micropores.

In the urea and EDA treated samples similar total contents of nitrogen are found regardless of the pretreatment applied. However, in the case of melamine treated samples, the nitrogen content is significantly higher when the oxidized activated carbon treated with thionyl chloride is the starting material.

Phenol removal by CWPO in the presence of carbon materials was slightly higher than those obtained by adsorption. However, the results lead to the conclusion that these materials are not particularly active for the reaction, the removal of phenol being mainly due to adsorption.

The iron supported catalysts based on N-containing AC show the highest phenol removal efficiency, reaching values over 85% conversion after 3 h. This result revealed that there is a positive relation between the catalytic activity and the nitrogen content of the materials.

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Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol

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Abstract

Zero-valent iron supported catalysts were prepared through modifying an activated carbon (AC) support with different nitrogen containing precursors; (ethylenediamine, urea and melamine) and impregnating it with 3 wt% of iron. The supports were characterized by N_2 adsorption at -196 ºC, elemental analysis (EA), the pH at the point of zero charge (pH_{PZC}) and temperature programmed desorption (TPD). The iron catalysts were also characterized by temperature programmed reduction (TPR). Subsequently, the catalysts were tested in the adsorption and wet peroxidation of phenol. The results from the different characterization techniques demonstrate that the nitrogen-containing groups are successfully introduced into the carbon surface via all

the precursors used. The tests of the different modified carbons as adsorbents/catalysts indicated that the adsorption capacity and the efficiency in phenol oxidation are governed by the specific surface area and functional groups present. Both surface chemistry and textural properties of carbons are influenced by the nitrogen source and the type of oxygen functionalities preexisting on the surface. The modified carbons supported iron catalysts revealed significantly enhanced phenol removal efficiency, reaching over 85% conversion after 3 h, and showed interesting catalytic stability.

Keywords: Phenol; Activated carbon; Surface chemistry; Catalytic wet peroxide oxidation

1. Introduction

The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of wastewaters [1]. Besides, due to the increasing complexity and toxicity of organic pollutants in industrial wastewaters and the more increasingly strict environmental regulations, the toxicity nature must be reduced. Phenol is among the most common water pollutants [2, 3] because it is presented in the effluent of numerous industrial processes such as oil refineries, petrochemical and pharmaceutical industries [4, 5]. This draws the attention of policymakers and scientists to take the necessary measures by studying alternative technologies, such as Advanced Oxidation Processes (AOPs).

AOPs are technologies based on the action of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds towards by-products and eventually inert end products [6, 7]. Among others, hydrogen peroxide, ozone or

oxygen/air can be used as oxidizing agents, the processes being called wet peroxide oxidation (WPO), ozonation and wet air oxidation (WAO), respectively [8-10]. Fenton process mainly operates under relatively mild operating conditions using hydrogen peroxide as oxidant and iron as a catalyst [11].

Fenton process achieves good results so far. However, its application is mainly dependent on the narrow operational pH range, the loss of reagent activity and the need for a subsequent separation step to remove the homogeneous catalyst from the effluent, which significantly increases the cost of the operation [12]. Therefore, taking into consideration the aforementioned inconveniences of Fenton system, a strategy is proposed to prepare a heterogeneous catalyst containing both the catalytic metal (iron) and N-functional groups on the surface of activated carbon (AC).

On one hand, it is well known that AC is widely used as a good adsorbent and supporting material due to its excellent properties in mechanical strength and porous structures [13, 14]. On the other hand, the catalytic activity of AC is far from well understood. Besides the direct relationship with the physical properties (surface area, pore volume, etc.) of activated carbon [15], the surface chemistry can play an important role [16-18]. According to the recent work of Dominguez et al. [19], the effects of physicochemical characteristics of carbon materials on the rate of hydrogen peroxide decomposition were explained using cyclic voltammetry, and the main results indicated that the most important factor in the catalytic activity was the content of metals, in particular iron, this was followed by the specific surface area and finally the content of surface oxygen groups.

In addition, the presence of a chelating agent in homogeneous Fenton has demonstrated to enhance the oxidation capacity [20], either by powering the oxidation potential or keeping the iron in solution at higher pH, although the addition of a new

compound in solution is clearly an inconvenience [21]. Although, some interest has been showed in using nitrogen-containing carbon materials as metal catalyst supports [22], to the best of our knowledge, there are no data about their application in the catalytic wet peroxide oxidation (CWPO) process, but there are some recent studies on catalytic wet air oxidation (CWAO). Aminated activated carbon as a catalyst in the CWAO of cooking wastewater has been studied by Chen et al. [23]. The COD removal in CWAO of organic compounds by nitrogen containing AC was higher than that of the untreated AC and suggested that nitrogen-containing functional groups contributed to the enhanced activities of ACs. A similar study was reported by Ayusheev et al. [24], focusing on the effect of nitrogen content in N-doped carbon nanofibers (N-CNFs) on the catalytic activity of Ru/N-CNFs in the wet air oxidation of phenol. Ru-containing catalysts and nitrogen in N-CNFs was found to be responsible for both the increased activity and stability of the catalysts. Moreover, this study illustrates that the increase in catalytic activity is related with several factors: (1) introducing a heteroatom into carbon materials changes the acid-base properties of the support surface; (2) it makes possible to control the size of the supported metal particles; (3) using a support of higher conductivity leads to enhanced chemical reactivity for electron transfer process in a catalytic system.

Therefore, the main objective of this work is to prepare surface modified activated carbon materials (for utilisation as supports/catalysts) using different N-containing groups, i.e. ethylenediamine (EDA), urea or melamine. Prior to introducing the N-functional groups on the AC surface, the activated carbon was oxidized by HNO_3 and/or subsequently activated by thionyl chloride treatment. Later, iron impregnated and then their performances where evaluated on phenol adsorption and wet peroxide oxidation.

2. Experimental

2.1. Materials

Activated carbon Norit ROX 0.8 was used as starting material for further treatments. Phenol (99%) and sodium chloride (99%) were purchased from Panreac. Nitric acid (≥65%), hydrochloric acid (>37%), hydrogen peroxide (30%wt), urea (98%), sodium hydroxide (≥97%) and iron nitrate nonahydrate (>98%) were purchased from Sigma-Aldrich. Ethylenediamine (>99%) was obtained from Merck. Thionyl chloride (>99%), melamine (≥99%) and toluene (>99%) were purchased from Fluka. The main physico-chemical properties of these N-containing compounds are presented in Table 1. All chemicals were used as received without further purification. Deionised water was used throughout the work.

2.2. Modification of activated carbon supports and catalyst preparation

Prior to use, the Norit ROX 0.8 activated carbon was crushed and granules of 25 – 50 mesh size (0.3 – 0.7 mm) were separated and used as starting material (Sample AC0). Activated carbons were modified using a combination of surface modification protocols described below, in order to obtain supports having N-containing surface groups. Iron was then supported on these modified activated carbons by incipient wetness impregnation.

2.2.1. Oxidation with nitric acid in liquid phase

The starting activated carbon (sample AC0) was oxidized with HNO_3 using a 125 mL Soxhlet extraction apparatus containing 9 g of activated carbon, connected to a boiling flask and to a condenser. A volume of 250 mL of 6 M HNO_3 was introduced into a 500 mL Pyrex round-bottom flask and heated to boiling temperature with a heating mantle. The reflux was stopped after 3 h. The oxidized activated carbon was extensively washed with distilled water to neutral pH and then dried in an oven at 110 ºC for 24 h (sample AC1) [18].

2.2.2. Activation with thionyl chloride

Thionyl chloride was used as a linking agent on the surface of AC for the attachment of N-functional groups [25]. About 12 g of the oxidized activated carbon (AC1) was subsequently activated with 40 mL of 5% solution of thionyl chloride in toluene for 5 h at 70 ºC. The carbon was then rinsed at least two times with toluene, and then purified by Soxhlet extraction with toluene for 2 h, and dried in an oven at 110 ºC for 24 h (sample AC2) [26-28].

2.2.3. Functionalization with ethylenediamine, urea and melamine

Samples AC1 and AC2 were the starting materials for functionalization with N-containing compounds. The functionalization of activated carbons with EDA, urea or melamine can be conducted directly (using sample AC1) or indirectly (using sample AC2). In the direct method, amine groups of these compounds condense with carboxyl groups on AC to generate surface amide groups. In the indirect method, they are anchored on the surface via a linkage agent thionyl chloride ($SOCl_2$). In this case, first

151 the linking agent reacts with a carboxylic group of the surface to convert the surface
152 carboxylic groups into acyl chloride functionalities [25]; and in the second stage, the
153 amine groups of EDA/urea/melamine condense with anchored chlorine atoms [29].
154
155 *Ethylenediamine*: 2 g of AC1 (or AC2) were refluxed with 100 mL solution of EDA in
156 toluene (1 M) for 24 h. The amine grafted samples were washed in toluene under
157 sonication for 10 min and then were purified in a Soxhlet extraction unit for 2 h to
158 remove unattached or free EDA from activated carbon. The resulting activated carbons
159 were dried in an oven at 110 ºC for 24 h (samples AC1_EDA and AC2_EDA).
160
161 *Urea*: 2 g of AC1 (or AC2) were added into 100 mL of an aqueous urea solution (1 M),
162 and stirred at room temperature for 24 h. Then, the material was filtered and dried in the
163 oven. The sample treated with urea was carbonized under N_2 flow (100 cm^3 min^{-1}) at 10
164 ºC min^{-1} up to 450 ºC and held at this temperature for 50 min (samples AC1_Urea and
165 AC2_Urea)
166
167 *Melamine*: 2 g of AC1 (or AC2) were mixed with a melamine suspension (1.3 g of
168 melamine in 100 mL of 80% ethanol) and stirred at 70 ºC for 5 h. Then the mixture was
169 boiled to evaporate the solvent and the slurry was dried at 110 ºC for 24 h. The sample
170 impregnated with melamine was carbonized under N_2 flow (100 cm^3 min^{-1}) at 10 ºC
171 min^{-1} up to 450 ºC and held at this temperature for 50 min [30, 31]. After this treatment
172 the samples are labeled as AC1_Melamine and AC2_Melamine, respectively.
173
174 *2.2.4. Preparation of catalysts*
175

The active metal was supported on the original (AC0) and in all the modified activated carbons by incipient wetness impregnation of an aqueous solution of iron(III) nitrate nonahydrate. The impregnation was always conducted under vacuum and ultrasonic mixing. The precursor solutions with calculated concentration were added drop wise using a peristaltic pump and the slurry was left at room temperature under ultrasonic mixing for 90 min. After impregnation, the samples were dried at 110 ºC for 24 h and calcined under a nitrogen flow at 400 ºC for 1 h, then finally reduced at 400 ºC in hydrogen flow for 3 h (sample ZVI/support). The content of metal was maintained constant at 3 wt%. The reduction temperature for the iron catalysts was determined by temperature programmed reduction (TPR). The treatment methods for the activated carbon used in this work are summarized in Table 2.

2.3. Characterization of supports and catalysts

The supports were characterized by N_2 adsorption at -196 ºC, temperature programmed desorption (TPD), elemental analysis and determination of the pH at the point of zero charge (pH_{PZC}). The catalysts were also characterized by temperature programmed reduction (TPR).

2.3.1. Textural characterization

The textural characterization of all the materials was checked in order to evaluate if there had been significant textural changes after the modification of surface chemistry. This characterization was based on the N_2 adsorption isotherms, determined at -196 ºC with a Quanthachrome NOVA 4200e multi-station instrument. Prior to the measurements, the samples were outgassed at 120 ºC for 5 h under vacuum. The

specific surface area of the mesopores (S_{meso}) and the micropore volume (V_{micro}) were calculated by the t-method. Moreover, the surface area (S_{BET}) of the samples was calculated by the B.E.T. method.

2.3.2. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) analysis allows finding the most appropriate reduction temperature of the metal and to evaluate the effect of modified activated carbons on the reducibility. TPR profiles were obtained with a fully automated AMI-200 (Altamira Instruments). The catalyst (0.15 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 600 ºC under a flow of 5% (v/v) H_2 in Ar at 30 cm^3 min^{-1}. The H_2 consumption was monitored by a thermal conductivity detector (TCD). The temperature range where reduction occurs could be indicated directly from the H_2 consumption peaks.

2.3.3. Surface chemistry characterization

The surface chemistry of the starting and modified activated carbons was characterized by temperature-programmed desorption (TPD) [18]. The TPD spectra of CO and CO_2 were obtained with a fully automated AMI-300 (Altamira instruments). The carbon sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 1100 ºC under a constant flow rate of He at 25 cm^3 min^{-1} (STP). The amounts of CO (m/z = 28) and CO_2 (m/z = 44) released from the carbon samples were monitored with a mass spectrometer (Dymaxion, Ametek). CO and CO_2 were calibrated at the end of each analysis.

The pH at the point of zero charge (pH_{PZC}) was determined by mixing 0.05 g of each sample with 20 mL of 0.01 M NaCl solution with pH values adjusted between 2 and 11, by adding 0.1 M HCl or 0.1 M NaOH solutions. The final pH was measured after 48 h of shaking at room temperature. Blank experiments (without addition of carbon) were also performed for each pH and the values measured after 48 h are considered as the initial pH, in order to avoid the variation of pH caused by the effect of CO_2 present in head space. The pH_{PZC} value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH [32].

Carbon, hydrogen, nitrogen and oxygen (by difference) contents were determined using a Carlo Erba EA 1108 Elemental Analyzer. Prior to the analysis, water adsorbed on the surface of the supports was removed by drying at 110 ºC in the oven overnight.

2.4. Adsorption and Catalytic tests

Both adsorption and CWPO experiments were carried out in a magnetically stirred tank (batch reactor). The reactor was filled with 100 mL of a phenol aqueous solution (150 mg/L) and heated by immersion in a water bath at controlled temperature.

The solution pH was adjusted to a value of 3.0 using H_2SO_4 solution (1 M). When the desired temperature was reached (30 ºC), a calculated volume of H_2O_2 (0.25 mL) was added into the system after catalyst addition (100 mg), in order to reach a H_2O_2 concentration of 750 mg/L in the CWPO runs (the theoretical stoichiometric amount needed to completely mineralize phenol); at this moment the reaction was assumed to start. The CWPO oxidation runs were carried out both using the activated

carbons (without iron) and iron supported carbon as catalysts, in order to evaluate the ability of the supports alone to decompose H_2O_2, and subsequently to promote phenol oxidation. This may give an idea to discriminate between a potential catalytic surface chemistry and the catalytic activity owing to the presence of iron.

In addition, pure adsorption runs were performed in order to assess the contribution of adsorption to the removal of phenol. The experiments were carried out in the same conditions, but without H_2O_2 addition.

Selected experiments were performed in triplicate and the relative error of the experimental results was below ±4%.

2.5. Analytical methods

Both in pure adsorption and in CWPO, liquid samples were periodically withdrawn from the reactor. Then, each sample was filtered with a syringe filter of 0.20 µm nylon (Teknokroma, ref._TR-200101) and placed in a glass vial (Agilent) for immediate analysis.

The determination of phenol concentration was performed by High Performance Liquid Chromatograph (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm from Agilent Technologies). The analyses were carried out with a mobile phase (flow rate 1 mL/min) of a 40/60% mixture of methanol and ultrapure water (Milli-Q water). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL.

Total Organic Carbon (TOC) was also determined at the end of the experiments

277 in a TC Multi Analyzer 2100 N/C equipment from Analytic Jena with a non-diffractive
278 IR detector.

279 Fe leached to the reaction media was determined by using Atomic Absorption
280 Spectroscopy (AAS) at 249 nm.

281 The main parameters used to compare the results in the discussion section are
282 the removal of phenol (X_{PhOH}) and TOC abatement (X_{TOC}), which are respectively
283 defined as:

284 $$X_{PhOH}(\%) = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \quad (2)$$

285 where $[PhOH]_0$ is the initial phenol concentration and $[PhOH]_t$ is the concentration at
286 time t, and

287 $$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \quad (3)$$

288 where TOC_0 is the initial TOC concentration and TOC_t is the concentration at time t.

289

290 **3. Results and discussion**

291

292 *3.1. Characterization of activated carbons and catalysts*

293 *3.1.1. Textural properties*

294 BET surface area (S_{BET}), mesopore surface area (S_{meso}) and micropore volume
295 (V_{micro}) of the original AC, modified AC and one iron supported catalyst are
296 summarized in Table 3. The results revealed that the original AC (AC0) is highly
297 microporous and has high BET surface area, 984 m^2/g. In the case of acid-treated (AC1)
298 and HNO_3 plus $SOCl_2$-treated (AC2) activated carbons, the BET surface area decreased
299 following the treatments by 13% and 35%, respectively. The slight change in the
300 surface area of AC1 can be explained by the abundant presence of oxygen-containing

groups on the surface of the activated carbon, which are introduced by the HNO_3 treatment. In spite of having similar micropore volumes, AC0 and AC1 present different mesopore areas, suggesting that the mesostructure of activated carbon was partially destroyed after treatment with HNO_3. In the case of AC2, which is treated with HNO_3 and $SOCl_2$, the reduction in the surface area can be explained by the introduction of both oxygen and sulfur-containing groups. Such sulfur moieties (sulfones, sulfides, sulfoxides, and sulfur atoms) may lead to active sites occlusion inside the pores and on the surface of AC, as reported by Khayoon et al. [33]. Treatments with EDA and melamine lead to a drastic reduction of the surface area. This may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of N_2 molecules to the micropores. However, an appreciable increase of surface area and pore volume can be noticed only for urea treated samples (compared to AC1 and AC2). In general, the textural properties of carbons are highly influenced by the nitrogen containing precursor; specially, for the AC2_Melamine sample, for which the micropore volume decreased up to nearly zero and also affects the mesostructure according to the S_{meso} value. On the other hand, the impregnation of iron did not substantially change the textural properties of the original carbon material due to the small load of iron (3 wt%) used, which is in agreement with the previous literature [34].

3.1.2. TPR

TPR profiles of iron catalyst on the different supports are shown in Fig. 1. For comparison purpose, the TPR analyses of selected modified activated carbons were also performed and no additional peaks were observed. As it can be seen from Fig. 1, the position, width and intensity of the peaks mainly depend on the nature of the support. The major reduction peak is at a temperature around 400 ºC for original (AC0) and

oxidized AC (AC1). The second peak observed at temperature above 550 ºC in AC0 profile could be related to iron oxide which is strongly interacting with the support. In general, the reduction peak for samples treated with N-containing compounds is shifted to the right irrespective of the starting material (AC1 or AC2). The reduction temperature depends on the degree of interaction between the active species and the support. For all samples treated with N-containing compounds using either AC1 or AC2 as a starting material, the iron reduction peaks shift to higher temperatures. Exceptions are the samples treated with urea, which present a reduction peak at lower temperature.

3.1.3. Surface chemistry characterization

3.1.3.1. TPD and pH_{PZC}

TPD analyses were carried out to evaluate the surface chemistry of the different AC supports. The nature of the groups can be assessed by the decomposition temperature and the type of gas released. CO and CO_2 are released by thermal decomposition of oxygen containing groups on the surface of carbon materials at different temperatures [18]. The TPD profiles of the original and modified activated carbons are depicted in Fig. 2. From the TPD profiles, it is possible to identify and quantify the amounts of the oxygenated groups of each sample. CO_2 peaks result from carboxylic acids at low temperatures (150 – 450 ºC), or lactones at higher temperatures (600 – 800 ºC); carboxylic anhydrides originate both CO and CO_2 (400 – 650 ºC); groups such as phenols (600 – 800 ºC) and carbonyls/quinones (750 – 1000 ºC) originate CO peaks [35].

It can be seen that the nitric acid treatment (AC1) increase the amount of oxygenated surface groups, which is evidenced by the increase of CO_2 (Fig. 2a) and CO

(Fig. 2b) released. The samples treated with EDA originate CO peaks at lower temperatures (200-400 ºC) than the others.

The total amounts of CO and CO_2 released from the AC materials were calculated from the corresponding TPD spectra. This information as well as the point of zero charge of the samples with different surface chemistries are shown in Table 4.

As expected, AC1 has a low pH_{PZC} and the highest amount of CO and CO_2, due to the introduction of oxygen-containing surface groups having acidic properties, mainly carboxylic acids. After thionyl chloride treatment (sample AC2), the carboxyl groups were mostly converted into acid chloride groups, resulting a decrease of the amount of CO and CO_2, but this material (AC2) still has acidic properties with the corresponding pH_{PZC} value similar to that of sample AC1. With the exception of AC2_EDA, all materials obtained after the treatment with N-containing precursors using sample AC1 or AC2 as starting materials have approximately neutral or slightly basic properties. This can be explained by the presence of nitrogen groups having basic properties.

In general, the TPD profile shows that it is important to have high density of oxygenated groups on the surface of carbon before functionalization with the N-containing compounds. The N-containing groups (EDA, urea and melamine) strongly interact with carboxylic acids, anhydrides and lactones [28, 36]. Whereas, in the case of AC2, the N-functional groups were effectively introduced on the carbon surface via $SOCl_2$ linkage.

3.1.3.2. Elemental analysis

The carbon, hydrogen, nitrogen and oxygen contents obtained by elemental analysis are summarized in Table 5. Considering the treatment carried out, it was

expected that AC2 and AC2-based samples may contain some sulphur, which is summed with the oxygen content as oxygen determined by difference.

The original AC contains a small amount (about 1%) of nitrogen. Significant amounts of nitrogen were introduced on the surface after treatment with N-containing compounds. The highest amount of nitrogen incorporated into the structure was obtained when melamine was the source of nitrogen, as its molecule contains up to six nitrogen atoms.

Thus, the differences in the amounts of nitrogen may be related to the content of nitrogen in the precursors (67% in melamine; 47% in urea and EDA) and the promoting effect of surface acidity, enhanced by oxidation/activation of $SOCl_2$ on the retention of N-containing organic bases [31,37]. On the other hand, the EDA treated samples contain a relatively high content of hydrogen compared to others; this is probably due to the higher content of hydrogen found in the compound. It is interesting to note that in the urea and EDA treated samples similar total contents of nitrogen are found regardless the pretreatment applied, either using oxidized (AC1) or activated with thionyl chloride (AC2). However, in the case of melamine treated samples, the nitrogen content is higher when the AC2 sample is the starting material in comparison to the inactivated (only oxidized) sample AC1.

3.2. Catalytic activity

Although it is difficult to compare the performance of catalysts having different textural properties and surface chemistries, we performed some tests using the activated carbons as adsorbents or catalysts and the iron supported on modified AC as catalysts for the removal of phenol in solution.

The phenol removal on the original and modified activated carbons was studied as a function of time under the following conditions: 100 mL of solution having 150 mg/L of phenol, adsorbent/catalyst amount = 1 g/L, initial pH of the solution = 3.0, T = 30 ºC, atmospheric pressure and stoichiometric amount of H_2O_2.

3.2.1. Adsorption experiments

Adsorption experiments were carried out to evaluate the effect of textural and surface properties of the original and modified activated carbons on phenol removal by adsorption. The results of phenol removal in adsorption runs performed with the original and modified activated carbons are compiled in Fig. 3.

Even though the difference is not big compared to the original AC, it is clear that urea treated samples (AC1_Urea and AC2_Urea) improve the adsorption capacity of the original AC (AC0). These samples (AC0, AC1_Urea and AC2_Urea) present similar surface areas and pore volumes, their difference being mainly related with their surface chemistry. All the other materials showed lower adsorption capacities compared to the original AC. These adsorption results confirm that the textural properties of the carbon materials have a primary role in adsorption of phenol, irrespective of surface chemistry, but closely following the available surface area.

In the adsorption of aromatic compounds in liquid phase on activated carbons, there are mainly two types of interactions: (1) electrostatic and (2) dispersive [38]. The first mechanism is involved when the adsorbate is dissociated under the experimental conditions. For example, if solution pH > pH_{PZC}, then the carbon surface is negatively charged, the opposite occurs when the solution pH < pH_{PZC} as described elsewhere [39]. In the case of the second mechanism, the existence of π-π dispersion interactions is commonly accepted [38, 40]. Taking this in consideration, at pH of 3.0, phenol

(pK_a=9.89) is found in solution predominantly in the molecular form and only the dispersive interactions are most probably involved in its adsorption on the carbon surface [41, 42].

Among the materials tested, the best performance was obtained with AC2_Urea, reaching 67% of phenol removal after 3 h. The BET surface area of this adsorbent is slightly lower and the pH_{PZC} is higher compared to the original AC. The EDA treated samples show moderate adsorption performance having moderate surface area and pH_{PZC}. However, the melamine treated samples show a poor adsorption performance due to the drastic decrease of surface area, though having a higher pH_{PZC} compared to AC1 and AC2 (pH_{PZC} of 2.5).

The presence of N-containing groups on the surface, increases the electronic density, and therefore the basicity of samples (see pH_{PZC} in Table 4), which generally favors adsorption of aromatic compounds. Recently, ammonia-modified activated carbon was prepared for the adsorption of 2,4-dichlorophenol (2,4-DCP), which enhances the adsorption capacity in comparison with the parent activated carbon [43]. This was explained due to the basic surface functional groups created by nitrogen-incorporation. Similar results also presented by Yang et al [44] for phenol adsorption using aminated activated carbon.

Moreover, the analysis of the results shows that there is a correlation between the phenol removal efficiency by adsorption and the S_{BET} of the tested activated carbons. The correlation is shown in Fig. 4. The figure clearly shows that the phenol removal efficiency increases linearly with the S_{BET}, irrespective of the surface chemistry. This indicates that the surface area of activated carbons is the principal responsible for the phenol adsorption capacity. Fierro and co-workers [45] also

observed that the amount of adsorbed phenol in microporous activated carbons increases linearly with the increase in micropore volume.

As mentioned above, the textural and chemical properties of the tested samples are different. So, an additional study is needed to take conclusions about the effect of textural properties and surface functionalities. For this purpose, the apparent rate constants for the first-order (k_1) and second-order (k_2) adsorption models were determined for all samples tested. The constants of the two models are listed in Table 6. The ratio between k_1 or k_2 and S_{BET} is presented in the same table. Even though, both the first-order and the second-order model fit the experimental data quite well with R^2 values close to unity, the second-order model was suitable for the adsorption of lower molecular weight adsorbates on smaller adsorbent particles as reported by Wu et al. [46] and therefore the corresponding kinetic constants are used in the following discussion.

It is reported that phenol adsorption is dependent on both the surface area and the presence of surface groups [45, 47]. In order to evaluate the influence of the nitrogen content, the second-order apparent rate constants (k_2) are normalized by the specific surface area (S_{BET}). It can be observed in Fig. 5 that high normalized adsorption rate constants correspond to samples with high amounts of N-containing surface groups (see Table 5).

3.2.2. CWPO experiments

3.2.2.1. Modified activated carbons as catalysts

In order to evaluate the ability of the modified activated carbons to act as catalysts (without any supported metal) in the CWPO of phenol, runs were performed under the same conditions as the adsorption tests but now adding H_2O_2. The corresponding phenol removal curves are shown in Fig. 6.

Phenol removal by CWPO in the presence of modified activated carbons as catalysts was similar or slightly higher than those obtained by adsorption. However, the results of phenol removal by adsorption (Fig. 3) and CWPO (Fig. 6) lead to the conclusion that these modified carbon materials are not particularly active for CWPO of phenol. For instance, the phenol removal at 60 min for AC1_Urea is 43% without H_2O_2 and 42% in the presence of H_2O_2, or 65% and 64%, respectively, at 180 min, which suggests that both cases are governed by adsorption. So, the removal of phenol is mainly due to pure adsorption. Similar conclusion was obtained in a previous work for some dyes [48]. According to Dominguez et al [49], as the initial phenol concentration and the phenol/catalyst ratio used in the present work are relatively low, a large fraction of active sites on the carbon surface is available for hydrogen peroxide decomposition into hydroxyl radicals, which may be consumed by non-effective reactions. This probably explains the poor performance of activated carbon in CWPO compared to adsorption.

3.2.2.2. Iron supported catalysts

In order to study the influence of surface chemical characteristics of the support on the activity of iron catalysts in phenol oxidation, a set of runs were performed in CWPO for different ZVI supported catalysts. Fig. 7 shows the evolution of phenol removal in the presence of the iron catalyst supported on different supports. ZVI/AC2_Melamine and ZVI/AC2_EDA show a good and similar performance, reaching above 80% phenol conversion after 60 min. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of ZVI (i.e AC2_Melamine and AC2_EDA) shows low removal efficiency below 15 % after 60 min.

It must be strongly noted that the presence of ZVI on N-containing catalysts yields a better phenol removal, reaching values over 85% after 3 h. Here, ZVI acts as a heterogeneous catalyst for the degradation of phenol in aqueous solution by effectively decomposing hydrogen peroxide and generating hydroxyl radical, which reacts at high rate with phenol and its intermediates [50]. These results revealed that there is a direct and positive relation between the catalytic activity and the nitrogen content of the materials. Therefore, the activity of iron supported catalysts based on N-containing AC in CWPO of phenol is enhanced when compared to that of the untreated ones. It is thus observed that the presence of nitrogen groups on the surface of activated carbon, in addition to iron, clearly increases the phenol removal. This synergy can be probably assigned to the ability of retaining the iron ions close to the carbon surface due to the complexing properties of these N-containing groups.

Similar trends were observed for TOC removal at the end of adsorption and oxidation tests. Fig. 8 shows that the EDA and melamine treated AC present lower TOC removal performance in the adsorption or oxidation tests when these materials were used as adsorbents or catalysts, respectively. However, the ZVI supported catalysts on the EDA and melamine treated supports also promote the TOC removal. The main reason for this can be explained by the synergetic effect of the presence of nitrogen group and iron on the surface of activated carbon, promoting oxidation instead of adsorption. In this case, the access of H_2O_2 to the iron on the carbon surface could be easier than for the other samples and accelerates the hydroxyl radical generation for deep oxidation of phenol, as observed in Fig. 7. However, additional studies are still required to reveal the exact origin of these effects.

Leaching tests were performed in order to evaluate the stability and contribution of homogeneous reaction for each catalyst after 120 and 180 min of reaction. Leaching

of iron corresponds to values below 0.01% of the metal initially present in almost all catalysts; also limited values of 0.03 to 0.04% were measured in the case of AC1 and AC2 supported catalysts. This fact can be related with the pH_{PZC} of the support. In fact, AC1 and AC2 present the lowest pH_{PZC} and a relatively high iron leaching. In conclusion, the contribution of homogeneous system is quite negligible, as the amount of leached iron is quite low.

Since the stability of a catalyst is one important aspect in the general evaluation of its performance, the most efficient catalysts of this study (ZVI/AC2_Melamine and ZVI/AC2_EDA) were reused three times in consecutive CWPO reactions (Fig. 9). A slight loss of catalyst activity is observed with both catalysts from the 1st to the 2nd run, but the activity being practically maintained from the 2nd to the 3rd run, and the actual removal of phenol is around 80%. The decrease in the removal of phenol observed from the first to the second run may be due to the lower adsorption capacity of the used catalyst and/or the slight loss of the catalyst during the recovery process. In fact, at the end of the experiment, a fraction of organic compounds will remain adsorbed onto the catalyst under the employed operating conditions. These compounds can be either phenol or intermediates formed during the oxidation reaction, as discussed elsewhere [51]. In any case, both catalysts (ZVI/AC2_Melamine and ZVI/AC2_EDA) still present a good efficiency under consecutive runs.

4. Conclusions

Activated carbons with different N-containing precursors were modified, characterized and tested as adsorbents or catalysts for adsorption and peroxide oxidation

of phenol. Besides, these modified carbons were also impregnated with iron and used as catalysts for CWPO.

Treatments with EDA and melamine lead to a drastic surface area reduction. This may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of N_2 molecules to the micropores.

In the urea and EDA treated samples similar total contents of nitrogen are found regardless of the pretreatment applied. However, in the case of melamine treated samples, the nitrogen content is significantly higher when the oxidized activated carbon treated with thionyl chloride is the starting material.

Phenol removal by CWPO in the presence of carbon materials was slightly higher than those obtained by adsorption. However, the results lead to the conclusion that these materials are not particularly active for the reaction, the removal of phenol being mainly due to adsorption.

The iron supported catalysts based on N-containing AC show the highest phenol removal efficiency, reaching values over 85% conversion after 3 h. This result revealed that there is a positive relation between the catalytic activity and the nitrogen content of the materials.

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Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol

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Abstract

Zero-valent iron supported catalysts were prepared through modifying an activated carbon (AC) support with different nitrogen containing precursors; (ethylenediamine, urea and melamine) and impregnating it with 3 wt% of iron. The supports were characterized by N_2 adsorption at -196 ºC, elemental analysis (EA), the pH at the point of zero charge (pH_{PZC}) and temperature programmed desorption (TPD). The iron catalysts were also characterized by temperature programmed reduction (TPR). Subsequently, the catalysts were tested in the adsorption and wet peroxidation of phenol. The results from the different characterization techniques demonstrate that the

nitrogen-containing groups are successfully introduced into the carbon surface via all the precursors used. The tests of the different modified carbons as adsorbents/catalysts indicated that the adsorption capacity and the efficiency in phenol oxidation are governed by the specific surface area and functional groups present. Both surface chemistry and textural properties of carbons are influenced by the nitrogen source and the type of oxygen functionalities preexisting on the surface. The modified carbons supported iron catalysts revealed significantly enhanced phenol removal efficiency, reaching over 85% conversion after 3 h.

Keywords: Phenol; Activated carbon; Surface chemistry; Catalytic wet peroxide oxidation

1. Introduction

The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of wastewaters [1]. Besides, due to the increasing complexity and toxicity of organic pollutants in industrial wastewaters and the more increasingly strict environmental regulations, the toxicity nature must be reduced. Phenol is among the most common water pollutants [2, 3] because it is presented in the effluent of numerous industrial processes such as oil refineries, petrochemical and pharmaceutical industries [4, 5]. This draws the attention of policymakers and scientists to take the necessary measures by studying alternative technologies, such as Advanced Oxidation Processes (AOPs).

AOPs are technologies based on the action of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds towards by-products and

eventually inert end products [6, 7]. Among others, hydrogen peroxide, ozone or oxygen/air can be used as oxidizing agents, the processes being called wet peroxide oxidation (WPO), ozonation and wet air oxidation (WAO), respectively [8-10]. Fenton process (Fe^{2+}/H_2O_2) belongs to catalytic wet peroxide oxidation (CWPO) technologies and operates under relatively mild operating conditions (room temperature and atmospheric pressure) using hydrogen peroxide as oxidant and iron as a catalyst [11].

Fenton process achieves good results so far. However, its application is mainly dependent on the narrow operational pH range, the loss of reagent activity and the need for a subsequent separation step to remove the homogeneous catalyst from the effluent, which significantly increases the cost of the operation [12].

Therefore, taking into consideration the aforementioned inconveniences of Fenton system, a strategy is proposed to prepare a heterogeneous catalyst containing both the catalytic metal (iron) and N-functional groups on the surface of activated carbon (AC).

On one hand, it is well known that AC is widely used as a good adsorbent and supporting material due to its excellent properties in mechanical strength and porous structures [13, 14]. On the other hand, the catalytic activity of AC is far from well understood. Besides the direct relationship with the physical properties (surface area, pore volume, etc.) of activated carbon [15], the surface chemistry can play an important role [16-18]. Moreover, it has been reported [19] that the mineral content (in particular Fe content) of AC is a key to display catalytic activities.

In addition, the presence of a chelating agent in homogeneous Fenton has demonstrated to enhance the oxidation capacity [20], either by powering the oxidation potential or keeping the iron in solution at higher pH, although the addition of a new compound in solution is clearly an inconvenience [21]. Ideally, heterogenisation of this

originally homogeneous catalytic system should mostly overcome the mentioned inconveniences. Therefore, the attachment of a ligand (N-functional groups) on the AC surface is expected to help the oxidative power of H_2O_2. However, care should be given to the load of iron or ligand to be incorporated on the AC.

Therefore, the main objective of this work is to prepare surface modified activated carbon materials (for utilisation as supports/catalysts) using different N-containing groups, i.e. ethylenediamine (EDA), urea or melamine, which are later iron impregnated and then their performances where evaluated on phenol adsorption and wet peroxide oxidation.

2. Experimental

2.1. Materials

Activated carbon Norit ROX 0.8 was used as starting material for further treatments. Phenol (99%) and sodium chloride (99%) were purchased from Panreac. Nitric acid (≥65%), hydrochloric acid (>37%), hydrogen peroxide (30%wt), urea (98%), sodium hydroxide (≥97%) and iron nitrate nonahydrate (>98%) were purchased from Sigma-Aldrich. Ethylenediamine (>99%) was obtained from Merck. Thionyl chloride (>99%), melamine (≥99%) and toluene (>99%) were purchased from Fluka. The main physico-chemical properties of these N-containing compounds are presented in Table 1. All chemicals were used as received without further purification. Deionised water was used throughout the work.

2.2. Modification of activated carbon supports and catalyst preparation

Prior to use, the Norit ROX 0.8 activated carbon was crushed and granules of 25 – 50 mesh size (0.3 – 0.7 mm) were separated and used as starting material (Sample AC0). Activated carbons were modified using a combination of surface modification protocols described below, in order to obtain supports having N-containing surface groups. Iron was then supported on these modified activated carbons by incipient wetness impregnation.

2.2.1. Oxidation with nitric acid in liquid phase

The starting activated carbon (sample AC0) was oxidized with HNO_3 using a 125 mL Soxhlet extraction apparatus containing 9 g of activated carbon, connected to a boiling flask and to a condenser. A volume of 250 mL of 6 M HNO_3 was introduced into a 500 mL Pyrex round-bottom flask and heated to boiling temperature with a heating mantle. The reflux was stopped after 3 h. The oxidized activated carbon was extensively washed with distilled water to neutral pH and then dried in an oven at 110 ºC for 24 h (sample AC1) [18].

2.2.2. Activation with thionyl chloride

About 12 g of the oxidized activated carbon (AC1) was subsequently activated with 40 mL of 5% solution of thionyl chloride in toluene for 5 h at 70 ºC. The carbon was then rinsed at least two times with toluene, and then purified by Soxhlet extraction with toluene for 2 h, and dried in an oven at 110 ºC for 24 h (sample AC2) [22-24].

2.2.3. Functionalization with ethylenediamine, urea and melamine

Samples AC1 and AC2 were the starting materials for functionalization with N-containing compounds. The functionalization of activated carbons with EDA, urea or melamine can be conducted directly (using sample AC1) or indirectly (using sample AC2). In the direct method, amine groups of these compounds condense with carboxyl groups on AC to generate surface amide groups. In the indirect method, they are anchored on the surface via a linkage agent thionyl chloride ($SOCl_2$). In this case, first the linking agent reacts with a carboxylic group of the surface to convert the surface carboxylic groups into acyl chloride functionalities [25]; and in the second stage, the amine groups of EDA/urea/melamine condense with anchored chlorine atoms [26].

Ethylenediamine: 2 g of AC1 (or AC2) were refluxed with 100 mL solution of EDA in toluene (1 M) for 24 h. The amine grafted samples were washed in toluene under sonication for 10 min and then were purified in a Soxhlet extraction unit for 2 h to remove unattached or free EDA from activated carbon. The resulting activated carbons were dried in an oven at 110 ºC for 24 h (samples AC1_EDA and AC2_EDA).

Urea: 2 g of AC1 (or AC2) were added into 100 mL of an aqueous urea solution (1 M), and stirred at room temperature for 24 h. Then, the material was filtered and dried in the oven. The sample treated with urea was carbonized under N_2 flow (100 cm^3 min^{-1}) at 10 ºC min^{-1} up to 450 ºC and held at this temperature for 50 min (samples AC1_Urea and AC2_Urea)

Melamine: 2 g of AC1 (or AC2) were mixed with a melamine suspension (1.3 g of melamine in 100 mL of 80% ethanol) and stirred at 70 ºC for 5 h. Then the mixture was boiled to evaporate the solvent and the slurry was dried at 110 ºC for 24 h. The sample impregnated with melamine was carbonized under N_2 flow (100 cm^3 min^{-1}) at 10 ºC min^{-1} up to 450 ºC and held at this temperature for 50 min [27, 28]. After this treatment the samples are labeled as AC1_Melamine and AC2_Melamine, respectively.

2.2.4. Preparation of catalysts

The active metal was supported on the original (AC0) and in all the modified activated carbons by incipient wetness impregnation of an aqueous solution of iron(III) nitrate nonahydrate. The impregnation was always conducted under vacuum and ultrasonic mixing. The precursor solutions with calculated concentration were added drop wise using a peristaltic pump and the slurry was left at room temperature under ultrasonic mixing for 90 min. After impregnation, the samples were dried at 110 ºC for 24 h and calcined under a nitrogen flow at 400 ºC for 1 h, then finally reduced at 400 ºC in hydrogen flow for 3 h (sample ZVI/support). The content of metal was maintained constant at 3 wt%. The reduction temperature for the iron catalysts was determined by temperature programmed reduction (TPR). The treatment methods for the activated carbon used in this work are summarized in Table 2.

2.3. Characterization of supports and catalysts

The supports were characterized by N_2 adsorption at -196 ºC, temperature programmed desorption (TPD), elemental analysis and determination of the pH at the

point of zero charge (pH_{PZC}). The catalysts were also characterized by temperature programmed reduction (TPR).

2.3.1. Textural characterization

The textural characterization of all the materials was checked in order to evaluate if there had been significant textural changes after the modification of surface chemistry. This characterization was based on the N_2 adsorption isotherms, determined at -196 ºC with a Quanthachrome NOVA 4200e multi-station instrument. Prior to the measurements, the samples were outgassed at 120 ºC for 5 h under vacuum. The specific surface area of the mesopores (S_{meso}) and the micropore volume (V_{micro}) were calculated by the t-method. Moreover, the surface area (S_{BET}) of the samples was calculated by the B.E.T. method.

2.3.2. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) analysis allows finding the most appropriate reduction temperature of the metal and to evaluate the effect of modified activated carbons on the reducibility. TPR profiles were obtained with a fully automated AMI-200 (Altamira Instruments). The catalyst (0.15 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 600 ºC under a flow of 5% (v/v) H_2 in Ar at 30 cm^3 min^{-1}. The H_2 consumption was monitored by a thermal conductivity detector (TCD). The temperature range where reduction occurs could be indicated directly from the H_2 consumption peaks.

2.3.3. Surface chemistry characterization

The surface chemistry of the starting and modified activated carbons was characterized by temperature-programmed desorption (TPD) [18]. The TPD spectra of CO and CO_2 were obtained with a fully automated AMI-300 (Altamira instruments). The carbon sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 1100 ºC under a constant flow rate of He at 25 cm^3 min^{-1} (STP). The amounts of CO (m/z = 28) and CO_2 (m/z = 44) released from the carbon samples were monitored with a mass spectrometer (Dymaxion, Ametek). CO and CO_2 were calibrated at the end of each analysis.

The pH at the point of zero charge (pH_{PZC}) was determined by mixing 0.05 g of each sample with 20 mL of 0.01 M NaCl solution with pH values adjusted between 2 and 11, by adding 0.1 M HCl or 0.1 M NaOH solutions. The final pH was measured after 48 h of shaking at room temperature. Blank experiments (without addition of carbon) were also performed for each pH and the values measured after 48 h are considered as the initial pH, in order to avoid the variation of pH caused by the effect of CO_2 present in head space. The pH_{PZC} value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH [29].

Carbon, hydrogen, nitrogen and oxygen (by difference) contents were determined using a Carlo Erba EA 1108 Elemental Analyzer. Prior to the analysis, water adsorbed on the surface of the supports was removed by drying at 110 ºC in the oven overnight.

2.4. Adsorption and Catalytic tests

Both adsorption and CWPO experiments were carried out in a magnetically stirred tank (batch reactor). The reactor was filled with 100 mL of a phenol aqueous solution (150 mg/L) and heated by immersion in a water bath at controlled temperature.

The solution pH was adjusted to a value of 3.0 using H_2SO_4 solution (1 M). When the desired temperature was reached (30 ºC), a calculated volume of H_2O_2 (0.25 mL) was added into the system after catalyst addition (100 mg), in order to reach a H_2O_2 concentration of 750 mg/L in the CWPO runs (the theoretical stoichiometric amount needed to completely mineralize phenol); at this moment the reaction was assumed to start. The CWPO oxidation runs were carried out both using the activated carbons (without iron) and iron supported carbon as catalysts, in order to evaluate the ability of the supports alone to decompose H_2O_2, and subsequently to promote phenol oxidation. This may give an idea to discriminate between a potential catalytic surface chemistry and the catalytic activity owing to the presence of iron.

In addition, pure adsorption runs were performed in order to assess the contribution of adsorption to the removal of phenol. The experiments were carried out in the same conditions, but without H_2O_2 addition.

Selected experiments were performed in triplicate and the relative error of the experimental results was below ±4%.

2.5. Analytical methods

Both in pure adsorption and in CWPO, liquid samples were periodically withdrawn from the reactor. Then, each sample was filtered with a syringe filter of 0.20

μm nylon (Teknokroma, ref._TR-200101) and placed in a glass vial (Agilent) for immediate analysis.

The determination of phenol concentration was performed by High Performance Liquid Chromatograph (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and C18 reverse phase column (Hypersil ODS, 5 μm, 25 x 0.4 cm from Agilent Technologies). The analyses were carried out with a mobile phase (flow rate 1 mL/min) of a 40/60% mixture of methanol and ultrapure water (Milli-Q water). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 μL.

Total Organic Carbon (TOC) was also determined at the end of the experiments in a TC Multi Analyzer 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector.

Fe leached to the reaction media was determined by using Atomic Absorption Spectroscopy (AAS) at 249 nm.

The main parameters used to compare the results in the discussion section are the removal of phenol (X_{PhOH}) and TOC abatement (X_{TOC}), which are respectively defined as:

$$X_{PhOH}(\%) = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \quad (2)$$

where $[PhOH]_0$ is the initial phenol concentration and $[PhOH]_t$ is the concentration at time t, and

$$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \quad (3)$$

where TOC_0 is the initial TOC concentration and TOC_t is the concentration at time t.

3. Results and discussion

3.1. Characterization of activated carbons and catalysts

Activated carbons were characterized by N_2 adsorption at -196 ºC, temperature programmed desorption (TPD), elemental analysis (EA), and by determination of the pH at the point of zero charge (pH_{PZC}). The catalysts were also characterized by temperature programmed reduction (TPR).

3.1.1. Textural properties

BET surface area (S_{BET}), mesopore surface area (S_{meso}) and micropore volume (V_{micro}) of the original AC, modified AC and one iron supported catalyst are summarized in Table 3. The results revealed that the original AC (AC0) is highly microporous and has high BET surface area, 984 m^2/g. In the case of acid-treated (AC1) and HNO_3 plus $SOCl_2$-treated (AC2) activated carbons, the BET surface area decreased following the treatments by 13% and 35%, respectively. The slight change in the surface area of AC1 can be explained by the abundant presence of oxygen-containing groups on the surface of the activated carbon, which are introduced by the HNO_3 treatment. These oxygen containing groups possibly block the entry of N_2 inside the small pores [30] or the carbon structure of activated carbon is partially destroyed and some micropores are vanished by treatment with HNO_3 [24]. Nevertheless, samples AC0 and AC1 have similar micropore volumes. In the case of AC2, which is treated with HNO_3 and $SOCl_2$, the reduction in the surface area can be explained by the introduction of both oxygen and sulfur-containing groups. Such sulfur moieties (sulfones, sulfides, sulfoxides, and sulfur atoms) may lead to active sites occlusion

inside the pores and on the surface of AC, as reported by Khayoon et al. [31]. Treatments with EDA and melamine lead to a drastic reduction of the surface area. This may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of N_2 molecules to the micropores. However, an appreciable increase of surface area and pore volume can be noticed only for urea treated samples compared to AC1 and AC2. This is probably due to significant carbon gasification and creation of additional microporosity [32]. In general, the textural properties of carbons are highly influenced by the nitrogen containing precursor; specially, for the AC2_Melamine sample, for which the micropore volume decreased up to nearly zero. On the other hand, the impregnation of 3 wt% iron did not substantially change the textural properties of the original carbon material.

3.1.2. TPR

TPR profiles of iron catalyst on the different supports are shown in Fig. 1. For comparison purpose, the TPR analyses of selected modified activated carbons were also performed and no additional peaks were observed. As it can be seen from Fig. 1, the position, width and intensity of the peaks mainly depend on the nature of the support. The major reduction peak is at a temperature around 400 ºC for original (AC0) and oxidized AC (AC1). The second peak observed at temperature above 550 ºC in AC0 profile could be related to iron oxide which is strongly interacting with the support. In general, the reduction peak for samples treated with N-containing compounds is shifted to the right irrespective of the starting material (AC1 or AC2). The reduction temperature depends on the degree of interaction between the active species and the support. For all samples treated with N-containing compounds using either AC1 or AC2

as a starting material, the iron reduction peaks shift to higher temperatures. Exceptions are the samples treated with urea, which present a reduction peak at lower temperature.

3.1.3. Surface chemistry characterization

3.1.3.1. TPD and pH_{PZC}

TPD analyses were carried out to evaluate the surface chemistry of the different AC supports. The nature of the groups can be assessed by the decomposition temperature and the type of gas released. CO and CO_2 are released by thermal decomposition of oxygen containing groups on the surface of carbon materials at different temperatures [18]. The TPD profiles of the original and modified activated carbons are depicted in Fig. 2. From the TPD profiles, it is possible to identify and quantify the amounts of the oxygenated groups of each sample. CO_2 peaks result from carboxylic acids at low temperatures (150 – 450 ºC), or lactones at higher temperatures (600 – 800 ºC); carboxylic anhydrides originate both CO and CO_2 (400 – 650 ºC); groups such as phenols (600 – 800 ºC) and carbonyls/quinones (750 – 1000 ºC) originate CO peaks [33].

It can be seen that the nitric acid treatment (AC1) increase the amount of oxygenated surface groups, which is evidenced by the increase of CO_2 (Fig. 2a) and CO (Fig. 2b) released. The samples treated with EDA originate CO peaks at lower temperatures (200-400 ºC) than the others.

The total amounts of CO and CO_2 released from the AC materials were calculated from the corresponding TPD spectra. This information as well as the point of zero charge of the samples with different surface chemistries are shown in Table 4.

As expected, AC1 has a low pH_{PZC} and the highest amount of CO and CO_2, due to the introduction of oxygen-containing surface groups having acidic properties,

mainly carboxylic acids. After thionyl chloride treatment (sample AC2), the carboxyl groups were mostly converted into acid chloride groups, resulting a decrease of the amount of CO and CO_2, but this material (AC2) still has acidic properties with the corresponding pH_{PZC} value similar to that of sample AC1. With the exception of AC2_EDA, all materials obtained after the treatment with N-containing precursors using sample AC1 or AC2 as starting materials have approximately neutral or slightly basic properties. This can be explained by the presence of nitrogen groups having basic properties.

In general, the TPD profile shows that it is important to have high density of oxygenated groups on the surface of carbon before functionalization with the N-containing compounds. The N-containing groups (EDA, urea and melamine) strongly interact with carboxylic acids, anhydrides and lactones [24, 34].

3.1.3.2. Elemental analysis

The carbon, hydrogen, nitrogen and oxygen contents obtained by elemental analysis are summarized in Table 5. Considering the treatment carried out, it was expected that AC2 and AC2-based samples may contain some sulphur, which is summed with the oxygen content as oxygen determined by difference.

The original AC contains a small amount (about 1%) of nitrogen. Significant amounts of nitrogen were introduced on the surface after treatment with N-containing compounds. The highest amount of nitrogen incorporated into the structure was obtained when melamine was the source of nitrogen, as its molecule contains up to six nitrogen atoms.

Thus, the differences in the amounts of nitrogen may be related to the content of nitrogen in the precursors (67% in melamine; 47% in urea and EDA) and the promoting

effect of surface acidity, enhanced by oxidation/activation of $SOCl_2$ on the retention of N-containing organic bases [28,35]. On the other hand, the EDA treated samples contain a relatively high content of hydrogen compared to others; this is probably due to the higher content of hydrogen found in the compound. It is interesting to note that in the urea and EDA treated samples similar total contents of nitrogen are found regardless the pretreatment applied, either using oxidized (AC1) or activated with thionyl chloride (AC2). However, in the case of melamine treated samples, the nitrogen content is higher when the AC2 sample is the starting material in comparison to the inactivated (only oxidized) sample AC1.

3.2. Catalytic activity

Although it is difficult to compare the performance of catalysts having different textural properties and surface chemistries, we performed some tests using the activated carbons as adsorbents or catalysts and the iron supported on modified AC as catalysts for the removal of phenol in solution.

The phenol removal on the original and modified activated carbons was studied as a function of time under the following conditions: 100 mL of solution having 150 mg/L of phenol, adsorbent/catalyst amount = 1 g/L, initial pH of the solution = 3.0, T = 30 ºC, atmospheric pressure and stoichiometric amount of H_2O_2.

3.2.1. Adsorption experiments

Adsorption experiments were carried out to evaluate the effect of textural and surface properties of the original and modified activated carbons on phenol removal by adsorption. The results of phenol removal in adsorption runs performed with the original and modified activated carbons are compiled in Fig. 3.

Even though the difference is not big compared to the original AC, it is clear that urea treated samples (AC1_Urea and AC2_Urea) improve the adsorption capacity of the original AC (AC0). These samples (AC0, AC1_Urea and AC2_Urea) present similar surface areas and pore volumes, their difference being mainly related with their surface chemistry. All the other materials showed lower adsorption capacities compared to the original AC. These adsorption results confirm that the textural properties of the carbon materials have a primary role in adsorption of phenol, irrespective of surface chemistry, but closely following the available surface area.

In the adsorption of aromatic compounds in liquid phase on activated carbons, there are mainly two types of interactions: (1) electrostatic and (2) dispersive [36]. The first mechanism is involved when the adsorbate is dissociated under the experimental conditions. For example, if solution pH > pH_{PZC}, then the carbon surface is negatively charged, the opposite occurs when the solution pH < pH_{PZC} as described elsewhere [37]. In the case of the second mechanism, the existence of π-π dispersion interactions is commonly accepted [36, 38]. Taking this in consideration, at pH of 3.0, phenol (pK_a=9.89) is found in solution predominantly in the molecular form and only the dispersive interactions are most probably involved in its adsorption on the carbon surface [39, 40].

Among the materials tested, the best performance was obtained with AC2_Urea, reaching 67% of phenol removal after 3 h. The BET surface area of this adsorbent is slightly lower and the pH_{PZC} is higher compared to the original AC. The EDA treated samples show moderate adsorption performance having moderate surface area and pH_{PZC}. However, the melamine treated samples show a poor adsorption performance due to the drastic decrease of surface area, though having a higher pH_{PZC} compared to AC1 and AC2 (pH_{PZC} of 2.5).

Moreover, the analysis of the results shows that there is a correlation between the phenol removal efficiency by adsorption and the S_{BET} of the tested activated carbons. The correlation is shown in Fig. 4. The figure clearly shows that the phenol removal efficiency increases linearly with the S_{BET}, irrespective of the surface chemistry. This indicates that the surface area of activated carbons is the principal responsible for the phenol adsorption capacity. Fierro and co-workers [41] also observed that the amount of adsorbed phenol in microporous activated carbons increases linearly with the increase in micropore volume.

As mentioned above, the textural and chemical properties of the tested samples are different. So, an additional study is needed to take conclusions about the effect of textural properties and surface functionalities. For this purpose, the apparent rate constants for the first-order (k_1) and second-order (k_2) adsorption models were determined for all samples tested. The constants of the two models are listed in Table 6. The ratio between k_1 or k_2 and S_{BET} is presented in the same table. Even though, both the first-order and the second-order model fit the experimental data quite well with R^2 values close to unity, the second-order model was suitable for the adsorption of lower molecular weight adsorbates on smaller adsorbent particles as reported by Wu et al. [42] and therefore the corresponding kinetic constants are used in the following discussion.

It is reported that phenol adsorption is dependent on both the surface area and the presence of surface groups [41, 43]. In order to evaluate the influence of the nitrogen content, the second-order apparent rate constants (k_2) are normalized by the specific surface area (S_{BET}). It can be observed in Fig. 5 that high normalized adsorption rate constants correspond to samples with high amounts of N-containing surface groups (see Table 5).

3.2.2. CWPO experiments

3.2.2.1. Modified activated carbons as catalysts

In order to evaluate the ability of the modified activated carbons to act as catalysts (without any supported metal) in the CWPO of phenol, runs were performed under the same conditions as the adsorption tests but now adding H_2O_2. The corresponding phenol removal curves are shown in Fig. 6.

Phenol removal by CWPO in the presence of modified activated carbons as catalysts was similar or slightly higher than those obtained by adsorption. However, the results of phenol removal by adsorption (Fig. 3) and CWPO (Fig. 6) lead to the conclusion that these modified carbon materials are not particularly active for CWPO of phenol. For instance, the phenol removal at 60 min for AC1_Urea is 43% without H_2O_2 and 42% in the presence of H_2O_2, or 65% and 64%, respectively, at 180 min, which suggests that both cases are governed by adsorption. So, the removal of phenol is mainly due to pure adsorption. Similar conclusion was obtained in a previous work for some dyes [44].

3.2.2.2. Iron supported catalysts

In order to study the influence of surface chemical characteristics of the support on the activity of iron catalysts in phenol oxidation, a set of runs were performed in CWPO for different ZVI supported catalysts. Fig. 7 shows the evolution of phenol removal in the presence of the iron catalyst supported on different supports. ZVI/AC2_Melamine and ZVI/AC2_EDA show a good and similar performance, reaching above 80% phenol conversion after 60 min. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of

ZVI (i.e AC2_Melamine and AC2_EDA) shows low removal efficiency below 15 % after 60 min.

It must be strongly noted that the presence of ZVI on N-containing catalysts yields a better phenol removal, reaching values over 85% after 3 h. These results revealed that there is a direct and positive relation between the catalytic activity and the nitrogen content of the materials. Therefore, the activity of iron supported catalysts based on N-containing AC in CWPO of phenol is enhanced when compared to that of the untreated ones. It is thus observed that the presence of nitrogen groups on the surface of activated carbon, in addition to iron, clearly increases the phenol removal. This synergy can be probably assigned to the ability of retaining the iron ions close to the carbon surface due to the complexing properties of these N-containing groups.

Similar trends were observed for TOC removal at the end of adsorption and oxidation tests. Fig. 8 shows that the EDA and melamine treated AC present lower TOC removal performance in the adsorption or oxidation tests when these materials were used as adsorbents or catalysts, respectively. However, the ZVI supported catalysts on the EDA and melamine treated supports also promote the TOC removal. The main reason for this can be explained by the synergetic effect of the presence of nitrogen group and iron on the surface of activated carbon, promoting oxidation instead of adsorption. In this case, the access of H_2O_2 to the iron on the carbon surface could be easier than for the other samples and accelerates the hydroxyl radical generation for deep oxidation of phenol, as observed in Fig. 7. However, additional studies are still required to reveal the exact origin of these effects.

Leaching tests were performed in order to evaluate the stability and contribution of homogeneous reaction for each catalyst after 120 and 180 min of reaction. Leaching of iron corresponds to values below 0.01% of the metal initially present in almost all

catalysts; also limited values of 0.03 to 0.04% were measured in the case of AC1 and AC2 supported catalysts. This fact can be related with the pH_{PZC} of the support. In fact, AC1 and AC2 present the lowest pH_{PZC} and a relatively high iron leaching. In conclusion, the contribution of homogeneous system is quite negligible, as the amount of leached iron is quite low.

Since the stability of a catalyst is one important aspect in the general evaluation of its performance, the most efficient catalysts of this study (ZVI/AC2_Melamine and ZVI/AC2_EDA) were reused three times in consecutive CWPO reactions (Fig. 9). A slight loss of catalyst activity is observed with both catalysts from the 1st to the 2nd run, but the activity being practically maintained from the 2nd to the 3rd run, and the actual removal of phenol is around 80%. The decrease in the removal of phenol observed from the first to the second run may be due to the lower adsorption capacity of the used catalyst and/or the slight loss of the catalyst during the recovery process. In fact, at the end of the experiment, a fraction of organic compounds will remain adsorbed onto the catalyst under the employed operating conditions. These compounds can be either phenol or intermediates formed during the oxidation reaction, as discussed elsewhere [45]. In any case, both catalysts (ZVI/AC2_Melamine and ZVI/AC2_EDA) still present a good efficiency under consecutive runs.

4. Conclusions

Activated carbons with different N-containing precursors were modified, characterized and tested as adsorbents or catalysts for adsorption and peroxide oxidation of phenol. Besides, these modified carbons were also impregnated with iron and used as catalysts for CWPO.

Treatments with EDA and melamine lead to a drastic surface area reduction. This may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of N_2 molecules to the micropores.

In the urea and EDA treated samples similar total contents of nitrogen are found regardless of the pretreatment applied. However, in the case of melamine treated samples, the nitrogen content is significantly higher when the oxidized activated carbon treated with thionyl chloride is the starting material.

Phenol removal by CWPO in the presence of carbon materials was slightly higher than those obtained by adsorption. However, the results lead to the conclusion that these materials are not particularly active for the reaction, the removal of phenol being mainly due to adsorption.

The iron supported catalysts based on N-containing AC show the highest phenol removal efficiency, reaching values over 85% conversion after 3 h. This result revealed that there is a positive relation between the catalytic activity and the nitrogen content of the materials.

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Table 1. Chemical properties of the N-containing compounds used

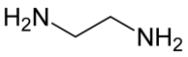
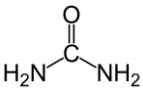
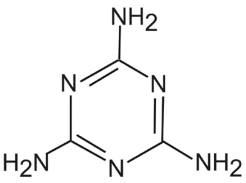
N-containing compounds	Molecular formula	Molar mass (g mol^{-1})	Chemical structure	N content (wt. %)
Ethylenediamine	$C_2H_8N_2$	60.10		46.59
Urea	CH_4N_2O	60.06		46.62
Melamine	$C_3H_6N_6$	126.12		66.60

Table 2. Abbreviations and description of original, modified and iron supported activated carbons

Abbreviation	Description
AC0	Untreated AC
AC1	HNO_3-treated AC0
AC2	$SOCl_2$-treated AC1
AC1_EDA	EDA-treated AC1
AC2_EDA	EDA-treated AC2
AC1_Urea	Urea- treated AC1
AC2_Urea	Urea- treated AC2
AC1_Melamine	Melamine- treated AC1
AC2_Melamine	Melamine- treated AC2
ZVI/ACx_y	Iron impregnated on sample ACx_y

x_y: represents the modification undergone on activated carbon

Table 3. Textural properties of samples

Sample	S_{BET} (±10 m^2 g^{-1})	S_{meso} (±10 m^2 g^{-1})	V_{micro} (±0.01 cm^3 g^{-1})
AC0	984	207	0.351
AC1	853	141	0.342
AC2	635	178	0.165
AC1_EDA	335	148	0.086
AC2_EDA	242	175	0.030
AC1_Urea	949	180	0.339
AC2_Urea	939	200	0.342
AC1_Melamine	194	111	0.038
AC2_Melamine	47	47	0.000
ZVI/AC0	975	216	0.348

Table 4. Surface chemistry data of activated carbon supports (total amounts of CO and CO_2 released, and pH_{PZC}).

Sample	CO (±20 µmol g^{-1})	CO_2 (±20 µmol g^{-1})	pH_{PZC} (±0.1)
AC0	598	164	6.7
AC1	2311	754	2.5
AC2	1660	565	2.4
AC1_EDA	927	150	6.8
AC2_EDA	616	102	5.3
AC1_Urea	1481	193	7.6
AC2_Urea	1096	118	7.9
AC1_Melamine	1305	175	6.2
AC2_Melamine	739	102	6.7

Table 5. Elemental analysis of the original and modified AC

Sample	C (wt%)	H (wt%)	N (wt%)	O[a](wt%)
AC0	90.95	0.92	0.92	7.66
AC1	85.79	0.18	1.80	12.24
AC2	84.43	1.36	1.23	12.97
AC1_EDA	83.00	1.88	5.74	9.38
AC2_EDA	81.49	1.99	5.53	10.99
AC1_Urea	85.24	0.30	3.20	11.26
AC2_Urea	88.38	0.57	2.38	8.68
AC1_Melamine	81.69	0.74	15.95	1.62
AC2_Melamine	74.06	0.98	22.07	2.90

[a] Oxygen determined by difference.

Table 6. Kinetics parameters of the first-order and second-order adsorption models

Sample	Pseudo-first-order				Pseudo-second-order			
	qe (mg/L)	k_1 (min^{-1})	R^2	10^3 k_1/S_{BET}	qe (mg/L)	10^3 k_2 ($g_{AC}mg^{-1}min^{-1}$)	R^2	10^6 k_2/S_{BET}
AC0	80.87	0.017	0.988	0.017	104.10	0.268	0.981	0.272
AC1	54.52	0.011	0.891	0.013	73.52	0.336	0.951	0.394
AC2	37.35	0.014	0.915	0.022	52.08	0.706	0.983	1.111
AC1-EDA	25.27	0.016	0.978	0.047	33.89	1.060	0.982	3.164
AC2-EDA	36.29	0.015	0.987	0.062	47.39	0.522	0.972	2.157
AC1-Urea	84.76	0.020	0.992	0.021	108.69	0.228	0.995	0.240
AC2-Urea	83.62	0.021	0.995	0.022	107.52	0.309	0.996	0.329
AC1-Melamine	19.13	0.017	0.985	0.087	25.57	1.410	0.987	7.268
AC2-Melamine	3.39	0.028	0.965	0.596	4.65	1.640	0.995	34.890

FIGURE CAPTIONS

Fig. 1. TPR profiles of supported iron catalysts using AC1 (a) and AC2 (b) as starting material.

Fig. 2. TPD spectra of the activated carbon supports (a) and (c) CO; (b) and (d) CO_2.

Fig. 3. Phenol removal obtained in pure adsorption experiments (150 mg/L of phenol, pH 3.0, T = 30 ºC and adsorbent load = 1 g/L) with different carbon supports.

Fig. 4. Correlation between specific surface area and phenol removal obtained in pure adsorption for original and treated activated carbons.

Fig. 5. Plot of the normalized rate constants for phenol adsorption (k_2/S_{BET}) versus N-content for original and treated activated carbons.

Fig. 6. Phenol removal obtained in CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and catalyst load = 1 g/L) with different activated carbons.

Fig. 7. Phenol removal obtained in CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and catalyst load = 1 g/L) with ZVI supported on different activated carbons.

Fig. 8. TOC removal after 180 min obtained in adsorption and CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and

adsorbent/catalyst load = 1 g/L) with carbon samples and ZVI supported on activated carbons.

Fig. 9. Phenol removal obtained by CWPO in sequential experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and catalyst load = 1 g/L) using ZVI/AC_EDA and ZVI/AC2_Melamine catalysts.

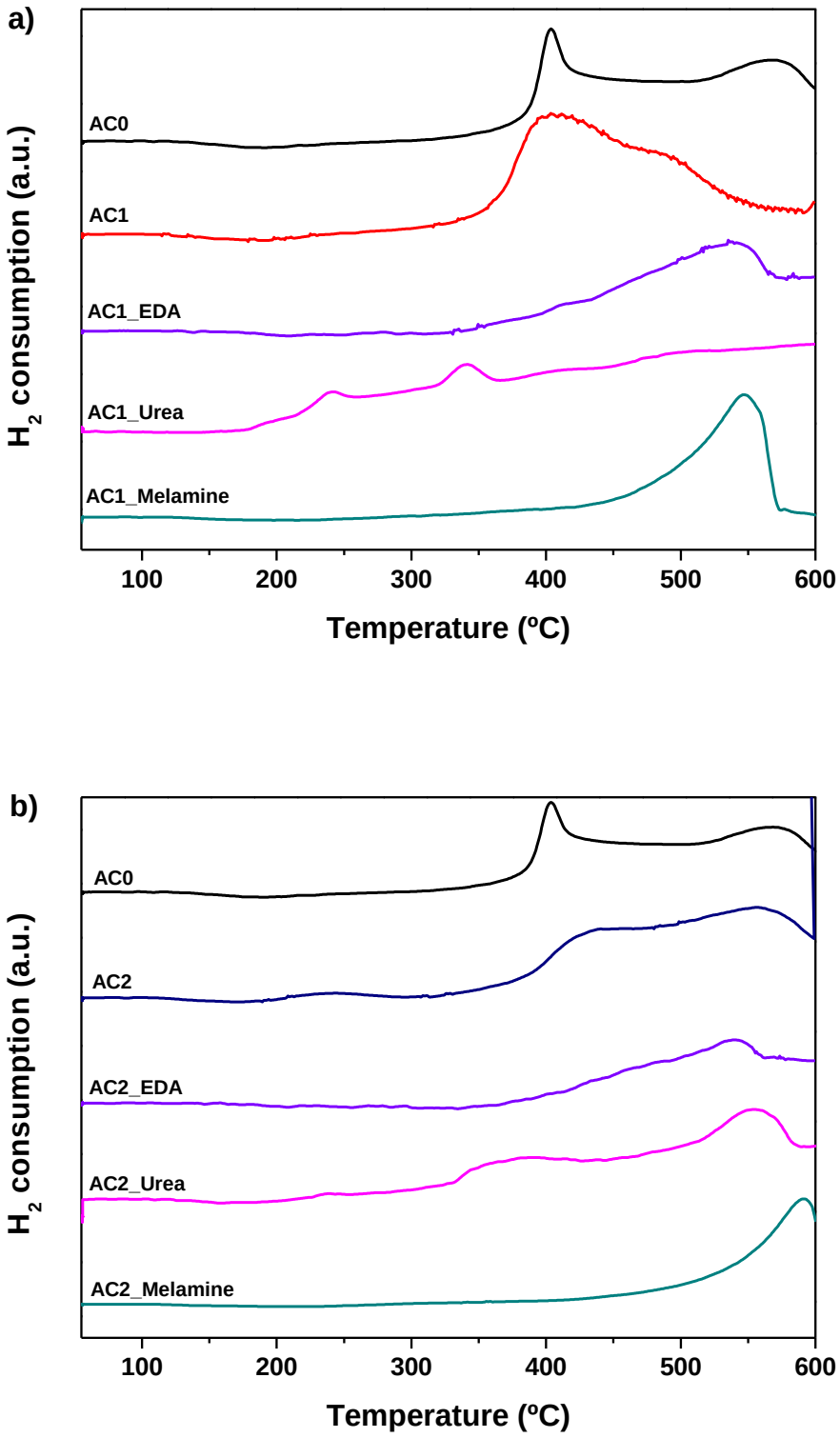

a)
AC0
AC1
AC1_EDA
AC1_Urea
AC1_Melamine
H2 consumption (a.u.)
100
200
300
400
500
600
Temperature (ºC)
b)
AC0
AC2
AC2_EDA
AC2_Urea
AC2_Melamine
H2 consumption (a.u.)
100
200
300
400
500
600
Temperature (ºC)

Fig. 1.

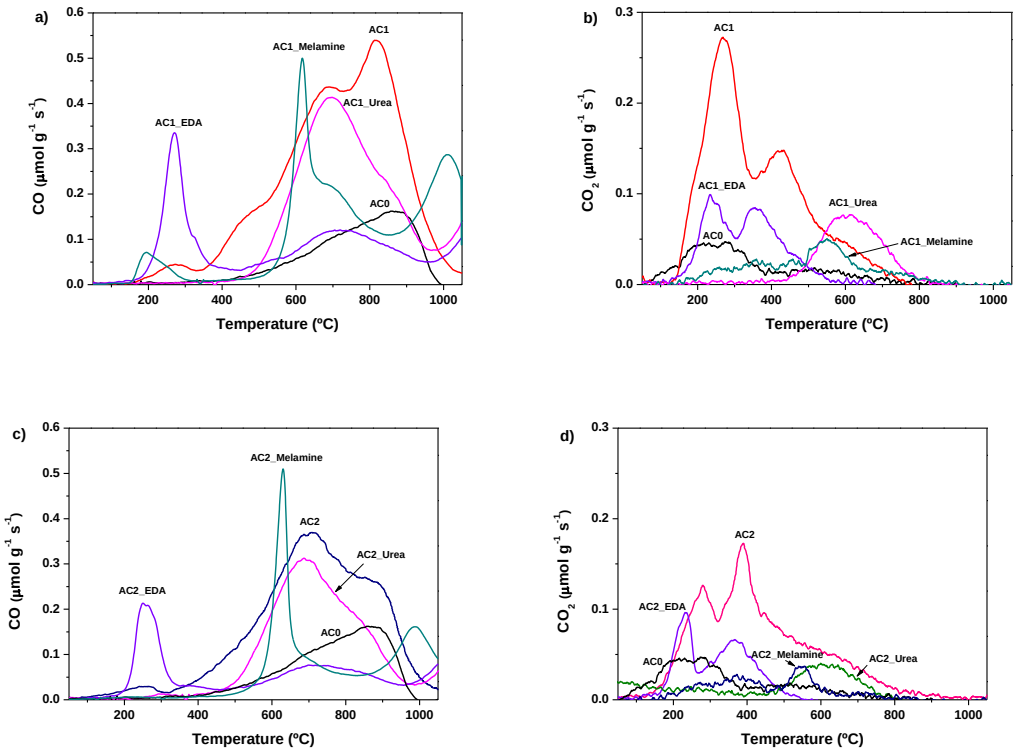

a)
CO (µmol g-1 s-1)
AC1
AC1_Melamine
AC1_Urea
AC1_EDA
AC0
Temperature (ºC)
b)
CO2 (µmol g-1 s-1)
AC1
AC1_EDA
AC1_Urea
AC0
AC1_Melamine
Temperature (ºC)
c)
CO (µmol g-1 s-1)
AC2_Melamine
AC2
AC2_Urea
AC2_EDA
AC0
Temperature (ºC)
d)
CO2 (µmol g-1 s-1)
AC2
AC2_EDA
AC0
AC2_Melamine
AC2_Urea
Temperature (ºC)

Fig. 2.

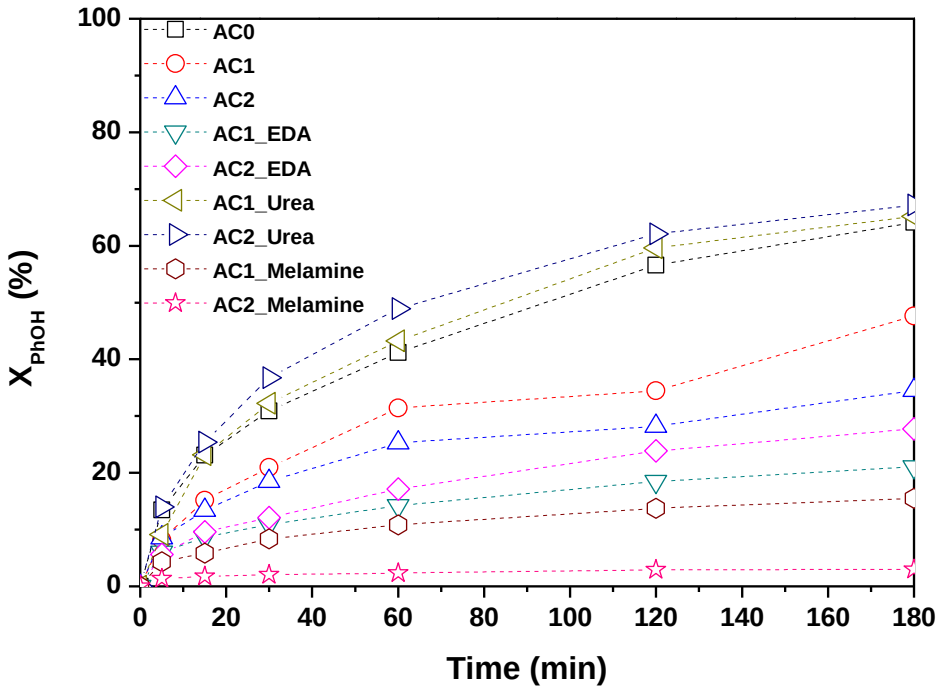

AC0
AC1
AC2
AC1_EDA
AC2_EDA
AC1_Urea
AC2_Urea
AC1_Melamine
AC2_Melamine
X_{PhOH} (%)
Time (min)
0
20
40
60
80
100
120
140
160
180

Fig. 3.

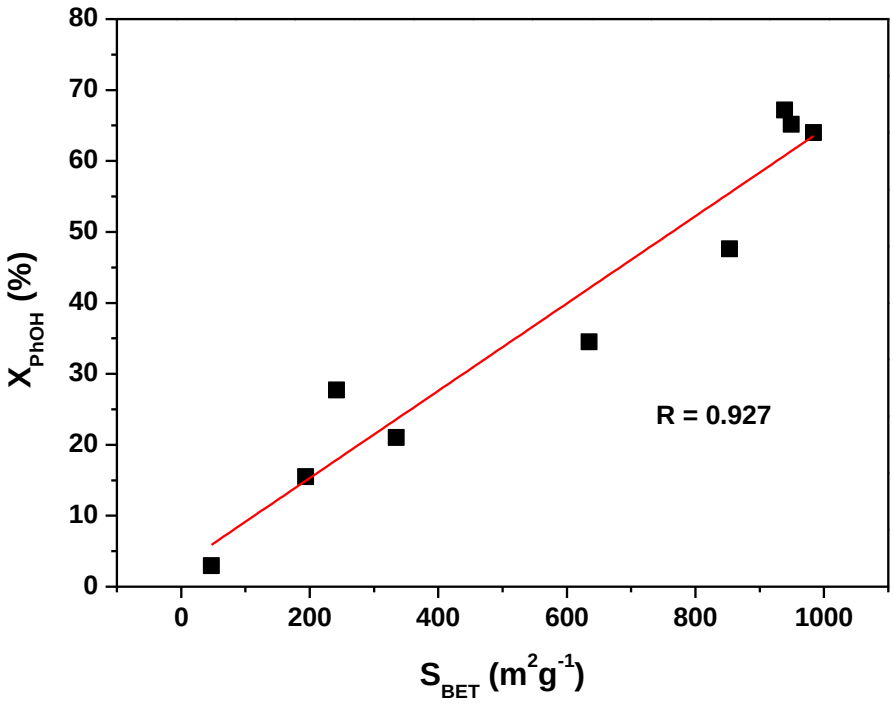

80
70
60
50
40
30
20
10
0
0
200
400
600
800
1000
X_{PhOH} (%)
S_{BET} (m^2g^{-1})
R = 0.927

Fig. 4.

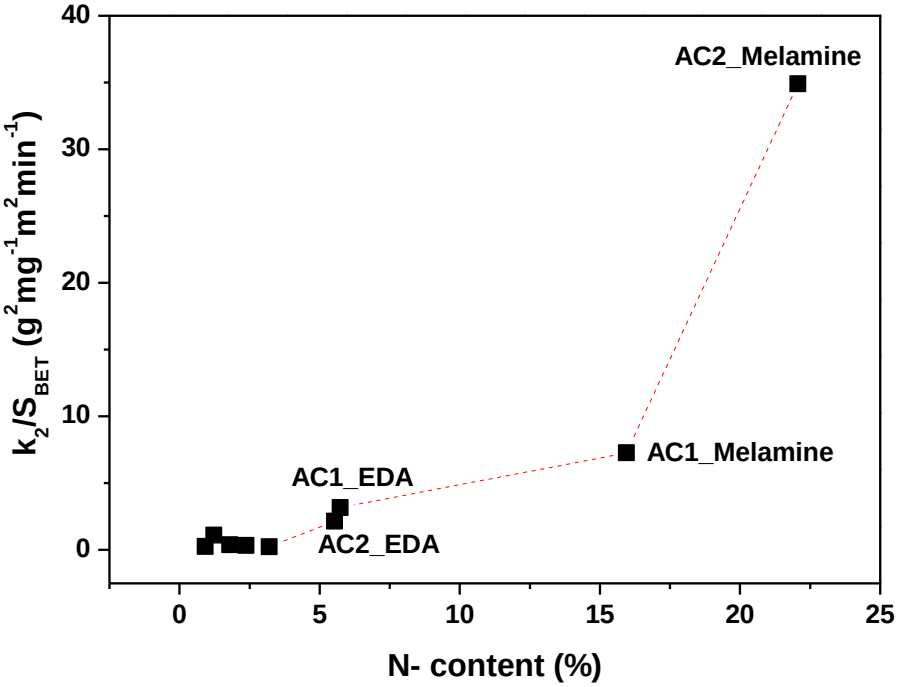

AC2_Melamine
AC1_Melamine
AC1_EDA
AC2_EDA
k_2/S_{BET} ($g^2mg^{-1}m^2min^{-1}$)
N- content (%)
0
10
20
30
40
0
5
10
15
20
25

Fig. 5.

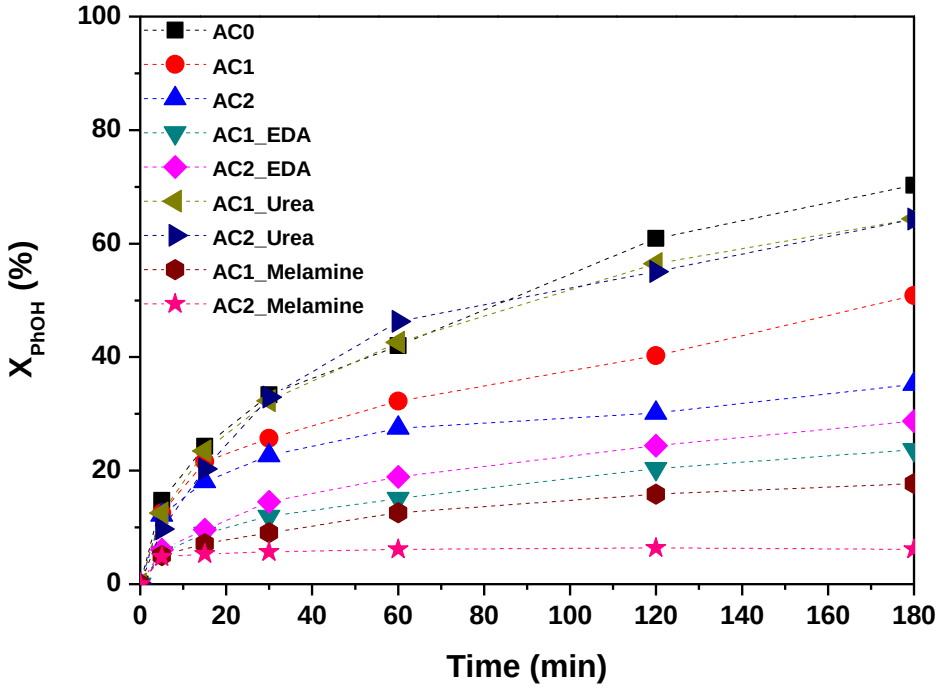

AC0
AC1
AC2
AC1_EDA
AC2_EDA
AC1_Urea
AC2_Urea
AC1_Melamine
AC2_Melamine
X_{PhOH} (%)
Time (min)
0
20
40
60
80
100
120
140
160
180

Fig. 6.

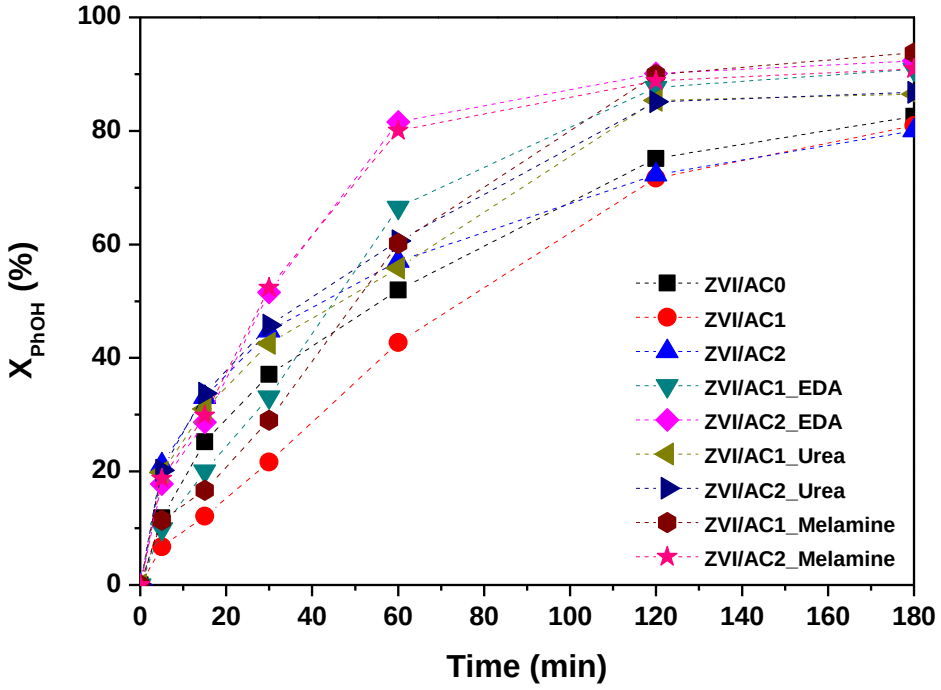

100
80
60
40
20
0
X_{PhOH} (%)
0
20
40
60
80
100
120
140
160
180
Time (min)
ZVI/AC0
ZVI/AC1
ZVI/AC2
ZVI/AC1_EDA
ZVI/AC2_EDA
ZVI/AC1_Urea
ZVI/AC2_Urea
ZVI/AC1_Melamine
ZVI/AC2_Melamine

Fig. 7.

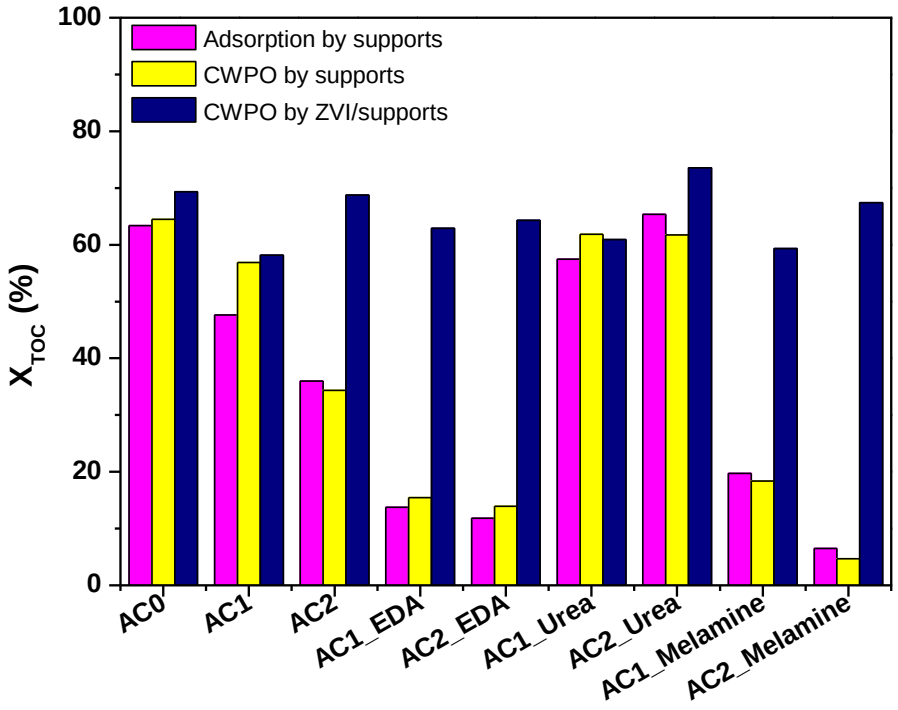

Adsorption by supports
CWPO by supports
CWPO by ZVI/supports
X_{TOC} (%)
100
80
60
40
20
0
AC0
AC1
AC2
AC1_EDA
AC2_EDA
AC1_Urea
AC2_Urea
AC1_Melamine
AC2_Melamine

Fig. 8.

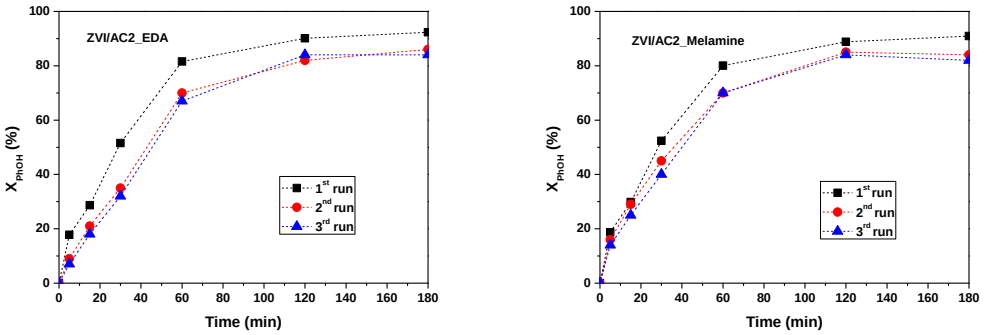
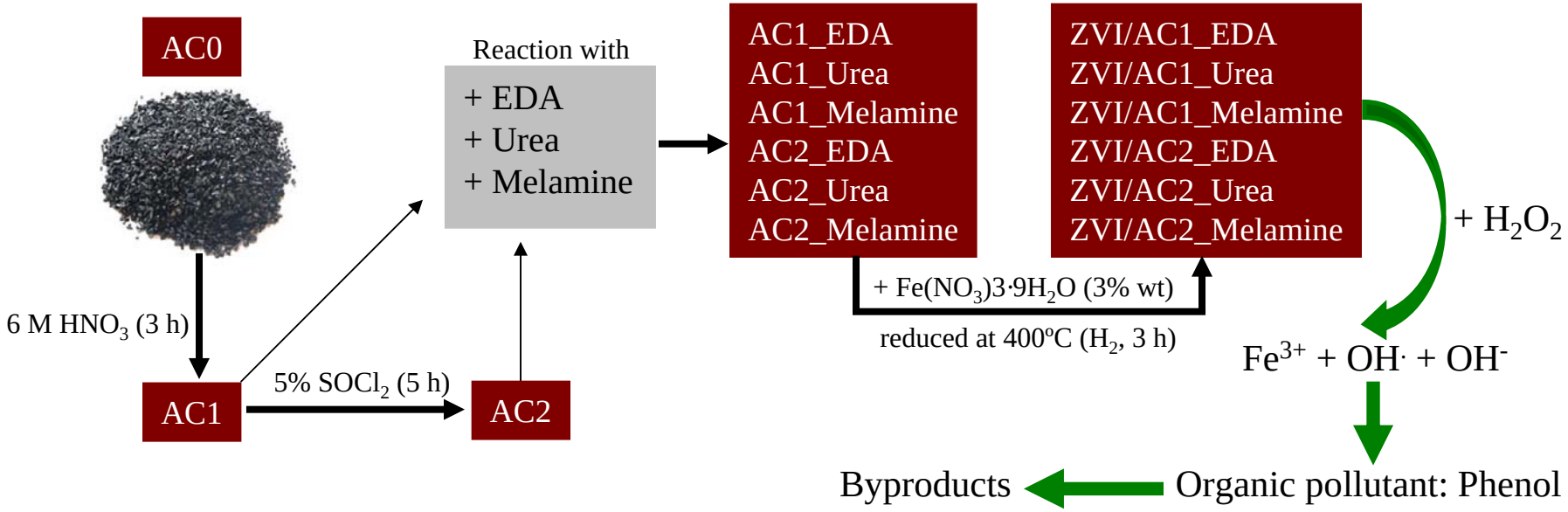

ZVI/AC2_EDA
ZVI/AC2_Melamine
X_{PhOH} (%)
Time (min)
1st run
2nd run
3rd run
0
20
40
60
80
100
120
140
160
180

Fig. 9.


AC0
6 M HNO3 (3 h)
AC1
5% SOCl2 (5 h)
AC2
Reaction with
+ EDA
+ Urea
+ Melamine
AC1_EDA
AC1_Urea
AC1_Melamine
AC2_EDA
AC2_Urea
AC2_Melamine
+ Fe(NO3)3·9H2O (3% wt)
reduced at 400ºC (H2, 3 h)
ZVI/AC1_EDA
ZVI/AC1_Urea
ZVI/AC1_Melamine
ZVI/AC2_EDA
ZVI/AC2_Urea
ZVI/AC2_Melamine
+ H2O2
Fe3+ + OH· + OH-
Organic pollutant: Phenol
Byproducts

Highlights

- Activated carbons were successfully modified with different N-containing precursors.
- Urea and EDA treated samples have similar total contents of nitrogen regardless of the pretreatment applied.
- The nitrogen content of melamine treated samples is significantly higher.
- The iron supported catalysts based on N-containing AC show the highest phenol removal efficiency.