

## Artigo

## Iron-doped Alfa-Alumina Applied in the Degradation of Phenol Solutions

Souza, J. J. N.;\* Meireles, B. R. L. A.; Cordeiro, A. M. T. M.; Santos, I. M. G.; Maia, A. S.

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### Alfa-alumina Dopada com Ferro Aplicada na Degradação de Soluções de Fenol

**Resumo:** Neste trabalho buscou-se avaliar a atividade catalítica de alumina dopada com ferro na degradação do fenol, pelo processo Fenton heterogêneo, que foi quantificado por dois métodos diferentes, Folin-Ciocalteu e cromatografia líquida de alta eficiência. A alumina foi caracterizada por difração de raios-X, espectroscopia de infravermelho, fluorescência de raios-X e área superficial pelo método de BET. Após os testes catalíticos, foi observado que houve degradação de 94 % do fenol com duas horas de reação, chegando ao máximo de 99 % com quatro horas. Esta alumina foi reutilizada por três vezes para o mesmo processo catalítico, mantendo o percentual de degradação após quatro horas de reação. A estabilidade química do material foi avaliada e observou-se que não há lixiviação do ferro.

**Palavras-chave:** Alumina dopada com ferro; Fenol; Degradação.

### Abstract

This work aimed at evaluating the catalytic activity of alumina doped with iron in phenol degradation by Fenton heterogeneous process, which was quantified by two different methods, Folin-Ciocalteu and high-performance liquid chromatography. The alumina was characterized by X-ray diffraction, infrared spectroscopy, X-ray fluorescence, and surface area measurement by the BET method. After the catalytic tests, the phenol degradation of 94 % was obtained after two hours of reaction, reaching a maximum of 99 % after four hours. This alumina was reused three times for the same catalytic process, maintaining the percentage of degradation after four hours of reaction. The chemical stability of the material was assessed no iron leaching was noticed.

**Keywords:** Iron doped alumina; Phenol; Degradation.

\* Universidade Federal da Paraíba, Centro de Ciências Exatas da Natureza, Departamento de Química, Campus João Pessoa. Cidade Universitária, s/n - Castelo Branco III, CEP 58051-900, João Pessoa-PB, Brazil.

✉ [jarllys@hotmail.com](mailto:jarllys@hotmail.com)

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## Iron-doped Alfa-Alumina Applied in the Degradation of Phenol Solutions

João Jarllys N. de Souza,<sup>a,\*</sup> Bruno R. L. de Albuquerque Meireles,<sup>b</sup> Angela Maria T. M. Cordeiro,<sup>c</sup> Ieda Maria G. dos Santos,<sup>a</sup> Ary da S. Maia<sup>a</sup>

<sup>a</sup> Universidade Federal da Paraíba, Centro de Ciências Exatas da Natureza, Departamento de Química, Campus João Pessoa, João Pessoa-PB, Brazil.

<sup>b</sup> Universidade Federal de Campina Grande, Centro de Ciências e Tecnologia Agroalimentar, Unidade acadêmica de Tecnologia de Alimentos, Campus Pombal, Brazil.

<sup>c</sup> Universidade Federal da Paraíba, Centro de Tecnologia e Desenvolvimento Regional/ Departamento de Tecnologia de Alimentos, Campus João Pessoa, João Pessoa-PB, Brazil.

\* [jarllys@hotmail.com](mailto:jarllys@hotmail.com)

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## 1. Introduction

Phenol and its derivatives have been widely used in different areas as in veterinary medicine, refinery, construction, automotive and appliance industries.<sup>1</sup> In spite of its important applications, phenol represents a meaningful threat to environment due to its toxicity and ability to remain in the environment for long periods, compromising aqueous systems.<sup>2</sup> For these reasons,

removal of phenol from water bodies is a very important task.<sup>3-5</sup>

Advanced oxidation processes, AOP's, have been widely studied for the abatement of recalcitrant substances, just as phenol, by a simple low cost system, based on hydroxyl radicals.<sup>6-7</sup> AOP's include, among others, homogeneous and heterogeneous Fenton processes. In spite of being widely studied in recent years, homogeneous Fenton systems have important drawbacks as the use of acidic media to promote reaction and sludge

formation, which is difficult to remove. These drawbacks may be overcome by the use of heterogeneous Fenton systems.<sup>8-9</sup>

In addition to the iron oxides directly used as Fenton catalysts, iron has also been incorporated onto different materials. For instance, two reviews were published in 2010, reporting the incorporation of iron onto materials as zeolites, mesoporous silicas, clays and pillared clays.<sup>9-11</sup> Moreover, recent researches show the application of gamma-alumina impregnated with iron oxide by wetness impregnation method, for the Fenton degradation of phenol and derivatives in aqueous media.<sup>12-14</sup> Fe (II) compound was deposited onto mesoporous Al<sub>2</sub>O<sub>3</sub>,<sup>15</sup> while impregnated Fe<sub>2</sub>O<sub>3</sub> onto mesoporous gamma-Al<sub>2</sub>O<sub>3</sub>,<sup>16</sup> both used for phenol degradation by Fenton reactions with a high efficiency. Recently, Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>/CuO/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by ultrasonic impregnation and obtained a high conversion, especially for the CuO containing catalyst.<sup>17</sup>

In the present work, iron was incorporated into alumina lattice, by a doping process using the modified Pechini method.<sup>18-19</sup> The use of doping instead of impregnation was chosen in order to decrease the risk of iron leaching, as iron replaces aluminum inside the unit cell. The synthesized materials were applied for phenol degradation by a heterogeneous Fenton catalysis.

## 2. Experimental

### 2.1. Synthesis and characterization of catalysts

Catalysts composed of pure and Fe-doped Al<sub>2</sub>O<sub>3</sub> were obtained by the modified-Pechini method.<sup>20</sup> During synthesis, Fe or Al solutions were prepared using Citric acid (Cargill, 99.5%), Iron nitrate (Synth, 99.1%) and Aluminum nitrate (Vetec, 99%) as precursors, respectively. These solutions were added into a citric acid solution in order to obtain a

molar ratio citric acid:metal of 3:1 and Fe-doping amounts of 5 % (Fe5) and 10 % (Fe10). Ethylene glycol was added at the end of the synthesis with a mass ratio citric acid:ethylene glycol of 3:2. The resin was heat treated at 350 °C for 2 h in order to obtain the precursor powders, which were milled in a Spex mill for 10 min and passed through a 100 mesh sieve. The milled powder precursor was heat treated in oxygen atmosphere at 300 °C for 12 h and subsequently in stagnated air atmosphere with a heating rate of 10 °C.min<sup>-1</sup> up to 1000 °C for 4 h. The pure Al<sub>2</sub>O<sub>3</sub> powder precursor was also heat treated at 1100 °C using the same conditions (Al<sub>2</sub>O<sub>3</sub>-1100).

Samples were characterized by X-ray diffraction (XRD) by a XRD-6000 diffractometer (Shimadzu), using K<sub>α</sub> Cu radiation. Infrared spectra (IR) were obtained in a spectrometer (Shimadzu), using KBr pellets. Composition was evaluated in a EDX-7000 X-ray fluorescence spectrometer (Shimadzu). Surface area was determined by a BELSORP II-MINI equipment from BEL JAPAN. UV-visible spectra were obtained in a 2550 spectrometer (Shimadzu) in the range from 190 to 900 nm.

### 2.2. Catalytic test

The catalysts were tested in the phenol oxidation in aqueous solution at pH = 3, heated at 70 °C, using a 50 mL reactor connected to a condenser. Catalysts were added into 20 mL of a phenol solution with a concentration of 250 ppm and 0.5 mL of H<sub>2</sub>O<sub>2</sub> (30% v/v), according to di Luca and collaborators (2015).<sup>16</sup> Tests were realized using 20, 10, 5 and 1 mg of catalysts, with duration varying from 1 to 4 h. A blank tested was realized using phenol (Sigma-Aldrich, 99%) and H<sub>2</sub>O<sub>2</sub> solutions, without the catalysts.<sup>21</sup>

Further tests were performed by varying the phenol concentrations, using 1000, 500 and 125 ppm, in the reaction time of 4 hours. The degradation of phenol in alkaline (pH =

11) and neutral media was also evaluated.

Hydrogen peroxide consumption was evaluated through UV-Vis spectrophotometry using acidic ammonium metavanadate, which reacts with  $\text{H}_2\text{O}_2$  to form the red-orange peroxovanadium cation, detected at the wavelength of 450 nm.<sup>24</sup>

### 2.3. Phenol quantification

Phenol degradation was initially monitored by the Folin-Ciocalteu method,<sup>22</sup> applied in the determination of total phenolics. This method uses the Folin-Ciocalteu reagent, which consists of a mixture of phosphomolybdic and phosphotungstic acids, with a yellow coloration. In the presence of reducing agents, the change in coloration to blue occurs, directly proportional to the concentration of the reducing substances, in this case, phenolic compounds. UV-visible absorbance was measured at 765 nm and phenol concentration was calculated using the previously determined calibration curve.

Phenol quantification was determined by the high-performance liquid chromatography (HPLC), using the separation method (LC-20 AT, Shimadzu Corporation, Japão), equipped with a C18 column (SUPELCOSIL™ LC-PAH HPLC Column, 250 x 4,6 mm, particle size 5  $\mu\text{m}$ , Sigma-Aldrich, St. Louis, MO, EUA) and a UV-visible detector (Rheodyne, EUA), in agreement to the previous methodology.<sup>23</sup>

## 3. Results and discussion

### 3.1. Synthesis and Characterization of the Catalyst

Figure 1 shows the DRX of the samples, indicate that pure  $\text{Al}_2\text{O}_3$  calcined at 1000 °C

presents gamma and alpha phases, in agreement to the index cards ICDD 50-0741 and 42-1468, respectively, while  $\text{Al}_2\text{O}_3$ -1100 presents only the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase, as well as Fe-doped samples (Fe5 and Fe10), with a small displacement of peaks to smaller angles. This behavior may be explained by the  $\text{Fe}^{3+}$  larger ionic radii (65 pm) comparing to  $\text{Al}^{3+}$  one (54 pm), both in octahedral site.<sup>25</sup> Secondary phases were not observed, indicating that iron got into the alumina lattice.

This behavior is in agreement with authors who reported the formation of  $\alpha$ - $\text{Al}_2\text{O}_3$  after calcinations at and above 1100 °C, which decrease to lower temperatures due to the presence of impurities in the material that change the phase transformation barrier.<sup>26</sup>

The experimental doping amount was evaluated by XRF, using the internal standards of the equipment. For the 5 % doped sample, 4.8 % of Fe was found in the final sample, while 9.6 % was found for the 10 % doped sample. These results indicated that a satisfactory result was attained, with a good stoichiometric control.

The infrared spectra of all of the samples are presented in Figure 2. According to literature data,<sup>27</sup>  $\delta$ - $\text{Al}_2\text{O}_3$  presents absorption bands assigned to the Al-O bonds of  $\text{AlO}_4$  groups (around 750  $\text{cm}^{-1}$ ) and  $\text{AlO}_6$  groups (around 615 and 490  $\text{cm}^{-1}$ ). In the present work,  $\text{Al}_2\text{O}_3$  presents bands around 466, 553, 733 and 814  $\text{cm}^{-1}$ .

For  $\alpha$ - $\text{Al}_2\text{O}_3$  samples, literature data indicates bands at about 650, 600  $\text{cm}^{-1}$ , and nearby 450 and 780  $\text{cm}^{-1}$ , assigned to Al-O bond in octahedral coordination,  $\text{AlO}_6$ .<sup>28</sup> In the present work, these bands were observed at about 429, 581 and 630  $\text{cm}^{-1}$  for  $\text{Al}_2\text{O}_3$ -1100 and Fe-doped samples. These results are in agreement to XRD patterns, which indicated the formation of  $\delta$ - $\text{Al}_2\text{O}_3$  for the pure sample calcined at 1000 °C and  $\alpha$ - $\text{Al}_2\text{O}_3$  for the pure sample calcined at 1100 °C as well as for the Fe-doped samples.

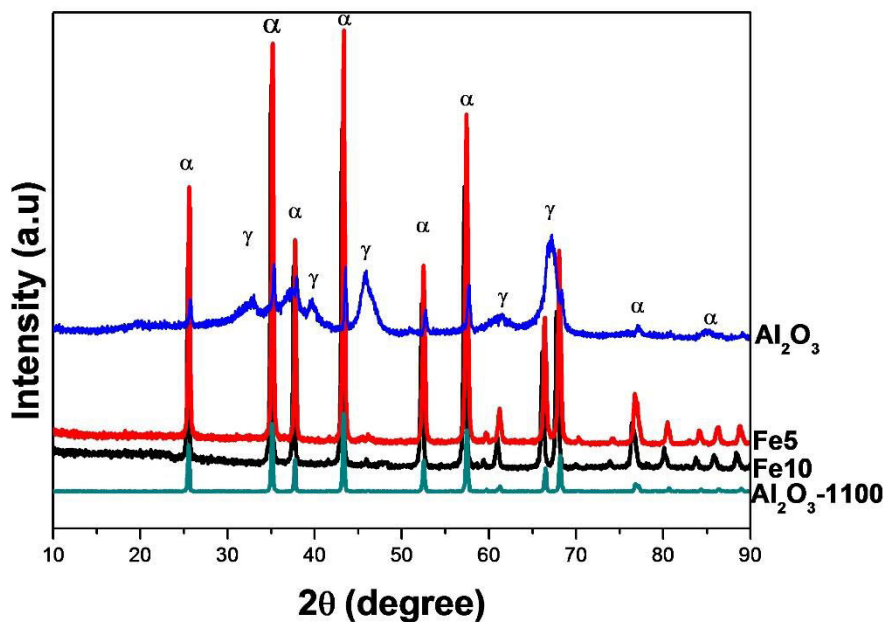


Figure 1. XRD patterns of pure and Fe-doped Al<sub>2</sub>O<sub>3</sub> samples

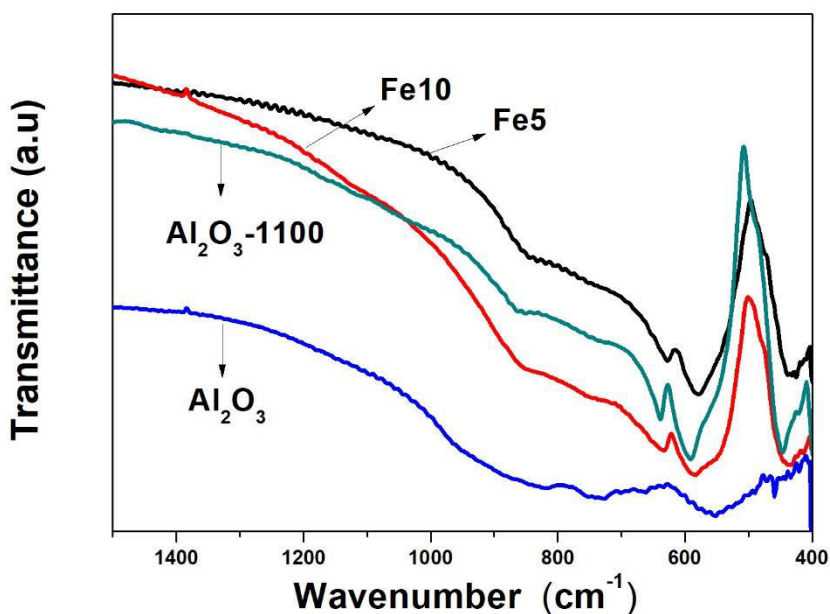


Figure 2. IR spectra of pure and Fe-doped Al<sub>2</sub>O<sub>3</sub> samples

UV-vis spectra of all samples are presented in Figure 3. Electronic transitions may also be observed in the UV-vis spectra. Fe<sup>3+</sup> containing materials have three types of

electronic transitions: (i) ligand-metal charge transfer; (ii) d-d transitions; (iii) pair excitations resulting from simultaneous excitations of two neighbouring Fe<sup>3+</sup> cations

that are magnetically coupled.<sup>29</sup> In the present work, the band at 250-400 nm was assigned to superposed ligand-metal charge transfers (Al-O and Fe-O) and Fe<sup>3+</sup> d-d

transitions; the band at 450-600 nm was assigned to pair excitation processes; the band at 650-800 nm was related to transitions of the Fe<sup>3+</sup> ligand field.

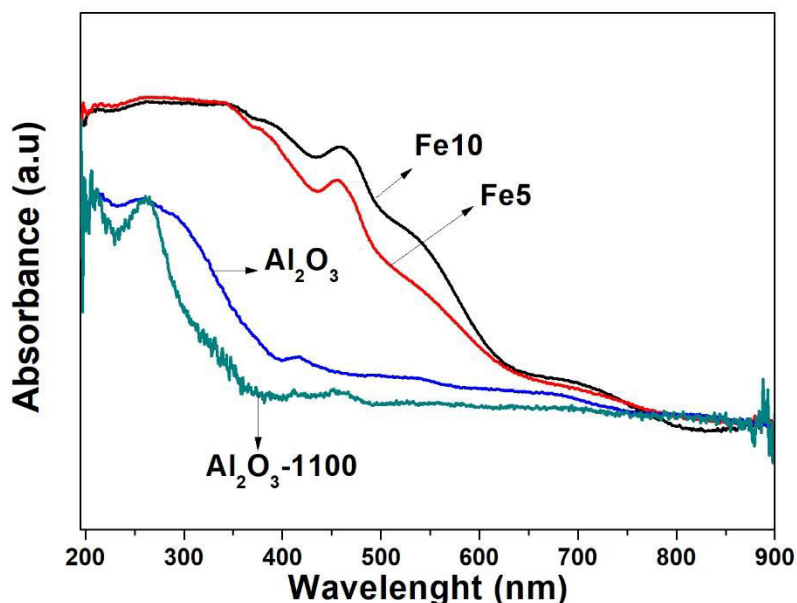


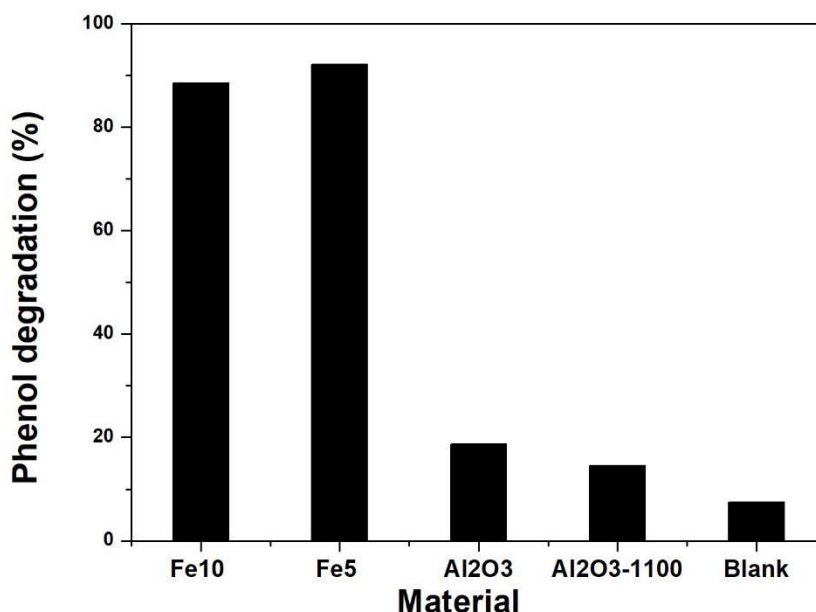
Figure 3. UV-vis spectra of pure and Fe-doped Al<sub>2</sub>O<sub>3</sub> samples

The band gap of the samples was calculated according to Wood and Tauc method. Pure Al<sub>2</sub>O<sub>3</sub> samples presented values of 2.8 and 3.5 eV for samples calcined at 1000 and 1100 °C, respectively. Fe-doped samples presented band gap values around 2 eV, indicating a possible use of these materials as photocatalysts sensitive to visible electromagnetic radiation.

Specific surface areas ( $S_{\text{BET}}$ ) of samples were measured using the BET method. For pure Al<sub>2</sub>O<sub>3</sub> calcined at 1000 °C,  $S_{\text{BET}}$  was 19.9 m<sup>2</sup>.g<sup>-1</sup>, while Fe-doped samples presented similar  $S_{\text{BET}}$  values, of 5.7 and 5.4 m<sup>2</sup>.g<sup>-1</sup> for 5 and 10 % doping, respectively.

### 3.2. Catalytic test and Phenol quantification

The first catalytic tests were realized at 70 °C for 4 h and quantified by the Folin-Ciocalteu method (Figure 4). Fe-doping leads to an improvement of the catalytic activity for phenol degradation, with a 5.5-fold increase for 10 % of Fe-doping and 5.8-fold increase for 5 % of doping, compared with non-doped material (Al<sub>2</sub>O<sub>3</sub>). This is a unusual result, especially considering that  $\delta$ -Al<sub>2</sub>O<sub>3</sub> has been the most used alumina phase applied as support for Fe<sub>2</sub>O<sub>3</sub> in previous works.<sup>30</sup> The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as support for Fe<sub>2</sub>O<sub>3</sub> and presented similar results.<sup>31</sup>



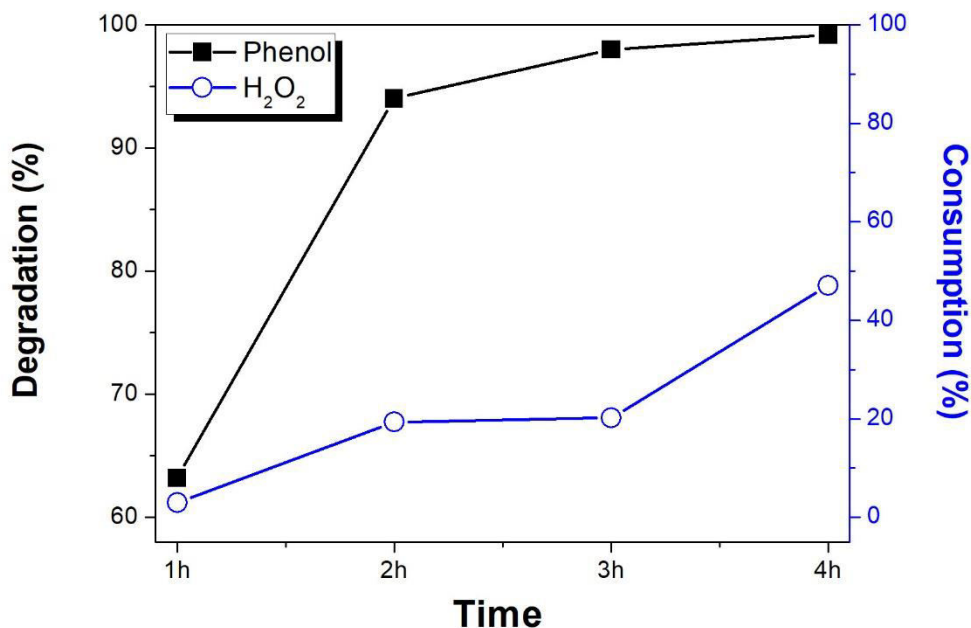
**Figure 4.** Phenol degradation after Fenton test, using 20 mg of the catalysts and 4 h of reaction. Quantification by Folin-Ciocalteu method

In relation to undoped alumina, two samples were evaluated  $\delta$ - $\text{Al}_2\text{O}_3$ , calcined at the same temperature of the doped samples and  $\alpha$ - $\text{Al}_2\text{O}_3$ , which presents the same crystalline phase of the doped samples. As expected, both presented a very small activity.

The doped materials exhibited similar catalytic activity and Fe5 was used in the posterior catalytic tests, with evaluation by HPLC. Figure 5 presents the Fenton tests done using 20 mg of catalyst ranging from 1 to 4 h. Results showed a high activity even in the first hours of reaction with almost 100% of degradation of 4 h, similarly to results obtained in literature, who used  $\text{Fe}_2\text{O}_3$

supported on mesoporous  $\delta$ - $\text{Al}_2\text{O}_3$ , a material with very high surface area.<sup>16</sup>

A blank test (phenol +  $\text{H}_2\text{O}_2$ , without catalyst) showed low phenol degradation (7% after 4 hours of reaction), suggesting that the  $\text{H}_2\text{O}_2$  decomposition occurs mainly on the surface of the material (Fe5 catalyst), since in the first hour of reaction, the phenol concentration was reduced to 94%, due to the consumption of approximately 20% of the initial  $\text{H}_2\text{O}_2$ , and consequently the phenol degradation was associated to the initial consumption of  $\text{H}_2\text{O}_2$  (3%). the greatest amount of OH radicals.<sup>21</sup> The maximum phenol breakdown was obtained in the time of 4h, close to 100%, which is linked to the increase in  $\text{H}_2\text{O}_2$  consumption (47%).



**Figure 5.** Phenol degradation and H<sub>2</sub>O<sub>2</sub> Consumption using 20 mg of the Fe5 catalyst and reaction periods ranging from 1 to 4 h. Quantification by HPLC and UV-Vis spectroscopy

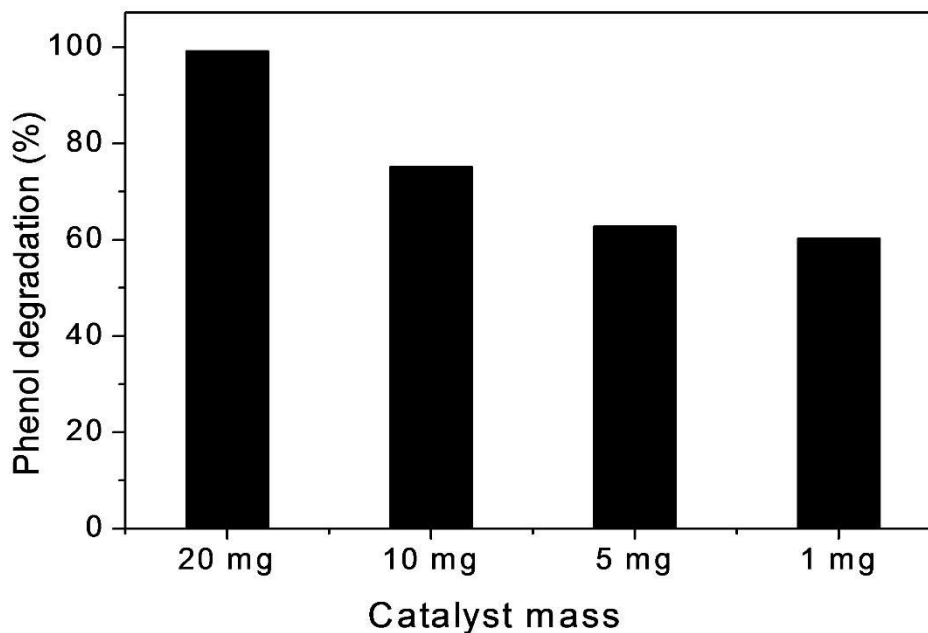
Comparison between quantification of degradation obtained by the Folin-Ciocalteu method and by HPLC for Fe5 catalyst after 4 h showed close results, indicating that the first one may be used as a good indicator to monitor phenol degradation.<sup>32</sup>

The influence of the catalyst amount on the phenol degradation was also evaluated for Fe5, for periods of 4 h and quantification by HPLC, as displayed in Figure 6. According

to these results, even a small amount of material (1 mg) leads to a high activity around 60 % of conversion.

Phenol degradation, after 4 hours of reaction, for solutions with different initial concentrations were tested using 20 mg of Fe5 catalyst. The results presented in Table 1 show that this degradation remained around 99% or higher.





**Figure 6.** Phenol degradation after Fenton test, using 1, 5, 10 or 20 mg of the Fe5 catalyst and reaction periods of 4 h. Quantification by HPLC

**Table 1.** Phenol degradation at different initial concentrations of phenol, after 4 hours of reaction. Quantification by HPLC

Initial concentration of phenol (ppm)	Degradation (%)
1000	99.1
500	99.1
250	99.2
125	99.6

The importance of the acidic pH in the degradation of phenol was evidenced by tests carried out in alkaline medium (20.3% phenol degradation) and in neutral medium (26% phenol degradation).

The reuse of the Fe5 catalyst was also evaluated and the same efficiency was observed even after the third Fenton test, with the same material. The degradation amount of 99 % was attained using the same initial mass (20 mg) after 4 h.

After the Fenton test, the catalyst was evaluated by XRF, in order to evaluate the Fe leaching from the material. Results indicated

the same Fe amount before and after test, confirming the high stability of the material. This result confirms that Fe incorporation as dopant into the alumina lattice consists in an interesting strategy for Fenton reaction, avoiding the risk of leaching as observed in literature,<sup>31</sup> who obtained 100 % of phenol conversion using  $\text{Fe}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ , however with 21 % of leaching of the active phase.

The rate of phenol consumption by mass of catalyst was calculated, as described by the equation 1:

$$-r = \frac{Nc \cdot \%}{t \cdot m} \quad \text{Equation 1}$$

At where: (-r) is the global rate of phenol consumption; (Nc) is the number of moles; (%) is the percent degradation of phenol; (t) is the time in hours; (m) is the mass of the catalyst in grams.

In this way, the phenol consumption rate calculated for Fe5 was  $3.2 \times 10^{-2}$  moles.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup>, even with a small surface area, but presenting high chemical stability, since iron leaching in the material was not observed.

#### 4. Conclusion

In this work, the use of Fe-doped  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as catalyst for phenol degradation using the Fenton process was successfully evaluated. A high efficiency was obtained using a relatively small time of reaction, with 90% of degradation after 2 h, according to HPLC results. Similar efficiencies were obtained after reuse for 3 times, with no Fe leaching from the material, indicating that a high stability was attained.

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