Artigo

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

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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.

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

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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.[1] 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.[2] For these reasons, removal of phenol from water bodies is a very important task.[3-5]

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.[6-7] 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.[8-9]

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.[9-11] 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.[12-14] Fe (II) compound was deposited onto mesoporous Al_2O_3,[15] while impregnated Fe_2O_3 onto mesoporous gamma-Al_2O_3,[16] both used for phenol degradation by Fenton reactions with a high efficiency. Recently, Fe_2O_3/Al_2O_3 and $Fe_2O_3/CuO/Al_2O_3$ catalysts were prepared by ultrasonic impregnation and obtained a high conversion, especially for the CuO containing catalyst.[17]

In the present work, iron was incorporated into alumina lattice, by a doping process using the modified Pechini method.[18-19] 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_2O_3 were obtained by the modified-Pechini method.[20] 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 ration citric acid: ethylene glycol of 3:2. The resin was heat treated at 350 ^{o}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 ^{o}C for 12 h and subsequently in stagnated air atmosphere with a heating rate of 10 ^{o}C.min^{-1} up to 1000 ^{o}C for 4 h. The pure Al_2O_3 powder precursor was also heat treated at 1100 ^{o}C using the same conditions (Al_2O_3-1100).

Samples were characterized by X-ray diffraction (XRD) by a XRD-6000 diffractometer (Shimadzu), using K_α 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 ^{o}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_2O_2 (30% v/v), according to di Luca and collaborators (2015).[16] 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_2O_2 solutions, without the catalysts.[21]

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 H_2O_2 to form the red-orange peroxovanadium cation, detected at the wavelength of 450 nm.[24]

2.3. Phenol quantification

Phenol degradation was initially monitored by the Folin-Ciocalteu method,[22] 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 µm, Sigma-Aldrich, St. Louis, MO, EUA) and a UV-visible detector (Rheodyne, EUA), in agreement to the previous methodology.[23]

3. Results and discussion

3.1. Synthesis and Characterization of the Catalyst

Figure 1 shows the DRX of the samples, indicate that pure Al_2O_3 calcined at 1000 ºC presents gamma and alpha phases, in agreement to the index cards ICDD 50-0741 and 42-1468, respectively, while Al_2O_3-1100 presents only the α-Al_2O_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 Fe^{3+} larger ionic radii (65 pm) comparing to Al^{3+} one (54 pm), both in octahedral site.[25] 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 α-Al_2O_3 after calcinations at and above 1100 ºC, which decrease to lower temperatures due to the presence of impurities in the material that change the phase transformation barrier.[26]

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,[27] δ-Al_2O_3 presents absorption bands assigned to the Al-O bonds of AlO_4 groups (around 750 cm^{-1}) and AlO_6 groups (around 615 and 490 cm^{-1}). In the present work, Al_2O_3 presents bands around 466, 553, 733 and 814 cm^{-1}.

For α-Al_2O_3 samples, literature data indicates bands at about 650, 600 cm^{-1}, and nearby 450 and 780 cm^{-1}, assigned to Al-O bond in octahedral coordination, AlO_6.[28] In the present work, these bands were observed at about 429, 581 and 630 cm^{-1} for Al_2O_3-1100 and Fe-doped samples. These results are in agreement to XRD patterns, which indicated the formation of δ-Al_2O_3 for the pure sample calcined at 1000 ºC and α-Al_2O_3 for the pure sample calcined at 1100 ºC as well as for the Fe-doped samples.
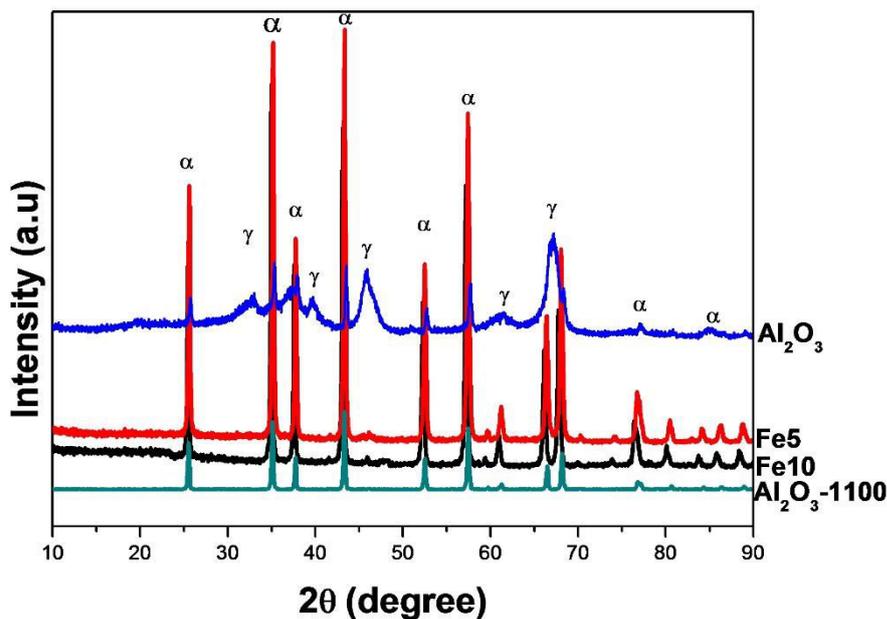
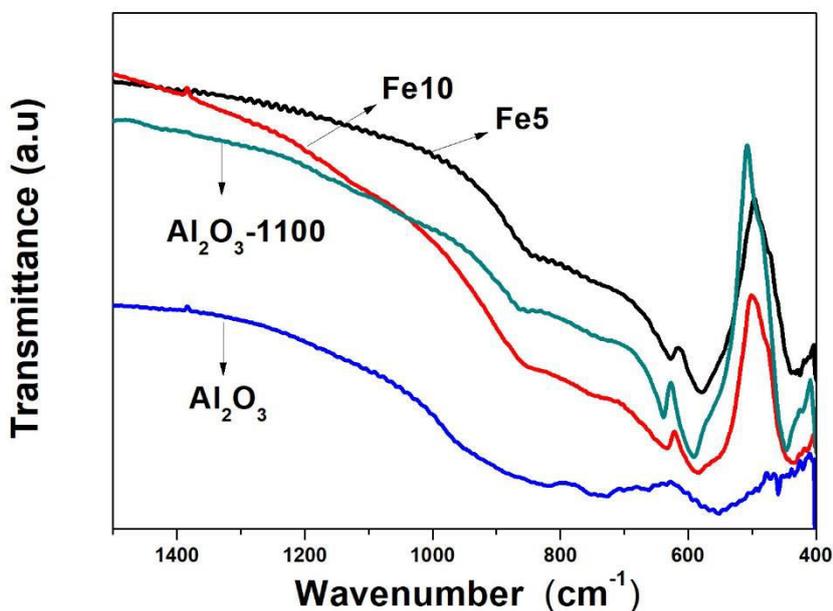**Figure 1**. XRD patterns of pure and Fe-doped Al_2O_3 samples

Figure 2. IR spectra of pure and Fe-doped Al_2O_3 samples

UV-vis spectra of all samples are presented in Figure 3. Electronic transitions may also be observed in the UV-vis spectra. Fe^{3+} 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^{3+} cations

that are magnetically coupled.[29] 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^{3+} 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^{3+} ligand field.
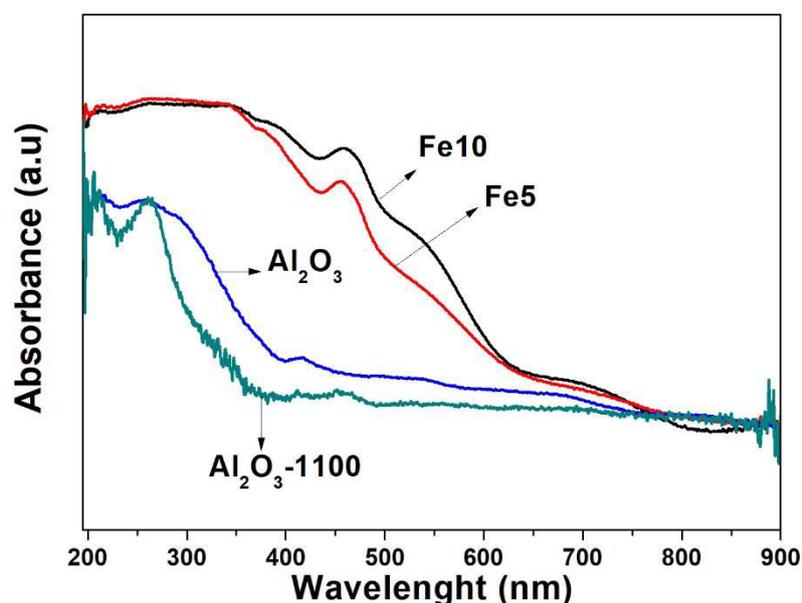

Figure 3. UV-vis spectra of pure and Fe-doped Al_2O_3 samples

The band gap of the samples was calculated according to Wood and Tauc method. Pure Al_2O_3 samples presented values of 2.8 and 3.5 eV for samples calcined at 1000 and 1100 ^{o}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_{BET}) of samples were measured using the BET method. For pure Al_2O_3 calcined at 1000 ^{o}C, S_{BET} was 19.9 $m^2.g^{-1}$, while Fe-doped samples presented similar S_{BET} values, of 5.7 and 5.4 $m^2.g^{-1}$ for 5 and 10 % doping, respectively.

3.2. Catalytic test and Phenol quantification

The first catalytic tests were realized at 70 ^{o}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_2O_3). This is a unusual result, especially considering that δ-Al_2O_3 has been the most used alumina phase applied as support for Fe_2O_3 in previous works.[30] The α-Al_2O_3 was used as support for Fe_2O_3 and presented similar results.[31]
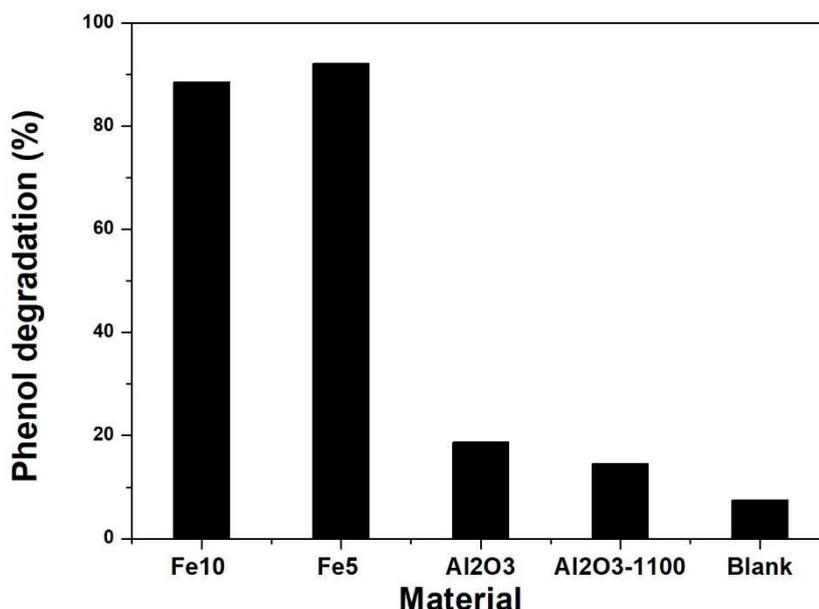
Figure 4. Phenol degradation after Fenton test, using 20 mg of the catalysts and 4 h of reaction. Quantification by Folin-Ciocalteu method

In relation to undoped alumina, two samples were evaluated δ-Al_2O_3, calcined at the same temperature of the doped samples and α-Al_2O_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 Fe_2O_3 supported on mesoporous δ-Al_2O_3, a material with very high surface area.[16]

A blank test (phenol + H_2O_2, without catalyst) showed low phenol degradation (7% after 4 hours of reaction), suggesting that the H_2O_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 H_2O_2, and consequently the phenol degradation was associated to the initial consumption of H_2O_2 (3%). the greatest amount of OH radicals.[21] The maximum phenol breakdown was obtained in the time of 4h, close to 100%, which is linked to the increase in H_2O_2 consumption (47%).
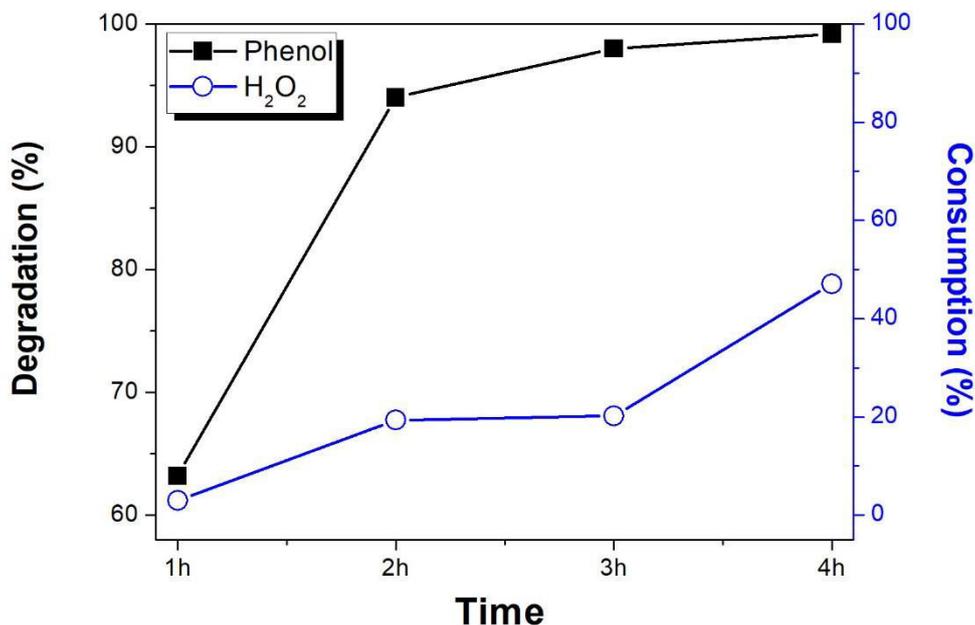
Figure 5. Phenol degradation and H_2O_2 Consumption using 20 mg of the Fe5 catalyst and reaction periods ranging from 1 to 4 h. Quantification by HPLC and UV-Vis spectroscopy

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.[32]

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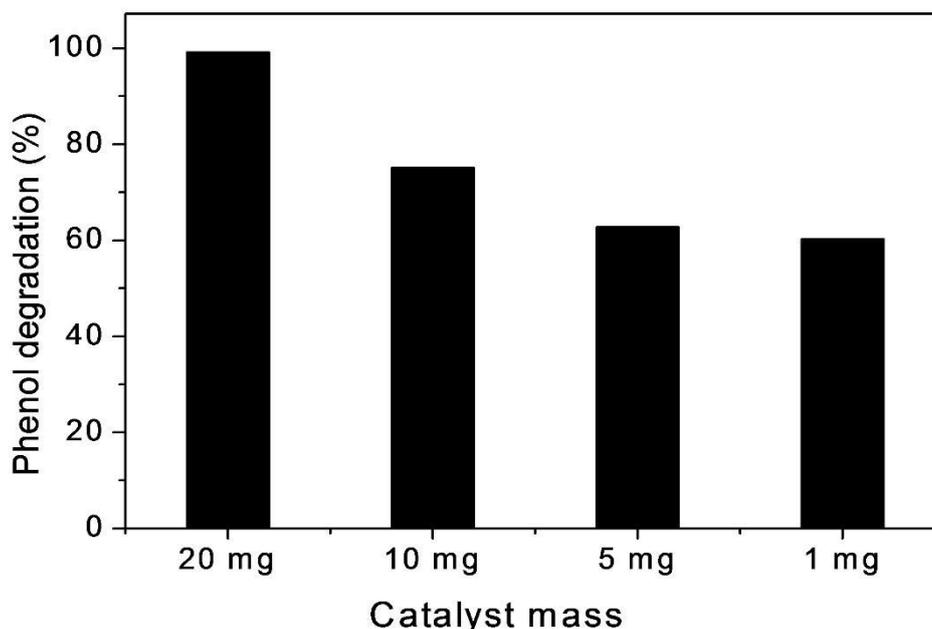
Figure 6. Phenol degradation after Fenton test, using 1, 5, 10 or 20 mg of the Fe5 catalyst and reaction periods of 4 h. Quantification by HPLC

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,[31] who obtained 100 % of phenol conversion using $Fe_2O_3/\alpha\text{-}Al_2O_3$, 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:

$$-r = \frac{Nc \,.\, \%}{t \,.\, m} \qquad \textbf{Equation 1}$$

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 3.2×10^{-2} $moles.g_{cat}^{-1}.h^{-1}$, 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 α-Al_2O_3 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.

Acknowledgements

References

[1] Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, L. Technologies for the removal of phenol from fluid streams: A short review of recent developments. *Journal of Hazardous Materials* **2008**, *160*, 265. [CrossRef]

[2] Abdelwahab, O.; Amin, N. K.; EL-Ashtoukhy, E. S. Z. Electrochemical removal of phenol from oil refinery wastewater. *Journal of Hazardous Materials* **2009**, *163*, 711. [CrossRef]

[3] Silva, K. S.; Zaidan, L. E. M. C.; Napoleão, D. C.; Dias, F. F. S.; Brandão, Y. B.; Checo Filho, J. G. A.; Barbosa, C. M. B. M.; Benachour, M.; da Silva, V. L. Análise da degradação e mineralização do fenol via processo oxidativo avançado para reuso de efluentes na indústria do petróleo. *Scientia Plena* **2014**, *10*, 074201. [Link]

[4] Kavitha, V.; Palanivelu, K. The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere* **2004**, *55*, 1235. [CrossRef]

[5] Lathasree, S.; Rao, N.; Sivashankar, B.; Sadasivam, V.; Rengaraj, K.; Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions. *Journal of Molecular Catalysis A: Chemical* **2004**, *223*, 101. [CrossRef]

[6] Vianna, V. B.; Torres, A. R.; Azevedo, E. B. Degradação de corantes ácidos por processos oxidativos avançados usando um reator com disco rotatório de baixa velocidade. *Química Nova* **2008**, *31*, 1353. [Link]

[7] Cao, Z.; Qin, M.; Jia, B.; Gu, Y.; Chen, P.; Volinsky, A. A.; Qu, X. One pot solution combustion synthesis of highly mesoporous hematite for photocatalysis. *Ceramics International* **2015**, *41*, 2806. [CrossRef]

[8] Araujo, F. V. F.; Yokoyama, L.; Teixeira, L. A. C.; Campos, J. C. Heterogeneous fenton process using the mineral hematite for the discolouration of a reactive dye solution. *Brazilian Journal of Chemical Engineering* **2011**, *28*, 605. [CrossRef]

[9] Navalon, S.; Alvaro, M.; Garcia, H. Heterogeneous Fenton catalysts based on clays, silicas and zeolites. *Applied Catalysis B: Environmental* **2010**, *99*, 1. [CrossRef]

[10] Hartmann, M.; Kullmann, S.; Keller, H. Wastewater treatment with heterogeneous Fenton-type catalysts based on

porous materials. *Journal of Materials Chemistry* **2010**, *20*, 9002. [CrossRef]

11 Wei X, Wu H, He G, Guan Y Efficient degradation of phenol using iron-montmorillonite as a Fenton catalyst: Importance of visible light irradiation and intermediates. *Journal of Hazardous Materials* **2017**, *321*, 408. [CrossRef]

12 Liu, P.; He, S.; Wei, H.; Wang, J.; Sun, C. Characterization of α-Fe_2O_3/γ-Al_2O_3 catalysts for catalytic wet peroxide oxidation of m-cresol. *Industrial & Engineering Chemistry Research* **2015**, *54*, 130. [CrossRef]

13 Grosh, P.; Kumar, C.; Samanta, N. A.; Ray, S. Comparison of a new immobilized Fe^{3+} catalyst with homogeneous Fe^{3+}–H_2O_2 system for degradation of 2,4-dinitrophenol. *Journal of Chemical Technology Biotechnology* **2012**, *87*, 914. [CrossRef]

14 Munoz, M.; Pedro, Z. M.; Menendez, N.; Casas, J. A.; Rodriguez, J. J. A ferromagnetic γ-alumina-supported iron catalyst for CWPO. Application to chlorophenols. *Applied Catalysis B: Environmental* **2013**, *136*, 218. [CrossRef]

15 Parida K.M.; Pradhan, A. C. Fe/meso-Al_2O_3: An efficient photo-Fenton catalyst for the adsorptive degradation of phenol. *Industrial & Engineering Chemistry Research* **2010**, *49*, 8310. [CrossRef]

16 di Luca, C.; Ivorra, P. Massa, R. Fenoglio. Iron–alumina synergy in the heterogeneous Fenton-type peroxidation of phenol solutions. *Chemical Engineering Journal* **2015**, *268*, 280. [CrossRef]

17 Zhang, J.; Zhang, X.; Wang, Y.; Degradation of phenol by a heterogeneous photo-Fenton process using Fe/Cu/Al catalysts. *RSC Advances* **2016**, 6, 13168. [CrossRef]

18 Melo, D.; Marinha, R.M. M.; Vieira. F. T. G.; Lima, S.J.G.; Longo, E. Souza, A.G.; Maia, A.S.; Santos, I.M.G. Influence of Cu(II) in the $SrSnO_3$ crystallization. *Journal of Thermal Analysis and Calorimetry* **2001**, *106*, 513. [CrossRef]

19 Vieira, F. T. G.; Oliveira, A. L. M.; Melo, D. S.; Lima, S. J. G.; Longo, E.; Maia, A. S.; Souza, A. G.; Santos, I. M. G. Crystallization study of $SrSnO_3$:Fe. *Journal of Thermal Analysis and Calorimetry* **2001**, *106*, 507. [CrossRef]

20 Alves, M. C. F.; Souza, S. C.; Silva, M. R. S.; Paris, E. C.; Lima, S. J. G.; Gomes R. M.; Longo, E.; Souza, A. G.; Santos, I. M. G. Thermal analysis applied in the crystallization study of $SrSnO_3$. *Journal of Thermal Analysis and Calorimetry* **2009**, *97*, 179. [CrossRef]

21 Biazati, L. B.; Moreira, T. F. M.; Neto, R. R.; Teixeira, A. L.; Freitas, M. B. J. G.; Lelis, M. F. F. Oxidação do benzo(a)pireno em matrizes aquosas por magnetita dopada com cobalto combinada com peróxido de hidrogênio. *Revista Virtual de Química* **2017**, *9*, 848. [CrossRef]

22 Chaves, M. H.; Citó, A. M. G. L.; Lopes, J. A. D.; Costa, D. A.; Oliveira, C. A. A.; Costa, A. F.; Júnior, F. E. M. B. Fenóis totais, atividade antioxidante e constituintes químicos de extratos de Anacardium occidentale L., Anacardiaceae. *Brazilian Journal of Pharmacognosy* **2010**, *20*, 106. [CrossRef]

23 Jiang, C.; Pang, S.; Ouyang, F.; Ma, J.; Jiang, J. A new insight into Fenton and Fenton-like processes for water treatment. *Journal of Hazardous Materials* **2010**, *174*, 813. [CrossRef]

24 Nogueira, R. F. P; Oliveira, M. C.; Paterlini, W. C. Simple and fast spectrophotometric determination of H_2O_2 in photo-fenton reactions using metavanadate. *Talanta* **2005**, *66*, 86. [CrossRef]

25 Zoppi, A.; Lofrumento, C.; Castellucci, E. M.; Sciau, P. H. Al-for-Fe substitution in hematite: the effect of low Al concentrations in the raman spectrum of Fe_2O_3. *Journal of Raman Spectroscopy* **2008**, *39*, 40. [CrossRef]

26 Matori, K. A.; Wah, L. C.; Hashim, M.; Ismail, I.; Zaid, M. H. M. Phase transformations of α-alumina made from waste aluminum via a precipitation technique. *International Journal of Molecular Sciences* **2012**, *13*, 16812. [CrossRef]

27 Saniger, J. M. Al-O infrared vibrational frequencies of γ-alumina. *Materials Letters* **1995**, *22*, 109. [CrossRef]

[28] Hernández, M. T.; González, M. Synthesis of resins as alpha-alumina precursors by the Pechini method using microwave and infrared heating. *Journal of the European Ceramic Society* **2002**, *22*, 2861. [CrossRef]

[29] Adhlakha, N.; Yadav, K. L. Structural, dielectric, magnetic, and optical properties of $Ni_{0.75}Zn_{0.25}Fe_2O_4$–$BiFeO_3$ composites. *Journal of Materials Science* **2014**, *49*, 4423. [CrossRef]

[30] di Luca, C.; Ivorra, F.; Massa, P.; Fenoglio, R. Alumina supported fenton-like systems for the catalytic wet peroxide oxidation of phenol solutions. *Industrial & Engineering Chemistry Research* 2012, *51*, 8979. [CrossRef]

[31] Pestunova, O. P.; Ogorodnikova, O. L.; Parmon, V. N. Studies on the phenol wet peroxide oxidation in the presence of solid catalysts. *Chemistry for Sustainable Development* **2003**, *11*, 227. [Link]

[32] Freire, L. F. A.; Fonseca F. V.; Yokoyama, L.; Teixeira, L. A. C. study of solar photo-fenton system applied to removal of phenol from water. *Water Science and Technology* **2014**, *70*, 780. [CrossRef]