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Nano-structured catalysts applied to heterogeneous photo-Fenton process to degrade herbicides in aqueous phase

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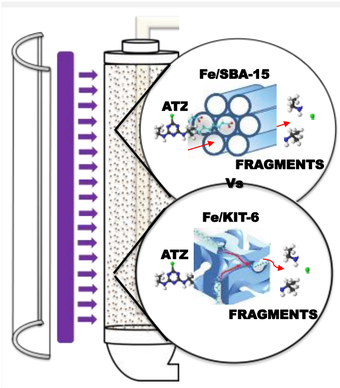

SBA-15 and KIT-6 materials have been synthesized and modified with iron salts by the wet impregnation method with different metal loadings. The different mesostructures obtained were characterized by N_2 adsorption-desorption at 77 K, TPR and UVVIS-RD. These iron-containing mesostructured materials have been successfully tested for the heterogeneous photo-Fenton degradation of atrazine (ATZ) aqueous solutions using UV-visible irradiation at room temperature and close to neutral pH. Depending on the dispersion and size of the different iron species, the nanocomposites showed different catalytic behaviors. The results showed that the Fe/SBA-15(10) and Fe/KIT-6(5) catalysts exhibited the highest activities. Thus, the high performance of these materials indicates that the heterogeneous via of photo-Fenton process can also be efficiently employed to treat wastewaters containing pollutants such as herbicides, in order to reduce them to simpler and less toxic molecules.

Introduction

The Fenton (Fe^{2+}/H_2O_2) and photo-Fenton (Fe^{2+}/H_2O_2/UV-Vis) reactions appear as very promising options for the oxidation of a wide range of recalcitrant organic pollutants [1]. The application of these processes to wastewater treatment has aroused great interest mainly due to the fact that Fe is a widely available and nontoxic element, and hydrogen peroxide is easy to handle and the excess decomposes to environmentally safe products [2].

Depending upon the phase, the Fenton and photo-Fenton reactions may be carried out under homogeneous or heterogeneous conditions. Under homogeneous conditions, the catalyst Fe^{2+}/H_2O_2 remains soluble in aqueous acidic medium, whereas under heterogeneous conditions, the metal ions like Fe^{2+} and Fe^{3+} get anchored on some low cost carriers.

Nevertheless, it has been reported that the conventional homogeneous Fenton process based methods suffer from some drawbacks such as (i) the precipitation of soluble iron ions as hydroxide precipitate under neutral pH or alkaline conditions [3], (ii) the requirement of strict pH regulation around 2.8 - 3 [4], and (iii) the requirement of post-treatment prior to discharge, such as neutralization of the treated solutions [5]. Some of the drawbacks of the conventional Fenton process can be avoided by the use of a heterogeneous catalyst.

Mesoporous materials have received widespread interest because of their good distribution of pore size / volume; this allows hundreds of molecules to effectively diffuse to internal active sites, increasing their activity per unit of volume [6]. Mesoporous photocatalysts are not only highly porous but orderly, with high specific surface areas [7] and high thermal stability. In previous works, mesoporous materials have been modified like SBA-15 and KIT-6 with iron showing excellent physical, optical and catalytic properties [8]. Mesoporous materials have received widespread interest because of their chemical, biochemical and environmental applications such as catalyst supports and adsorbents, particularly in reactions involving large molecules. In particular, mesoporous silica materials have attracted attention in materials science due to their morphological and textural properties, such as high specific surface area, large pore volumes, narrow pore-size distribution, wide pore dimensions and regular pore structure. As a result, such silica structures allow the access of large molecules and exhibit enhanced catalytic activity and adsorptive capacity compared to microporous materials.

It is known that, most herbicides are composed of very complex organic molecules, toxic and non-biodegradable. A chemical treatment, therefore, may originate the rupture of these organics into smaller, less toxic and more biodegradable fragments, thereby enabling a subsequent biological treatment.

In the present work, mesoporous photocatalysts supporting iron species on SBA-15 and KIT-6 were prepared, for their application in the photo-Fenton heterogeneous reaction for the degradation of the commercial herbicide (atrazine, ATZ) in water.

Material and Methods

SBA-15 and KIT-6 were synthesized and used as catalyst supports. Non-hydrothermal syntheses of both silica supports were carried out at room temperature based on synthesis processes described by Barrera et al [9] and Kleitz et al. [10], respectively. Catalysts were obtained by using these supports and the salt $Fe(NO_3)_3{\cdot}9H_2O$. Incipient impregnation was performed using ethanol as solvent in a volume ten times greater than the total pore volume of the supports. Mixture was kept in contact for 90 min in a rot evaporator with ultrasound at 50 °C. Subsequently, a drying process was carried out at 60 °C for 12 h and finally the samples were calcined at 350 °C for 3 h. Five impregnations were made using different percentages of theoretical iron and the samples were named as follows: Fe/SBA-15 (X) and Fe/KIT-6 (X), where X corresponds to 1, 2.5, 5, 10 y 15 % w/w.

Photo-Fenton tests were carried out in an isothermal, batch reactor (V_R = 85 cm^3) made of borosilicate glass tube, with four tubular UV-Vis lamps (ACTINIC BL 20, Philips). The system included a sintered glass piece placed at the bottom through which an air flow was introduced to provide good mixing conditions. Moreover, the reactor was equipped with a liquid sampling valve and temperature and pH controls.

Aliquots of the aqueous suspensions were collected to perform the following determinations: (i) ATZ concentration by HPLC; (ii) H_2O_2 by means of a modified iodimetric technique [11]; (iii) ferrous ions and total iron with a standard spectrophotometric technique (Fe^{2+}-phenanthroline complex) [12].

Textural characterization was carried out by using measurements of N_2 adsorption-desorption at 77 K in manometric equipment (Micromeritics ASAP 2000). Prior to the analysis, samples were degassed at 200 °C for 10 h. The specific surface area (S_{BET}) of the samples was estimated by the Brunauer, Emmet and Teller method using the N_2 adsorption data at 77 K in the following relative pressure (p/p^0) ranges: SBA-15 and Fe/SBA-15 (10%) (0.05-020), KIT-6 y Fe/KIT-6 (5%) (0.05-0.13). The α_S-plot method using LiChrospher Si-1000 macroporous silica gel as the reference adsorbent was used to calculate the micropore ($V_{\mu P}$), primary mesopores (V_{PMP}) volumes and primary mesopores surface (S_{PMP}). The total pore volume (V_{TP}) was obtained by applying the Gurvich rule at p/p^0 = 0.98. Pore size distributions (PSD) of the samples were obtained using the Non-Local Density Functional Theory (NLDFT) method "N_2 at 77 K on silica, cylindrical pore, equilibrium model" and "N_2 at 77 K on silica, cylindrical pore, adsorption branch" kernels for Fe/SBA-15 (10%) and Fe/KIT-6 (5%), respectively.

Temperature Programmed Reduction (TPR) experiments were carried out in ChemBET 3000 equipment, with a hydrogen flow (8 %) diluted in nitrogen with a heating ramp of 10 °C/min. Finally, samples were characterized by UV-Vis with diffuse reflectance in the wavelength range of 200 – 900 nm.

Results and Discussion

Catalytic tests

The atrazine degradation feasibility was researched applying the heterogeneous photo-Fenton reaction with synthesized catalysts. The used reaction conditions were reported elsewhere [13].

Figures 1(a) and 1(b) show the ATZ degradation as a function of time for the catalysts using SBA-15 and KIT-6 as supports, respectively. The initial concentration of the catalyst (C^0_{CAT}), hydrogen peroxide (C^0_{H2O2}) and the radiation remained constant. As can be seen in the samples obtained using KIT-6 as catalytic support an increase in the metal loading (1 to 5 % w/w) led to obtain a higher activity. Meanwhile, samples with higher iron content (10 and 15 % w/w) showed a decrease in the activity, leading to a lower ATZ degradation. Probably, the appearances of new iron species, inactive for the reaction, are the reason of this behavior.

In the case of catalyst obtained from SBA-15 as support, samples with lower iron loading (1, 2.5 and 5 % w/w) did not present meaningful differences among them. Samples with higher iron loading (10 and 15 % w/w) had similar and the best performance.

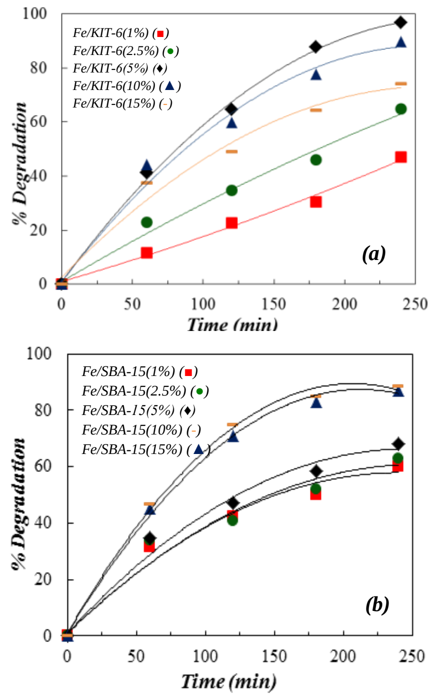

Figure 1. ATZ Degradation (%) as a function of time for **a)** Fe/KIT-6(X) and **b)** Fe/SBA-15(X).

Finally, as can be seen, the best behavior was found with the Fe/KIT-6(5) material, obtaining almost 100 % in the ATZ degradation at 240 min of the reaction. The second best material was Fe/SBA-15(10) which degraded approximately 90 % of ATZ. It should be noted that, in all cases, the consumption of H_2O_2 for these heterogeneous photo-Fenton reactions was lower than those obtained in homogeneous photo-Fenton reactions reported elsewhere [14].

Characterization

Figure 2(a) shows N_2 adsorption-desorption isotherms at 77 K of the supports and the catalysts which presented the best performance in ATZ degradation.

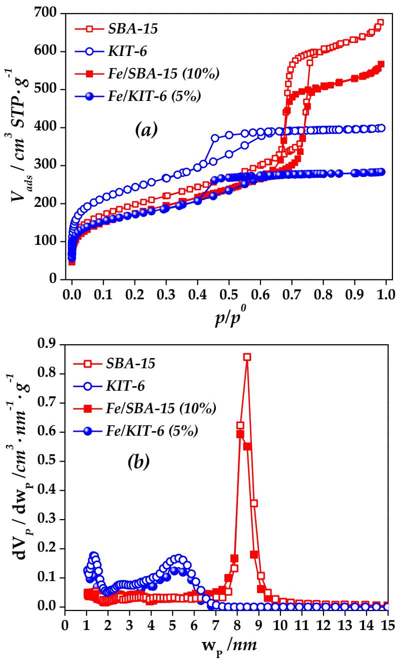

Figure 2. a) Adsorption-desorption isotherm of N_2 at 77 K b) Pore size distribution.

It can be seen that four materials exhibit Type IV isotherms (IUPAC classification) with typical hysteresis loops for this type of materials. A reduction in the catalysts adsorption capacity as well as in total pore volumes was obtained in comparison to their respective supports. This decrease can be related to the iron distribution in the surface and porosity material. There were no significant changes in the isotherms shapes between supports and catalysts, evidencing that the incorporation of the iron did not drastically affect the pore structure of the supports. In Figure 2(b) can be seen that there were no meaningful changes in the PSD of supports and catalysts. However, a difference between pore sizes of supports is observed. Table 1 shows textural properties of all materials.

Conclusions

Iron modified mesoporous photocatalysts were successfully synthesized by wet impregnation on mesoporous silica SBA-15 and KIT-6. This method appears as an effective, simple and low cost synthesis route. All the materials exhibited high specific surface areas, pore volumes, structural order retaining the original mesostructure.

The synthesized materials were evaluated in the photo-Fenton process in a heterogeneous phase applied to the degradation of aqueous solutions of commercial herbicide, atrazine. From these results it was possible to determine that both supports are suitable in order to obtain high conversions of the organic pollutant. The results showed that the Fe/KIT-6(5) and Fe/SBA-15(10) catalysts presented contaminant degradations above 90% in a reaction time of 240 min.

Obtained catalysts consumed low amounts of oxidant and they are stable and suitable materials for the atrazine degradation at the established reaction conditions in this research. Consequently, this heterogeneous photo-Fenton process appears as a very promising pre-treatment route capable of improving the biodegradability of contaminated water with recalcitrant chemicals as are the most agrochemicals used nowadays.

Acknowledgments

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Table 1. Textural properties of materials

Materials	S_{BET} (m^2/g)	S_{PMP} (m^2/g)	$V_{\mu P-\alpha}$ (cm^3/g)	V_{PMP} (cm^3/g)	V_{TP} (cm^3/g)
SBA-15	710	475	0.04	0.81	1.04
Fe/SBA-15 (10 %)	630	426	0.02	0.63	0.87
KIT-6	870	747	0.09	0.52	0.62
Fe/KIT-6 (5 %)	620	433	0.08	0.35	0.44

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