Influence of the concentration of iron on the structural, adsorption, and photocatalytic activity in the degradation of a textile dye in mesoporous catalysts

Influencia de la concentración de hierro sobre la actividad estructural, adsorción y la actividad fotocatalítica en la degradación de un colorante textil en catalizadores mesoporosos

José Manuel Barrera-A.*[a], Sayra Lissette Orozco-Cerros[a],
Raúl Campos-Gutiérrez[a], Antonio Esteban Jiménez-González[b],
María del Carmen Durán-Domínguez-de-Bazúa[a]

[a]Universidad Nacional Autónoma de México, Facultad de Química, Departamento de Ingeniería Química, Laboratorios 301, 302, 303 de Ingeniería Química Ambiental y de Química Ambiental. Edificio E-3. Conjunto E, Circuito de la Investigación Científica S/N, Ciudad Universitaria, Coyoacán, 04510 Ciudad de México, México
*Email (*correo-e*): jmanban@yahoo.com.mx, Phone: +1 52 55 5622 5301, Fax +1 52 55 5622 5300
[b]Universidad Nacional Autónoma de México, Instituto de Energías Renovables, Temixco, Morelos, México

*Corresponding author / *Autor a quien debe dirigirse la correspondencia*

Received / *Recibido*: Enero 15, 2022

Accepted / *Aceptado*: Febrero 14, 2022

Abstract

Mesoporous catalysts loaded with TiO_2 and doped with iron were prepared using the sol-gel method. They were physically characterized showing that iron in their structures favored the formation of the crystalline phase anatase. The surface area for all iron doped catalysts decreased, but at the same time the iron presence increased pore volume and diameter obtaining catalysts with greater catalytic activity by the modification of the textural properties. The principal specie of iron was Fe_2O_3, determined by X-ray photoelectron spectroscopy (XPS). The catalysts were tested in the degradation of the Reactive Blue 69 (RB69) dye. Results confirm that increasing the concentration of iron on the surface of the catalysts increased the removal percentage of organic matter measured as total organic carbon (TOC) and chemical oxygen demand (COD). The iron in those catalysts was strongly linked on their surface, the iron in titanium dioxide (P25) lost huge quantity of it immediately passing to the water where it performed a photo-Fenton process. The best result for the dye degradation was obtained using the catalyst doped with the highest concentration of iron supported on Santa Barbara amorphous catalyst (SBA-15). This catalyst can be used during four cycles without losing catalytic activity. This result has a better performance than the P25 and the P25 doped with the same concentration of iron.

Keywords: Reactive Blue 69, dye degradation, iron doping, mesoporous catalyst, SBA-15, titanium dioxide

Resumen

Los catalizadores mesoporosos cargados con TiO_2 *y dopados con hierro se prepararon utilizando el método sol-gel. Se caracterizaron físicamente mostrando que el hierro en sus estructuras favorecía la formación de la fase cristalina anatasa. El área superficial para todos los catalizadores dopados con hierro disminuyó, pero al mismo tiempo la presencia de hierro aumentó el volumen y el diámetro de los poros obteniendo catalizadores con mayor actividad catalítica por la modificación de las propiedades texturales. La principal especie de hierro fue* Fe_2O_3*, determinada porXPS (X-ray photoelectron spectroscopy). Los catalizadores se probaron en la degradación del colorante RB69 (Reactive Blue 69). Los resultados confirman que el aumento de la concentración de hierro en la superficie de los catalizadores aumentó el porcentaje de eliminación de materia orgánica medida como carbono orgánico total (TOC) y demanda química de oxígeno (DQO). El hierro en esos catalizadores estaba fuertemente ligado en su superficie, el hierro en dióxido de titanio (P25) perdió una gran cantidad pasando inmediatamente al agua donde realizó un proceso foto-Fenton. El mejor resultado para la degradación del tinte se obtuvo utilizando el catalizador dopado con la mayor concentración de hierro soportado sobre SBA-15 (Santa Barbara amorphous catalyst). Este catalizador se puede utilizar* *durante cuatro ciclos sin perder actividad catalítica. Este resultado muestra un mejor rendimiento que el P25 y el P25 dopado con la misma concentración de hierro.*

Palabras clave: *Azul Reactivo 69, degradación del colorante, dopado con hierro, catalizador mesoporoso, SBA-15, dióxido de titanio*

Introduction

The family of mesoporous materials are considered as an ideal class of catalyst supports because of their large surface areas and uniform pore size distributions. One of the most used mesoporous materials is SBA-15, which was synthesized in 1998 by Zhao et al. (1998a). Zhao and coworkers (1998a) used triblock copolymer surfactants to template the formation of SBA-15 silica molecular sieves. SBA-15 material contains hexagonal arrays of uniform mesopores (with pore diameters in the range of 5-30 nm), huge surface areas, narrow pore size distribution, and high pore volume (Busuioc et al., 2006; Khodakov et al., 2005). The immobilization of TiO_2 on mesoporous silica can be used to enhance adsorption and avoid agglomeration (López-Muñoz et al., 2005; De Witte et al., 2008). The huge surface area of SBA-15 helps to distribute one or more semiconductors on its surface, converting the new material into a supported photocatalyst (Acosta-Silva et al., 2011; De Witte et al., 2008; Wang et al., 2013). The synthesis of a siliceous support material and subsequent deposition of titanium dioxide on the surface by applying it with a post-synthesis method has also been reported (De Witte et al., 2008; Shah et al., 2007; Zhao et al., 2011). Introducing titanium species into mesoporous silicate materials has attracted much interest because the titanium containing mesoporous systems have much higher active surface areas (>200 m^2/g) in comparison to pure titanium (De Witte et al., 2008; Suraja et al., 2011) which makes them more effective (Bhattacharyya et al., 2004; Van Grieken et al., 2002). Titanium dioxide on the surface of SBA-15 has one disadvantage: When the concentration of TiO_2 increases, the surface area of the doped catalysts decreases, even destroying the structure of SBA-15. High quantities of TiO_2 provoke agglomeration of the particles (Li and Kim, 2005; Van Grieken et al., 2002).

Thus, in this work the SBA-15 was impregnated with an amount of TiO_2 that would preserve the characteristics of the original mesoporous material.

An additional doping was then carried with this TiO_2/SBA-15 out using iron. It has been amply proved this doped ion changes the characteristics and properties of the TiO_2 catalysts obtaining new materials useful in the degradation of textile dyes (Li and Kim, 2005). P25 was used as control both undoped and doped with the same concentrations of iron as the TiO_2/SBA-15.

Materials and Methods

Synthesis of the catalysts

SBA-15 synthesis

The reagents were mixed in a Teflon bottle to obtain 15 g of SBA-15: HCl (2N, T.J. Baker Co., Ltd.) (473 mL), Pluronic 123 (Aldrich) (16 g), and water (27 mL). The mixture was stirred until the Pluronic was completely dissolved. Then the TEOS (35 mL) was added to the Teflon bottle drop by drop. The solution was maintained in agitation and in a Maria bath at 38°C for 24 h. After the thermal treatment, the bottle was put in an oven at 95°C for 72 hours. When the thermal treatment was finished, the white solid was washed with enough quantity of distilled water to eliminate the surfactant. Finally, the material was dried at 95°C for 12 hours, and calcined at 550°C for 6 hours.

TiO_2/SBA-15 synthesis

The precursor of titanium dioxide was titanium tetrachloride (99.9% of purity, Aldrich). This precursor was treated before being added to the SBA-15 material. The treatment consisted in mixing 5.5 mL of titanium tetrachloride in water at 0°C using an ice bath. The addition of $TiCl_4$ was very slow and the reaction vessel was stirred during 6 hours. All the equipment was set in an extraction system to eliminate the gas formed during the reaction. After 6 hours, the value of the pH of the reaction was adjusted to 7.0 using ammonium hydroxide (10% volume, 30% purity, Baker). A white precipitate was formed. It was washed with 2 L of distilled water. Then, 300 mL of distilled water adjusted to pH 2.0 using nitric acid (10% volume, 70% purity, Sigma Aldrich) were mixed with the washed precipitate. The system was stirred and set in a bath at 70°C for 24 h. At the end of these 24 h the SBA-15 material was added at the recipient to support the TiO_2 in the SBA-15. The solution was stirred for 3 hours and the sol-gel method was applied. The catalyst was dried at 95°C for 12 h and calcined at 550°C for 6 hours.

Fe/TiO_2/SBA-15 catalysts

The TiO_2/SBA-15 catalysts were doped with four different concentrations of iron, 0.1, 0.2, 0.3, 0.5, and 0.7 mass%, using a wet conventional method. The different solutions of iron salt were prepared with distilled water at a pH value of 2.0 (10% volume, 70% purity, Sigma Aldrich), adding the required amount of ferric nitrate, $Fe(NO_3)_3.9H_2O$ (99.99%, Aldrich), and stirring until the iron salt was completely dissolved. Then, 10 g of TiO_2/SBA-15 were dispersed in each solution. The suspension was maintained in agitation for 4 hours. After that time, the value of the pH of the suspension was adjusted to 8.5 (ammonium hydroxide, 10% volume, 30% purity, Baker). One week was the time of aging for all the catalysts. Then they were first dried at 95°C for 12 hours and secondly calcined at 550°C for 6 hours.

Characterization

The crystalline structure for all the catalysts was analyzed by using a Bruker AXS D8 diffractometer equipped with a Ni filter for CuK_α line, operating with a pitch of 0.03-degree min^{-1}, at 2θ range from 5 to 75 grades and a power condition of 40 kV and 30 mA.

N_2 adsorption-desorption isotherms for all photocatalysts were obtained by using a nitrogen adsorption-desorption apparatus (Quantachrome, Autosorb-1) at a liquid nitrogen temperature of 77 K. The surface area of all the prepared photocatalysts was calculated by the Brunauer-Emmett-Teller method (BET method). Pore size distribution was calculated for all catalysts. Before adsorption, the catalysts were outgassed at 120°C for 24 hours to remove adsorbed impurities.

X-ray photoelectron spectroscopy (XPS) data were collected by a K Alpha X-ray photoelectron spectrometer under ultrahigh vacuum (2×10^{-9} mbar). A $K\alpha$ ($h\nu$= 1486.7 eV) monochromated X-ray source was operated at 3 mA corresponding to a spot size of 400 μm. The powders were mounted on double-stick carbon tape.

To study the light absorption of the catalysts, the diffuse reflectance spectra (DRS) of the samples in a wavelength range of 200-800 nm were obtained using a spectrophotometer Agilent Technologies Cary 500 with PTFG as reference.

Experimental procedure

The photocatalytic activity for the catalysts was measured considering the discoloration and degradation processes of a textile dye, Reactive Blue 69 (RB69). The experiment was divided into two parts: First part, the adsorption-desorption process and second part, the reaction process. Initially, the water solution with the dye was prepared at a concentration of 30 mgL^{-1}. The solution was set in a glass reactor of 500 mL. The reactor had a UV lamp (13 W) and was externally covered to avoid other radiations. Then, the value of the pH was adjusted to 3.0 adding nitric acid (10 volume%, 70% of purity, Sigma-Aldrich). One initial sample was taken for measuring the initial dye concentration using a Cintra 5 UV-Vis spectrophotometer at the wavelength of 600 nm. This value was the peak of maximum absorption energy for the dye. The catalyst, 1 gL^{-1}, and hydrogen peroxide, 32 mM, were then added to the reactor that was stirred during the whole experiment. After 15 minutes one sample was taken from the reactor. It was centrifuged at 4000 rpm for 7 minutes. Then the sample was analyzed in the UV-Vis spectrophotometer. The liquid sample and the solid catalyst were returned to the reactor to maintain a constant volume. The UV lamp was turned on to start the reaction process. The samples were collected during the first 30 minutes every 10 minutes, then every 15 minutes until 2 hours and, finally, every 30 minutes until 5 hours. All the samples were centrifuged at 4000 rpm for 7 minutes and analyzed in the UV-vis spectrophotometer.

To analyze the degradation of the dye carbonaceous components two techniques were used, chemical oxygen demand (COD) and total organic carbon (TOC). The samples were collected every 60 minutes to determine the evolution of the degradation of organic matter measured as COD. TOC was measured at the beginning and at the end of the photoreaction process.

Results and discussion

X-ray diffraction

Figure 1 displays all the patterns of X-ray diffractions for all catalysts. The SBA-15 material did not present any peaks with respect to the crystalline phase. It was an amorphous material. When the substrate SBA-15 was impregnated with 40 mass% of TiO_2, the catalyst presented two crystalline phases of TiO_2, anatase and rutile, being rutile in higher proportion. The crystalline planes of rutile were (110), (101), (111), and (211). For anatase phase the planes were (101), (004), and (200). When the catalyst was doped with different concentrations of iron the crystalline phases of TiO_2 completely changed. For all catalysts, the anatase phase appeared in higher proportion in comparison with the rutile phase. This mixture might have increased the catalytic activity. The addition of the iron in the catalyst completely modified the configuration in the surface of the catalysts, giving more stabilization in the formation of the crystalline anatase phase.

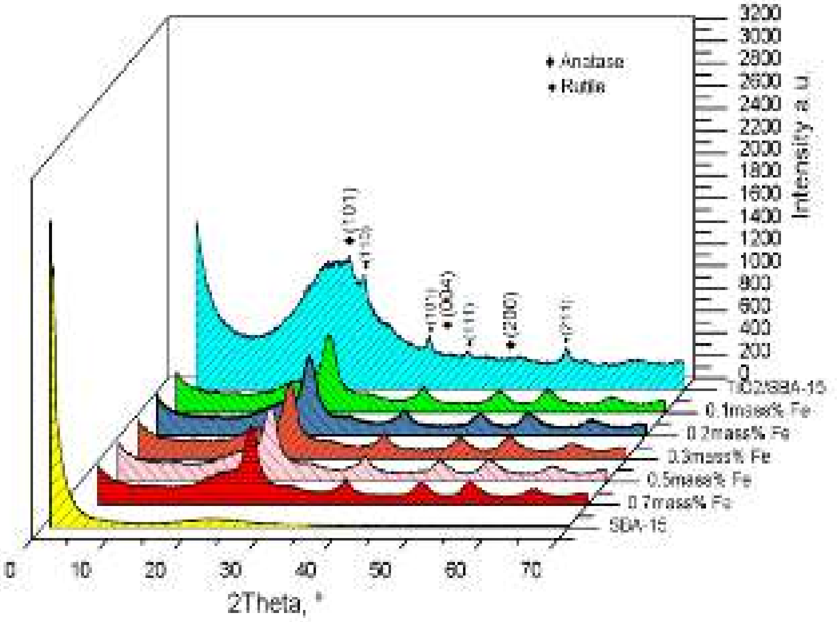

Fig. 1. Patterns of X ray diffractions for all the material prepared in the laboratory

The average size of the crystals was determined using the Squerrer equation calculating it from the FWHM (full-width at half-maximum) of the diffraction peak (101) crystal plane for the anatase phase for all the catalysts. In the equation, β is the crystal size of the catalyst, λ is the X-ray wavelength (1.54 Å), k=1, and θ is the diffraction angle.

For the catalyst impregnated with only TiO_2 the size of the particle was approximately 10 nm. When this catalyst was doped with the different iron amounts, the size of the particle was reduced. They had almost the same size of their particle in 5 nm.

For the P25 doped with the highest concentration of iron (0.7 mass%) the size of the particle was calculated using the same procedure, and it had a size of 26 nm. The differences in particle size for the catalysts modified their catalytic activity. Furthermore, the concentrations of iron were so low that perhaps for that reason in this determination did not appear crystalline phases of iron.

Surface area

All the mesoporous catalysts including the SBA-15 exhibited adsorption isotherms of type IV with H1 hysteresis loops (Lee et al., 2005; Zhao et al., 1998b). These isotherms are characteristic for mesoporous catalysts with a hexagonal pore arrangement (Ryoo et al., 2001; Zhao et al., 1998b). The catalyst impregnated with 40 mass% of TiO_2 on SBA-15 adsorbed a higher volume of N_2 than the supported material SBA-15. The SBA-15 presented the hysteresis loop in a well-defined range at relatively high pressures ($0.60 < P/P_0 < 0.78$) that represent the spontaneous filling of the mesopores due to capillary condensation indicating the presence of uniform mesopores. The catalyst impregnated with TiO_2 increased the absorption capacity of N_2 because it had more surface area. This behavior was due to the agglomeration of the particles of TiO_2 on the surface of the structure of the SBA-15. The effect of the iron in the surface of the catalysts reduced the surface area almost to one half in comparison with the catalyst impregnated only with TiO_2. The iron had another effect in the textural properties: It increased the pore diameter and the pore volume because the iron was supported on the SBA-15 structure. All the results of the characterization of surface area for the catalysts are shown in Table 1.

Table 1. Textural properties of the catalysts prepared in the laboratory

Catalysts	**Surface area ($m^2\,g^{-1}$)**	**Pore diameter Å**	**Pore volume ($cm^3\,g^{-1}$)**
SBA-15	672	13.4	0.22
TiO_2/SBA-15	770	13.7	0.26
0.1 mass% Fe	340.1	65.5	0.95
0.2 mass% Fe	325.1	65.7	0.89
0.3 mass% Fe	332.8	65.6	0.91
0.5 mass% Fe	313.5	56	0.80
0.7 mass% Fe	314.4	56.1	0.85

XPS characterization

The chemical composition for those catalysts that had the highest catalytic activity was analyzed by XPS. Those catalysts were doped with the highest concentration of iron. One was supported on SBA-15 and the other was supported on P25. For those catalysts, their spectrum was very similar, and for that reason only the catalyst impregnated with 40 mass% of TiO_2 and doped with 0.7 mass% of iron was presented in Figure 2.

In this spectrum iron was analyzed. Iron appeared as Fe_2O_3 for the value reported at 710.75 ± 0.85 eV. In this case the peak was approximately at 711 eV that corresponds to Fe^{3+} $2p_{1/2}$. The peak at 725 eV corresponds to the species Fe^{3+} $2p_{1/2}$. This other signal confirmed the formation of the Fe_2O_3. Other form that confirmed this was the signal of the satellite peaks at 719 eV and 734 eV (Figure 2). The binding energy at 714 eV and 727 eV indicated the presences of the γ-Fe_2O_3 species.

UV-Vis diffuse reflectance spectra

This analysis only was tested for the catalysts that presented the highest catalytic activity, those doped with the highest concentration of iron. Figure 3 displays their different spectra of light absorption. First, the SBA-15 catalyst impregnated with titanium dioxide was analyzed, absorbing energy in the UV region. Then, this catalyst doped with iron (0.7 mass%) was tested, also absorbing energy, but this began in the visible region at 550 nm.

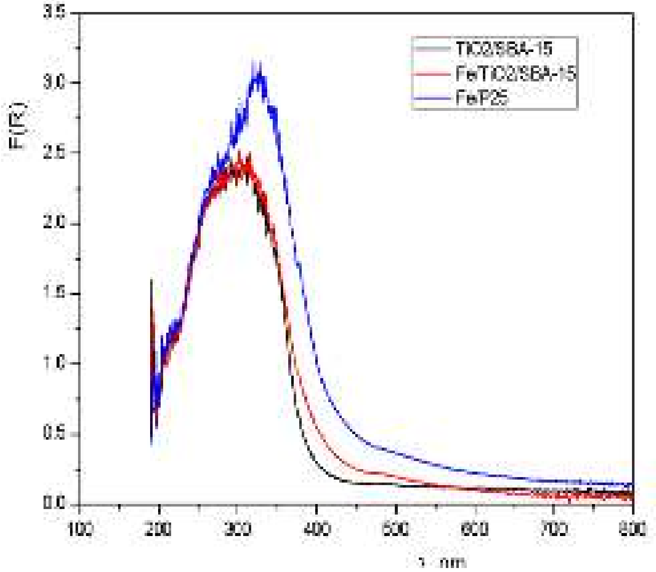

Fig. 2. XPS spectra of the 0.7 mass% of Fe in the catalyst supported in TiO_2/SBA-15

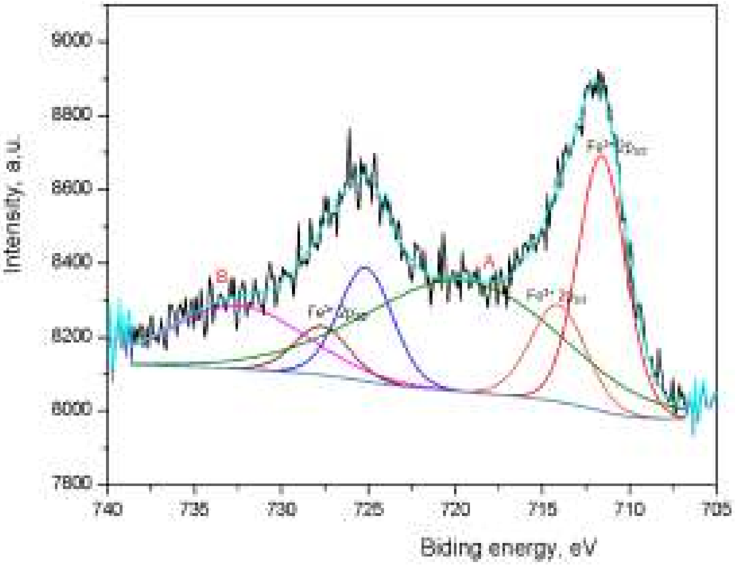

Fig. 3. UV-Vis diffuse reflectance spectra for the catalysts with high catalytic activity

This energy absorption was produced by the iron that was supported on the SBA-15 and the TiO_2. The P25 material doped with the same concentration of iron to compare its effect absorbed energy in the visible region, too. But it began at 700 nm. The band gap energies (Eg) of the catalysts impregnated with TiO_2 and doped with iron were estimated from the intersection of the extrapolated linear portion of the curve of $(\alpha h\nu)^{1/2}$ *vs*. photon energy ($h\nu$). When the SBA-15 material was impregnated with TiO_2, the band gap was 2.9 eV. This value is lower in comparison with the pure titanium dioxide (3.2 eV) for the anatase phase. This proved that the band gap of the TiO_2 was reduced when it was impregnated on SiO_2 (Bellardita et al., 2010). For the catalysts doped with iron the band gap of the catalyst supported on SBA-15 the value was 2.6 eV, since iron modified the surface of the catalyst. This technique showed that the band gap of the semiconductor was a combination of the TiO_2 and the iron. For that reason, this catalyst can absorb visible light to become active. In the case of P25 after doping with iron the value of the band gap was 2.5 eV. The iron interacted directly in the surface of the titanium dioxide decreasing the value of the TiO_2 band gap. By reducing the value of the band gap in the catalysts the catalytic activity will be increased. In both cases, the iron would act as an impurity to reduce the recombination of the pair electron-hole. All the patterns presented a big peak in the UV region for the titanium dioxide.

Photocatalytic activity

The catalytic activity for all the studied catalysts was tested through the discoloration process of the textile dye RB69. In Figure 4 all the patterns of the discoloration process of the RB69 using all the catalysts are displayed. Before evaluating the catalytic activity for all the catalysts, two experiments were made. One evaluated the effect of the light source and the addition of the hydrogen peroxide, and this experiment was named photolysis.

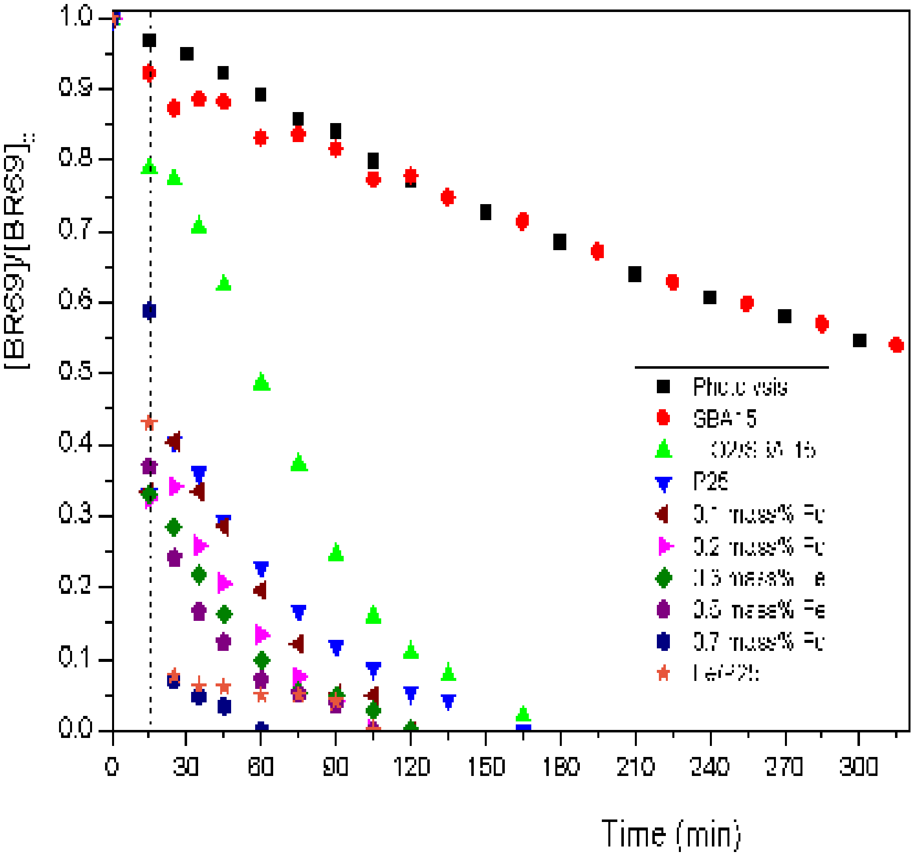

Fig. 4. Patterns of the discoloration process of the RB69 for all the catalysts

This experiment removed 45% of the color of the system. The light source did not have enough energy to break the textile dye molecule, but it could be fragmented by the hydroxyl radical generated from hydrogen peroxide molecule. The second experiment was done to evaluate the SBA-15 material used as catalyst. After 300 minutes, the system lost the 47% of the initial color. The reduction of the color in this experiment could have happened due to the adsorption process of the dye on the material surface. For all the experiments, a lapse of 15 minutes was taken for the adsorption-desorption process. This was identified in Figure 4 by a discontinue line. The catalyst TiO_2/SBA-15 discolored the system completely after 160 minutes. The control P25 decolorized the system in the same time as the TiO_2/SBA-15. The difference between them was in the adsorption process of the RB69.

Using the catalysts doped with iron the time of the discoloration process was reduced significantly. The P25 modified with iron decreased the time of discoloration of the system in 60 minutes with respect to the result using only P25. The shortest time of discoloration was the one presented for the catalyst doped with 0.7 mass% of iron supported on SBA-15 and impregnated with TiO_2. The catalysts synthesized in the laboratory using the SBA-15 material as support presented equal or less time for the discoloration process of the textile dye RB69 than the P25.

The catalytic activity for all the catalysts was measured considering the degradation of the RB69 molecule components. Results for the COD and TOC values determined by analyzing its removal percentage are given in Figure 5.

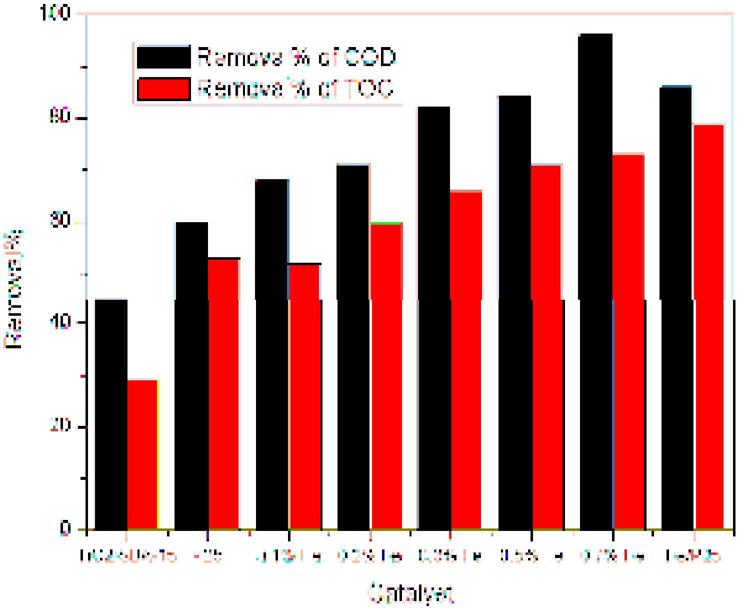

Fig. 5. Removal percentage of organic matter of the RB69 for all the catalysts

In the case of catalysts with TiO_2, the P25 yielded better results than the catalyst impregnated with TiO_2 and supported on SBA-15. When iron was incorporated in the structure of the catalysts the percent of removal in both parameters was also increased. The results were better that those obtained for the catalysts with only TiO_2. The P25 doped with iron gave a higher removal percentage of TOC than the other material. This might be due to the effect of the iron originally supported on its surface desorbing to a higher proportion. To corroborate this, an iron mass balance was determined for the catalysts with highest catalytic activity.

The results were the following: The iron losses for the TiO_2 catalyst supported on SBA-15 with 0.7 mass% of iron and for the Fe/P25 control were 5 and 11% of the initial iron, respectively. Iron in the solution followed the classical foto-Fenton reactions.

However, catalysts themselves were losing catalytic activity along the lapse when the amount of iron was becoming desorbed. For the case of the TiO_2 catalysts supported on SBA-15, the catalytic activity was almost the same, since the amount of iron adsorbed was strongly linked to both SBA-15 and TiO_2.

The cycles of reuse the different catalyst play a key role in the practical applications of photocatalytic nanomaterials. In this case the best catalyst Fe/TiO_2/SBA-15 was tested to find out how many cycles could be performed considering the degradation of RB69.

The different cycles are presented in Figure 6. The results indicate that the catalyst can be used during four cycles being only dried under the sun between cycles with equivalent results in the degradation of RB69 slightly higher than P25. After these four cycles, the catalyst was regenerated using a thermic treatment (400°C for 1 hours). After the regeneration treatment, the catalyst was tested again obtaining the same results as for the first cycle.

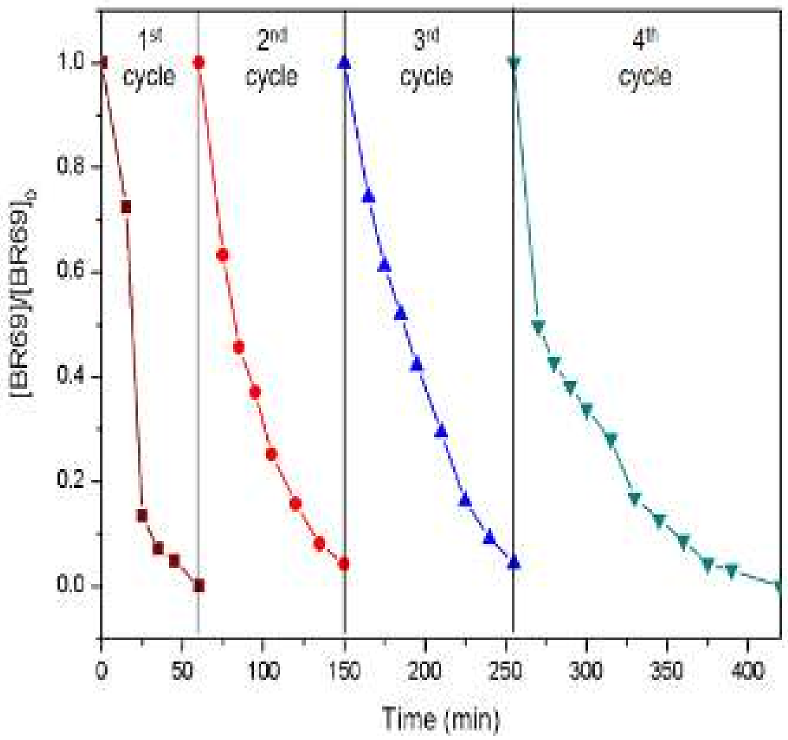

Fig. 6. The reusability test for the Fe/TiO_2/SBA-15 catalyst

Conclusions

The mesoporous catalysts impregnated with 40 mass% of TiO_2 and doped with five concentrations of iron using a wet conventional method were photocatalytic active in the degradation of the dye B R69 in aqueous solutions. The iron doped in the different catalysts increased the formation of the anatase phase in all catalysts. It reduced the band gap energy for the TiO_2, but at the same time this iron acted as semiconductor and adsorbed energy to generate the hydroxyl radicals increasing the percent removal of the organic matter. Using the catalyst supported on SBA-15 and impregnated with TiO_2 and doped with 0.7 mass% of iron the mineralization process of the RB69 achieved 73%, measured as TOC. This parameter indicated that the molecule of the textile dye was broken and had less carbon components. The Fe/TiO_2/SBA-15 catalyst demonstrated that it was more effective and efficient in the degradation of the textile dye RB69 than P25.

Acknowledgements

Authors gratefully acknowledge the collegial support and helpful academic discussions with Mrs. Dr. Silvia Lucila Gelover-Santiago from IMTA, Mexico.

Funding

Partial financial support to acquire materials, reagents, equipments use, etc., was granted by the Mexico's National Council for Science and Technology (*Consejo Nacional de Ciencia y Tecnología, CONACYT*, in Spanish) with the Project 214352, by the UNAM DGAPA-PAPIIT Project IT100615, as well as by the UNAM FQ PAIP 50009067. First and third authors received a graduate studies scholarship from *CONACYT* Mexico.

References

Acosta-Silva, Y.J., Nava, R., Hernández-Morales, V., Macías-Sanchez, S.A., Gómez-Herrera, M.L., Pawelec, B. 2011. Methylene blue photodegradation over titania-decorated SBA-15. Appl. Catal. B: Environ. 110: 108-117.

Bellardita, M., Addamo, M., Di Paola, A., Marcìa, G., Palmisano, L., Cassar, L., Borsa, M. 2010. Photocatalytic activity of TiO_2/SiO_2 systems. J. Hazard. Mat. 174: 707-713.

Bhattacharyya, A., Kawi, S., Ray, M.B. 2004. Photocatalytic degradation of orange II by TiO_2 catalysts supported on adsorbents. Catal. Today. 98: 431-439.

Busuioc, A.M., Meynen, V., Beyers, E., Mertens, M., Cool, P., Bilba, N., Vansant, E.F. 2006. Structural features and photocatalytic behaviour of titania deposited within the pores of SBA-15. Appl. Catal. A Gen. 312: 153-164.

De Witte, K., Busuioc, A.M., Meynen, V., Mertens, M., Bilba, N., Van Tendeloo, G., Cool, P., Vansant, E.F. 2008. Influence of the synthesis parameters of TiO_2–SBA-15 materials on the adsorption and photodegradation of rhodamine-6G. Micropor. Mesopor. Mat. 110: 100-110.

Khodakov, A.Y., Zholobenko, V.L., Bechara, R., Durand, D. 2005. Impact of aqueous impregnation on the long-range ordering and mesoporous structure of cobalt containing MCM-41 and SBA-15 materials. Micropor. Mesopor. Mat. 79: 29-39.

Lee, D.-W., Ihm, S.-K., Lee, K.-H. 2005. Mesostructure control using a titania-coated silica nanosphere framework with extremely high thermal stability. Chem. Mater. 17: 4461-4467.

Li, Y., Kim, S.J. 2005. Synthesis and characterization of nanotitania particles embedded in mesoporous silica with both high photocatalytic activity and adsorption capability. J. Phys. Chem. B. 109: 12309-12315.

López-Muñoz, M.J., Van Grieken, R., Aguado, J., Marugán, J. 2005. Role of the support on the activity of silica-supported TiO_2 photocatalysts: Structure of the TiO_2/SBA-15 photocatalysts. Catal. Today 101: 307-314.

Ryoo, R., Joo, S.H., Kruk, M., Jaroniec, M. 2001. Ordered mesoporous carbons. Adv. Mater. 13: 677-681.

Shah, P., Ramaswamy, A.V., Lazar, K., Ramaswamy, V. 2007. Direct hydrothermal synthesis of mesoporous Sn-SBA-15, materials under weak acidic conditions. Micropor. Mesopor. Mater. 100: 210-226.

Suraja, P.V., Yaakob, Z., Binitha, N.N., Resmi, M.R., Silija, P.P. 2011. Photocatalytic degradation of dye pollutant over Ti and Co doped SBA-15: Comparison of activities under visible light. Chem. Eng. J. 176-177: 265-271.

Van Grieken, R., Aguado, J., López-Muñoz, M.J., Marugán, J. 2002. Synthesis of size-controlled silica-supported TiO_2 photocatalysts. J. Photochem. Photobiol. A. 148: 315-322.

Wang, X.-J., Li, F.-T., Hao, Y.-J., Liu, S.-J., Yang, M.-L. 2013. TiO_2/SBA-15 composites prepared using H_2TiO_3 by hydrothermal method and its photocatalytic activity. Materials Letters. 99: 38-41.

Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G.H., Chmelka, B.F., Stucky, G.D. 1998a. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. Science. 279: 548-552.

Zhao, D., Huo, Q., Feng, J., Chimelka, B.F., Stucky, G.D. 1998b. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. J. Am. Chem. Soc. 120: 6024-6036.

Zhao, S., Su, D., Che, J., Jiang, B., Orlov, A. 2011. Photocatalytic properties of TiO_2 supported on SBA-15 mesoporous materials with large pores and short channels. Materials Letters. 65: 3354-3357.