Photocatalytic solar discoloration of Reactive Red 84 employing titanium dioxide modified with iron

Decoloración solar fotocatalítica de Rojo Reactivo 84 empleando dióxido de titanio modificado con hierro

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Abstract

In this investigation, TiO_2 and Fe/TiO_2 (0, 0.15, 0.25, 0.40 iron mass%) were compared as photocatalysts to determine its best efficiency with respect to decoloration time and mineralization measured as total organic carbon (TOC) of a textile dye, Reactive Red 84 (water solution at 50 mg/L). The catalysts were synthesized using the sol-gel method under specific conditions (450°C 2h, using titanium terbutoxide, TBT). Doping with ferric nitrate was carried out. At lab scale (first stage), the TiO_2 and Fe/TiO_2 and the controls were exposed to visible light lamps adding 1 mL/L H_2O_2 (8.6 mmol/L) and 1 g/L of each catalyst. The iron doped catalysts were activated using visible light lamps. The results obtained indicated that the best catalyst was Fe-0.25 iron mass% doped TiO_2 (TSGF-0.25, technique sol-gel Fe). Decoloration time was 120 minutes of reaction and mineralization reached approximately 50% measured as TOC after 240 minutes. At pilot scale (second stage) using a CPC (Compound Parabolic Collector) solar reactor, the best catalyst (TSGF-0.25) decolorized 100% requiring 3.87 kJ/L of accumulated energy (Q_{UV}) and degraded 77% of the initial dissolved dye measured as TOC. Visible light proved to be suitable when using iron-doped materials.

Keywords: Titania and titania iron doped catalysts, CPC (Compound Parabolic Collector), Decoloration, Photocatalysis, Reactive Red 84

Resumen

En esta investigación se compararon como catalizadores TiO_2 y Fe/TiO_2 (0, 0.15, 0.25, 0.40 % masa de Fe) para determiner su eficiencia respecto del tiempo de decoloración y la mineralización de un colorante textil, Rojo Reactivo 84 en solución acuosa a 50 mg/L, medida como carbono orgánico total (COT). Los catalizadores se sintetizaron usando el método sol-gel en condiciones específicas (450°C, 2 h, usando terbutóxido de titanio, TBT). Se realizó el dopaje con nitrato férrico. A escala de laboratorio (primera etapa), el TiO_2 , Fe/TiO_2 y los controles se expusieron a lámparas de luz visible añadiendo 1 mL/L de H_2O_2 (8.6 mmol/L) y 1 g/L de cada catalizador. Los catalizadores dopados con hierro se activaron usando lámparas de luz visible. Los resultados obtenidos indicaron que el mejor catalizador era el de TiO_2 dopada con Fe-0.25% en masa (TSGF-0.25, technique sol-gel *Fe). El tiempo de decoloración fue de 120 minutos de reacción y la mineralización alcanzó aproximadamente el 50% medido como TOC después de 240 minutos. A escala piloto (segunda etapa) utilizando un reactor solartipo CPC (*Compound Parabolic Collector*), el mejor catalizador (TSGF-0.25) decoloró al 100% requiriendo 3.87 kJ / L de energía acumulada (Q_{UV}) y degradó el 77% del colorante disuelto inicial medido como TOC. La luz visible demostró ser adecuada cuando se utilizan materiales dopados con hierro.*

Palabras clave: *Catalizadores de titania y titania dopada con hierro, reactortipo CPC (Compound Parabolic Collector), decoloración, fotocatálisis, Rojo Reactivo 84*

Introduction

On average, from 10 to 15 per cent of the dyes are lost during the coloring process textiles (Pearce et al., 2003). Even at very low concentrations (10 to 50 mg/L) the azo dyes which are soluble in water present negative effects on the receiving environment (Bae and Freeman, 2007).

The implementation of processes of advanced oxidation as the heterogeneous photocatalysis to treat effluents with dye textiles is feasible as it has presented important results (Asiltürk et al., 2008; Barrera-Andrade, 2011; Garcés-Giraldo and Peñuela-Mesa, 2007; Gutiérrez-Díaz, 2015; Muñoz-Rábago and Rodríguez-Ortiz, 2011; Pey-Clemente, 2008). The catalysts of TiO_2 in their pure state have been widely studied, but with the aim of increasing its effects photocatalytic studies have been conducted with catalysts of TiO_2 doped with transition metal ions (Lettmann et al., 2001; Rajeshwar et al., 2001; Subramonian et al., 2017). The iron has been considered a suitable candidate for the doping of TiO_2, due to its atomic radius Fe^{3+} (0.64 Å) being similar to the Ti^{4+} (0.68 Å). That is why it is inferred that the iron can enter in the crystal lattice of the TiO_2 and reduce its bandwidth by increasing the efficiency of absorption of visible light. Another reason why iron is used as doping agent is its ability to act as a center of charge increasing the catalytic efficiency (Li et al., 2008; Luu et al., 2010; Nasralla et al., 2013; Yamashita et al., 2003).

On this basis, it is imperative to expand the capacity of absorption of visible light of TiO_2 for its activation in processes photocatalytic using solar reactors due to the solar radiation its component of UV light is less than 5%. There are a great number of studies that have used catalysts of TiO_2 doped with different concentrations of iron for the elimination of various pollutants as are the colorants Reactive Black 5 (Soo et al., 2016), Reactive Blue 69 (Gutiérrez-Díaz, 2015; Barrera-Andrade, 2016), Orange Bromide (Barrera-Andrade, 2011), Reactive Orange 84 (Garcés-Giraldo and Peñuela-Mesa, 2007), Reactive Red 120 and Reactive Blue 4 (Reyes-Calle, 2015), Reactive Red 198 (Moradi et al., 2016), and Reactive Orange 16 (Safari et al., 2014).

With this background, in this work there were tested different catalysts that have as an array the TiO_2 doped with different iron concentrations (0.15, 0.25 and 0.40 mass%) to determine which concentration of iron was idoneous to provide the highest percentage of mineralization of the molecule of Reactive Red 84 textile dye measured as total organic carbon (TOC).

Experimental

Materials

Titanium terbutoxide, $Ti(C_4H_9O)_4$ (Fluka) was used as a precursor of TiO_2. For doping ferric nitrate, $Fe(NO_3)_3.9H_2O$ (Fermont) was employed. Hydrogen peroxide was added as oxidizing agent H_2O_2 (Fermont). Reactive Red 84 was provided by a cooperating textile industry.

TiO_2 and Fe/TiO_2 synthesis and characterization

The catalysts of TiO_2 synthesized by the technique sol-gel (TSG) were prepared by mixing 44 mL of titanium terbutoxide, 48 mL anhydrous butanol, and 28 mL of distilled water at 4°C. The mixture was stirred for 24 hr and stored at room temperature by other 24 h, dried at 100°C for 24 h, and calcined for 2 hr to 450°C with a ramp of temperature of 5°C/min. The catalysts doped with different concentrations of iron Fe/TiO_2 were prepared by the wet impregnation method. The catalysts were synthesized by sol-gel doped with 0.15, 0.25 and 0.40% iron mass%. For the preparation of the catalysts of Fe doped TiO_2 (TSGF), iron was dissolved in distilled water at pH 2 set with HNO_3 (10 v/v), then added to TiO_2 and stirred for 4 hours. Subsequently the pH was adjusted to 8.5 with NH_4OH (10 v/v) and was left to stand 7 days. Finally, the material was dried by 10 hours to 100°C and calcined at 450°C with a ramp of temperature of 5°C/min during 2 hours. The crystalline structure of nanomaterials was determined using an X-ray difractometer (XRD Rigaku DMAX 2200, CuKα radiation λ=1.5406 Å). The catalysts were analyzed by diffuse reflectance spectroscopy (DRS) in a UV-Vis spectrophotometer (Cintra 5 UV-VIS). An integrating sphere of $BaSO_4$ was used as standard in the experiments of diffuse reflectance. The energy band prohibited for each catalyst was determined with the Kubelka-Munk function and the measuring range was 200 to 800 nm:

$$(R)=\frac{(1-R)^2}{2R} \qquad (1)$$

where R is the reading of reflectance of the spectrum. Applying a linear extrapolation from [F(R)*hv*]n *vs*. *hv*, where *hv* is the photon energy and n=1/2 is managed to find the energy band gap (EG) for each catalytic converter.

Photocatalytic activity

The photocatalytic activity of the nano-catalysts was measured through the process of discoloration and mineralization of the Reactive Red 84 (RR84) molecule. The samples were measured in a spectrophotometer dual beam Cintra Model 5 UV-Vis and the mineralization of RR84 was evaluated as total organic carbon, cot in a computer Shimadzu (TOC-VCSN). The first stage at laboratory scale consisted in the evaluation of the photocatalytic activity TSG doped with iron (0.15, 0.25, 0.40% mass%) under irradiation with visible light lamps (λ= 400 to 650 nm) coupled to a filter of acrylic material. In each experiment 1 g/L of catalyst was dispersed in 600 mL of an aqueous solution with 50 mg/L of RR84 adding 1 mL/L of H_2O_2 (8.6 mmol/L) as oxidizing agent and keeping a pH value of the system at 3.0 set with HNO_3 to 10 v/v (Merck). Before the reaction stage, solutions were set for 30 min in total darkness to reach equilibrium adsorption-desorption with the surface photocatalyst. The reactor containing the colored aqueous solution of RR84 the catalyst and the hydrogen peroxide was taken to complete a time of irradiation of 240 min (Fig. 1a). The second stage consisted in the evaluation of the photocatalytic activity the best catalyst (TSGF-0.25) under solar irradiation using a Compound Parabolic Collector (CPC) reactor of 3 L with glass tubes with a mass flow of 20 L/min generated by a submersible pump and a tank of recirculation (Fig. 1b). The conditions in this experiment were the same as at the laboratory level.

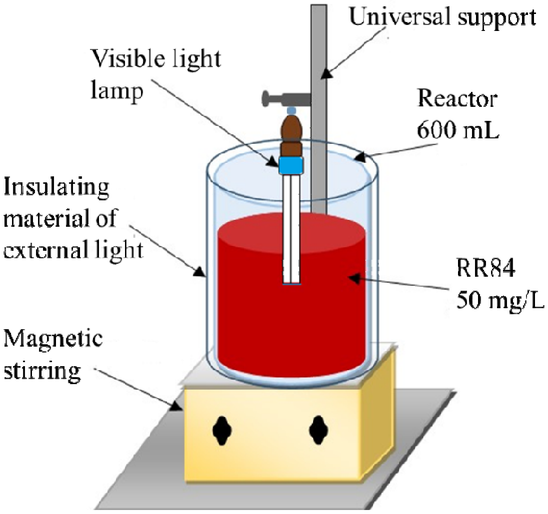

Fig. 1a. Lab scale photorector of 0.6 L with a visible light lamp (λ=400-650 nm) to test the catalysts on an aqueous solution of Reactive Red 84

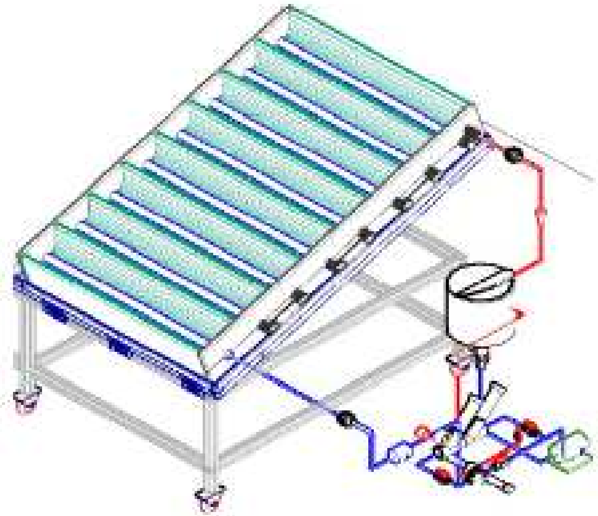

Fig. 1b. Compound Parabolic Collector (CPC) solar reactor of 3 L with glass tubes to test the catalysts on an aqueous solution of Reactive Red 84 (Campos-Gutiérrez, 2017)

Results and Discussion

Photocatalysts characterization

Fig. 2 shows XRD patterns of the nanocatalysts TiO_2 and Fe/TiO_2. TSG presented as the majority anatase phase, being to 2θ=25.26, 37.801 and 48.041°, corresponding to the planes of reflection (1 0 1), (0 0 4) and (2 0 0). Brookite phase was present to the 2θ=38.0° with index (1 3 1) with peaks of low intensity. The measurements obtained by XRD showed that the catalysts TSG and TSGF (0.15, 0.25, 0.40 mass% Fe) showed the same crystalline phases. It was not observed another phase attributed to the iron oxides probably due to the low concentrations of iron tested.

The optical properties of the catalysts TiO_2 and Fe/TiO_2 were examined with diffuse reflectance spectroscopy UV-VIS (DRS). Fig. 3 shows the results of DRS of catalysts TSG and TSGF-0.25. It is noted that the absorption edge of the catalysts Fe/TiO_2 in comparison with the TiO_2 without doping extends toward the visible light.

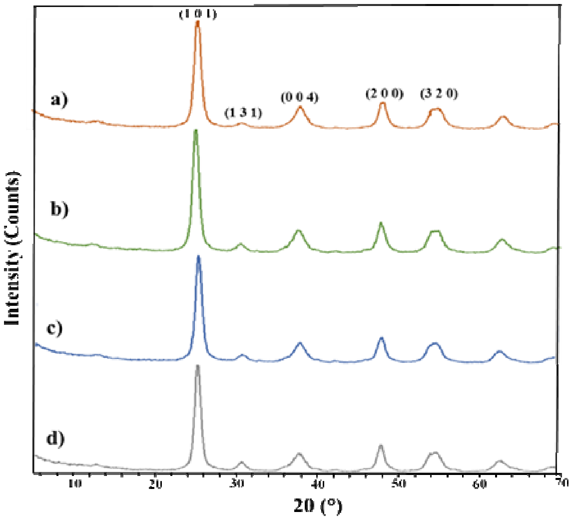

Fig. 2. XRD patterns of the Fe doped TiO_2 and TiO_2 catalysts

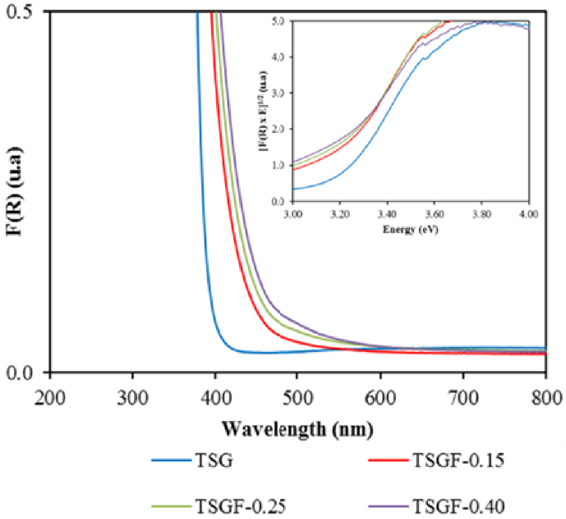

Fig. 3. UV-Vis diffuse reflectance spectra for the Fe doped TiO_2 and TiO_2 catalysts

The absorption edge extends more toward the visible spectrum as the concentration increases. This effect might be due to the electronic transition of the orbiting Fe3d to the conduction band of TiO_2. Despite that doping with iron does not alter the position of the TiO_2 valence band (VB), this introduces new levels of energy (Fe^{3+}/Fe^{4+}) of the transition of the ions within the TiO_2 prohibited energy band (Moradi et al., 2016).

The band gap energy (EG) of the catalysts was calculated by linear extrapolation between [F(R)E]1/2 where (E= *hv*) and *hv* to [F(R)E]1/2 = 0.

For the catalysts TSG the band gap energy for materials doped with 0.0, 0.15, 0.25 and 0.40 mass% was 3.16, 3.11, 3.10, and 3.06, respectively. It was found that by increasing the concentration of iron on the TiO_2 energy band gap decreases. The doping with iron decreases the band gap energy due to the level of catch of electrons between the valence band and the conduction band (Wu, 2008).

Decoloration and mineralization of RR84 using TiO_2 and Fe/TiO_2 at the laboratory level

The time of equilibrium adsorption-desorption of RR84 on the TiO_2 and Fe/TiO_2 was evaluated in terms of the time of contact between the dye and the catalysts. The time of adsorption was 30 min. Figure 4 represents the profiles of discoloration of the RR84 with TiO_2 and Fe/TiO_2.

The photocatalytic activity of materials TiO_2 and Fe/TiO_2 was determined using the discoloration and mineralization of RR84 under visible light. It is clear that the catalysts doped with iron are more efficient in the discoloration of the RR84 that the catalyst without doping under visible light. The catalytic converter doped with 0.25 mass% Fe was the most efficient one in the treatment (Fig. 4).

$$TiO_2 + hv \rightarrow e^- + h^+ \tag{2}$$

$$Fe^{3+} + h^+ \rightarrow Fe^{4+} \tag{3}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{4}$$

$$Fe^{3+} + O_{2(ads)} \rightarrow Fe^{3+} + O_2^- \tag{5}$$

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+} \tag{6}$$

$$Ti^{3+} + O_{2(ads)} \rightarrow Ti^{4+} + O_2^- \tag{7}$$

$$Fe^{3+} + OH^-{}_{(ads)} \rightarrow Fe^{3+} + OH^{\bullet}(ads) \tag{8}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{9}$$

$$Fe^{2+} + h^+ \rightarrow Fe^{3+} \tag{10}$$

$$Fe^{3+} + h^+ \rightarrow Fe^{4+} \tag{11}$$

$$Fe^{4+} + e^- \rightarrow Fe^{3+} \tag{12}$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \tag{13}$$

$$Fe^{3+} + hv \rightarrow Fe^{4+} + e^- \tag{14}$$

$$Fe^{4+} + OH^- \rightarrow Fe^{3+} + OH^{\bullet} \tag{15}$$

$$e^- + O_{2(ads)} \rightarrow O_2^- \tag{16}$$

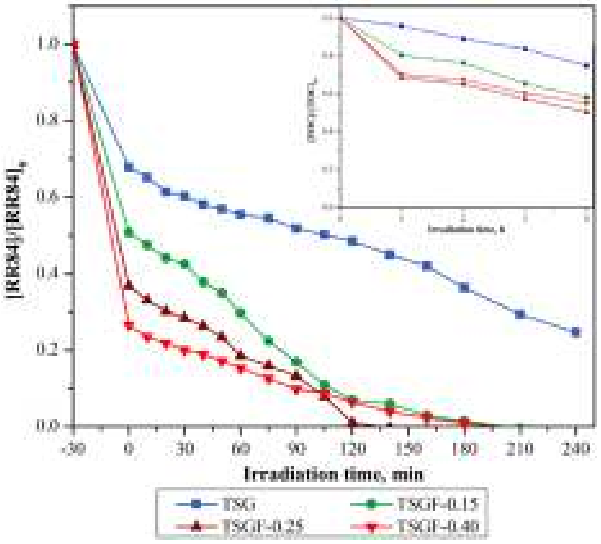

Fig. 4. Patterns of the decoloration process of the RR84 for all the catalysts under visible light

It has been emphasized that the photocatalytic oxidation of organic pollutants is carried out by the generation of electron-hole pairs. However, the recombination of electron-hole pairs generated can decrease the photocatalytic efficiency of TiO_2.

The high levels of recombination may be limited by the insertion of traps of electrons and/or gaps, thus postponing the time of recombination. The effect of the Fe^{3+} described considering the efficiency of separation of electrons and holes generated. As a result of introducing the appropriate amount of Fe^{3+} the generated electron-hole pair, necessary for the discoloration of the RR84 and delay the degree of recombination of catalysts Fe/TiO_2 exposed to visible light was obtained.

However, when the concentration of Fe^{3+} is exceeded, the ions of Fe^{3+} can act as centers of recombination of electron-hole pair, decreasing the efficiency of Fe/TiO_2 catalysts. In this work, the best amount of Fe^{3+} was 0.25 mass%, and it could be observed that at a concentration greater than this the efficiency decreases.

Unlike the excitement inherent in the TiO_2 under UV light, the excitement of the Fe/TiO_2 under visible light arises from the electronic transfer of the energy levels of the ion doping (Fe^{3+} /Fe^{4+}) to the conduction band of TiO_2.

The ion Fe^{3+} absorbs a photon (λ≥400 nm) to produce an ion Fe^{4+} and an electron in the conduction band of TiO_2. The electron from the conduction band reacts with the O_2 adsorbed to form O_2^-, where the ion Fe^{4+} reacts with the hydroxyl ion to produce a hydroxyl radical (OH•) (Moradi et al., 2016).

When ions of iron are exposed to radiation visible pass Fe^{3+} to Fe^{4+} (oxidation). Subsequently, the electron ceded by the iron passes to titanium and it is taken advantage of by another ion of Fe^{3+}.

Once the Fe^{3+} is in contact with a molecule of oxidizing agent (H_2O_2) The dissociates in an ion hydroxyl (OH-) and a hydroxyl radical (OH•) (Fig. 5).

Mineralization of RR84 using Fe/TiO₂ at pilot scale

The assessment with the CPC reactor was conducted controlling the initial pH of the sample and the concentration of catalytic converter; while the factor that was not handled was the amount of energy accumulated in the reactor. It was calculated using the following equation:

$$Q_n = Q_{n-1} + \Delta t_n \overline{G_n} \frac{A_c}{V_T} \tag{17}$$

where t_n is the time experimental of each sample; $\overline{G_n}$ is the average of the radiation during t_n; A_C is the catchment area solar, V_T is the total volume of the solution occupied, Q_n is the incident energy used in the reactor and Q_{n-1} is the incident energy used in the reactor in the time prior to Q_n.

Figure 6 shows the results of the experiments with solar irradiation. It was observed that when using the catalysts doped with iron are required less energy to discolor the system with RR84 compared with the process of photolysis plus the H_2O_2.

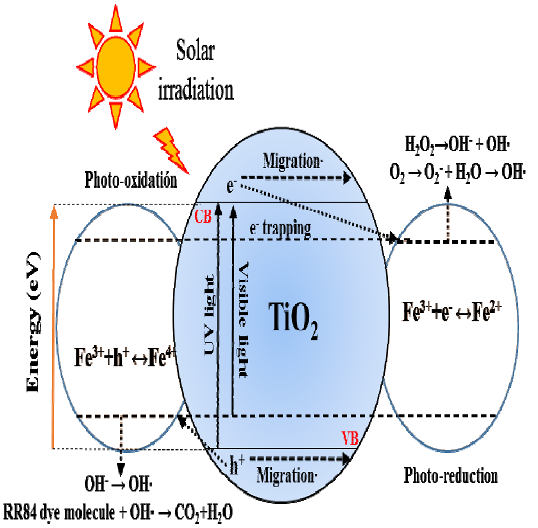

Fig. 5. Proposed mechanism for mineralization of RR84 under UV light and visible

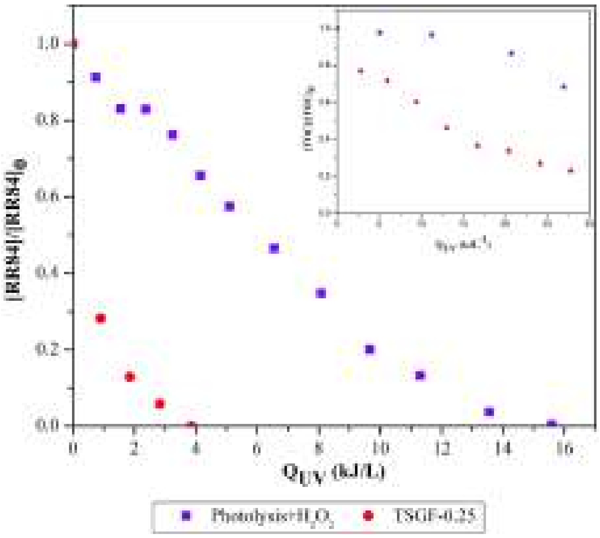

Fig. 6. Decoloration and mineralization of the RR84 depending on the accumulated energy

The TSGF-0.25 catalyst required 3.87 kJ/L and photolysis plus the H_2O_2 needed 15.59 kJ/L, respectively to discolor to 100% the system. The TSGF-0.25 downgraded 77% of COT requiring 27.81 kJ/L and photolysis more the oxidizing agent degraded 32% of COT requiring 26.99 kJ/L. On the basis of these results it was confirmed the activation of Fe/TiO_2 under visible light using solar energy by doping with iron.

Conclusions

Experiments succeeded in synthesizing catalysts of TiO_2 and Fe/TiO_2 at the level of laboratory and bench scale that presented efficiencies of 100% with respect to the discoloration of the RR84. The visible light allowed the activation of the catalysts due to doping with iron. The doping with iron achieved absorption in the visible spectrum of the catalysts. The dose of iron to the doping that allowed the best efficiency under visible light was TiO_2-0.25 mass% Fe. An increase of the percentage of iron might be increasing the recombination of pair electron/hollow.

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