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Fe_3O_4/TiO_2-βCD MAGNETIC PARTICLES: SYNTHESIS AND APPLICATION IN SOLAR PHOTOCATALYSIS FOR THE DEGRADATION OF ORANGE DYE II

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Abstract: Water pollution is one of the most important problems in our days, the wastewater discharged by the textile industry exemplifies this problem because high concentrations of colorants and other organic compounds (additives, surfactants, etc.) have been reported from of this sector in aquatic ecosystems. The colorants in water bodies are slowly degraded, generating byproducts of greater toxicity that are easily bioaccumulative, consequently dissolved oxygen is reduced, and biogeochemical cycles are altered, affecting organisms at different trophic levels. The results obtained from the photocatalytic evaluation of Fe_3O_4 and the Fe_3O_4/TiO_2 and Fe_3O_4/TiO_2-βCD complexes indicated that Fe_3O_4 is the material that degrades in the highest percentage to the orange II azo dye, under a process of exposure to natural sunlight, in addition to showing adequate recoverability and reuse efficiency. Fe_3O_4 was synthesized by a simple precipitation technique, shows a particle size of 100.617 ± 42.043 nm, a surface charge of -12.133 ± 0.32 mV, a reflectance of 48.218 ± 0.258% at 900 nm wavelength and bandgap energy of 2.95 eV. The experiments related to the reuse of Fe_3O_4 for 5 cycles indicated that it maintained adequate efficiency, since the degradation percentages remained above 90% for up to three consecutive cycles. However, for the fourth and fifth cycles, the percentages of degradation obtained were lower, these being 86.925 ± 0.407% and 78.119 ± 1.770%, respectively. Thanks to its paramagnetic properties, the easy recovery through the use of a magnet and the degradation percentages obtained, the synthesized Fe_3O_4 proves to be an alternative for the environmental restoration of contaminated water, this textile dye in areas with optimal solar radiation conditions.

Keywords: Day; Paramagnetic properties; Photocatalytic evaluation; Solar radiation; Water pollution.

INTRODUCTION

Water pollution is one of the most important problems nowadays, this resource is constantly affected by the discharge of untreated effluents from the industrial sector and whose composition varies according to each process. Such is the case of the textile industry, which worldwide generates around one trillion dollars, contributing approximately 7% of total world exports, employing more than 35 million workers worldwide, however, it is one of the activities that involves a significant consumption of water, because it is estimated that about 200 L are used per kg of textile product is dyed (Desore and Narula, 2018).

Contamination of bodies of water by this sector is related to the discharge of dyes (mainly of the azoic type) and other organic compounds (additives, surfactants, etc.) that are not adhered to the cloth and that are generated during the process of fixing and washing cloth (Yaseen and Scholz, 2019).

The presence of these dyes significantly alters aquatic ecosystems, as it increases the biochemical oxygen demand, the chemical oxygen demand , reduces photosynthetic activity, favors the bioaccumulation of recalcitrant compounds, in addition to promoting mutagenic and carcinogenic alterations in surrounding organisms (Khan and Malik, 2014).

Azo dyes are the most used and represent more than 60% of the total dyes on the market, mainly because their reduction in the environment leads to the formation of aromatic amines, which generally do not degrade and accumulate under anaerobic conditions (sediments), because about 20 to 50% of a dye of this category is not adhered to the cloth during washing processes, as is the case with the dye of orange II, methyl orange, scattered yellow, acid black 210 and reactive black 5, to name a few (Lellis et al., 2019).

Different technologies have been studied for the degradation of dyes in wastewater, such as biological treatments, coagulation/flocculation; electrochemical reactions such as Fenton, ozonation, adsorption and heterogeneous photocatalysis (Almazán-Sánchez et al., 2016). The latter shows greater advantages than the former because degradation occurs in relatively short times (180 min on average), the formation of by-products of greater toxicity is avoided and, when appropriate photocatalysts are used. These can be used continuously for up to 5 operating cycles and promote reaction within the visible spectrum, thus reducing the operational costs of the process. (Pawar and Lee, 2015)

Photocatalysis is an advanced oxidation process (AOP), where a catalyst and energy radiation is used to modify the rate at which a reaction occurs. This happens when an adequate wavelength is irradiated that manages to affect the surface of the catalyst, generating electron-hollow pairs (e^-/h^+), capable of promoting oxide-reduction (redox) processes allowing the reduction and in some cases the mineralization of dyes (Anandan and Yoon, 2004; Douthwaite, 2017). The study of different catalysts has been extensive in recent years, so it is increasingly necessary to look for photocatalysts capable of harnessing the electromagnetic energy emitted by the sun for its activation, as well as its easy recovery and reuse in the photocatalytic process.

This paper presents a proposal for the degradation of the residual orange dye II, through the use of heterogeneous photocatalysis with β-cyclodextrin (βCD) supported in easy recovery micromaterials (Fe_3O_4/TiO_2) making use of direct solar radiation, as the evaluation of the Fe_3O_4/TiO_2-βCD configuration for the degradation of dyes under natural solar radiation has not been reported to date, becoming a topic of interest and relevance to be investigated in order to provide further information in this field, as an alternative application to contribute to the solution of current problems relating to water pollution.

SYNTHESIS OF Fe_3O_4

The Fe_3O_4 particles were synthesized taking as reference the chemical precipitation technique proposed by Li and collaborators (Li et al., 2015). 40 mL of $FeCl_2·4H_2O$ [0.5 M] was placed in a solution containing 3.8 g of polyethylene glycol (PEG) previously dissolved in 25 mL of water, the mixture was homogenized, later 8 mL of H_2O_2 was added, see Fig. 1(a). The precipitation process was carried out by adding NaOH [1M] to a pH value of 12, the solution was introduced into an orbital agitator with heating at a temperature of 50 °C for 3 h, producing a turn color from yellow to grayish blue (Fig. 1b).

At the end of the reaction, the particles showed a brown coloration (Fig. 1c), characteristic of the formation of Fe_3O_4, later recovered with the aid of a magnet and washed three times with deionized water. Finally, the particles obtained were thermally oxidized in an oven at 80 °C for 200 minutes, to obtain powdered particles.

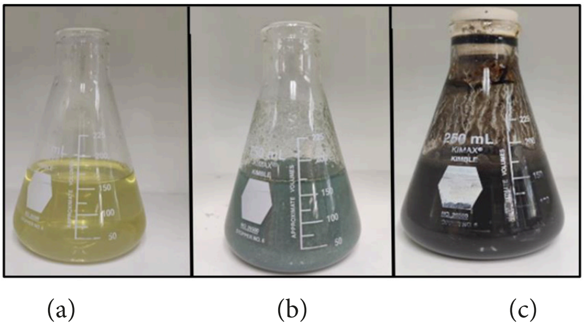

(a) (b) (c)

Figure 1. Experimental synthesis of Fe_3O_4: (a) Erlenmeyer flask with the homogeneous mixture of precursors, (b) Erlenmeyer flask with the mixture of precursors at pH 12, (c) Erlenmeyer flask with the Fe_3O_4 particles obtained.

FORMATION OF THE Fe_3O_4/TiO_2 COMPLEX

The TiO_2 layer that coated the Fe_3O_4, was synthesized taking as reference the technique proposed by Li and collaborators (Li et al., 2015), for this purpose a mixture of the suspension of particles of Fe_3O_4 with the precursor solution of titanium was prepared. The suspension consisted of 0.3 g of Fe_3O_4 in 40 mL of water, which was then sonicated in a BRASON 2800 ultrasound for 3 hours to obtain a uniform particle size (solution I, Fig. 2a).

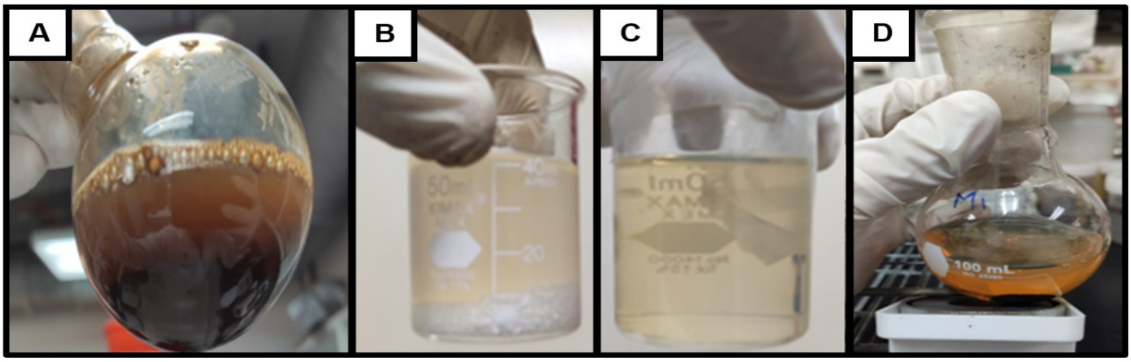
The titanium precursor solution consisted of 10 mL ethanol and 20 mL nitric acid [1M], to which 8.5 mL of titanium n-butoxide (TBOT) were subsequently added drop by drop (solution II, Fig. 2b). This solution was mixed with a magnetic stirrer in heating plate at 60 °C and 200 rpm for 1 hour, the magnetic bar was removed and left to stand for 24 hours in dark conditions to favor the complete dissolution of the TBOT and obtain a homogeneous solution, see Fig. 2(c).

The solution II was slowly added to the Fe_3O_4 particulate suspension until a pH 2 value (2.5-3.0 mL) was obtained, the mixture was placed in an orbital stirrer with heating at 50 °C for 3 hours. After the reaction time the particles were magnetically recovered, and washed with deionized water, Fig. 2(d).

FORMATION OF THE PHOTOCATALYTIC COMPLEX Fe_3O_4/TiO_2 – βCD

For the addition of the βCD layer, the procedure developed by Chalasani and Vasudevan was performed (Chalasani and Vasudevan, 2013). For this purpose, the precursor carboxymethyl βCD (CMCD) was initially prepared by mixing two solutions. The first solution contained 3 g βCD in 3 mL of water. The second solution was formed with 2.79 g NaOH in 10 mL of deionised water. The solutions were mixed, 8.1 mL of monochloroacetic acid was added. The resulting mixture was placed in an orbital agitator heated to 50 °C for 4 hours.

After the reaction time the pH of the mixture was adjusted to 4 by adding concentrated HCl, the CMCD was obtained by precipitation by adding 100 mL methanol and 100 mL acetone, the mixture was homogenized and left at rest for 20 minutes, after precipitating, the liquid phase was extracted and the CMCD was dried at 50 °C for 1.5 h.



(a) (b) (c) (d)

Figure 2. Experimental synthesis of the Fe_3O_4/TiO_2 complex: (a) Balloon flask with 40 mL of solution I, (b) Beaker with sample of fresh solution II, (c) Beaker with sample of solution II after 24 hours of rest, (d) Magnetic separation process.

To obtain the photocatalytic complex Fe_3O_4/TiO_2-βCD, immediately synthesized the Fe_3O_4/TiO_2 particles were resuspended in 20 mL of deionized water (Fig. 3a), pH was adjusted to 6 with a phosphate buffer solution. 100 mg of CMCD were added and the resulting solution was placed in an orbital stirrer with heating at 50 °C for 4 hours (Fig. 3b). After the reaction time, the particles recovered magnetically (Fig. 3c) and washed with deionized water until βCD was detected in the supernatant liquid by 1% phenolphthalein, finally the particles obtained were dried at 90 °C (Fig. 3d).

CHARACTERIZATION OF THE MICROMATERIALS

ZETA SIZER

For Fe_3O_4 a hydrodynamic size of 986,433 ± 88.929 nm was obtained (brown line in Fig.4), when the TiO_2 layer was placed the size increased to 1,408.33 ± 321.547 nm (purple line in Fig. 4), finally after adding the β-layer CD, formation of the photocatalytic complex, a hydrodynamic size of 1,914 ± 91.148 nm (green line in Fig. 4) was obtained.

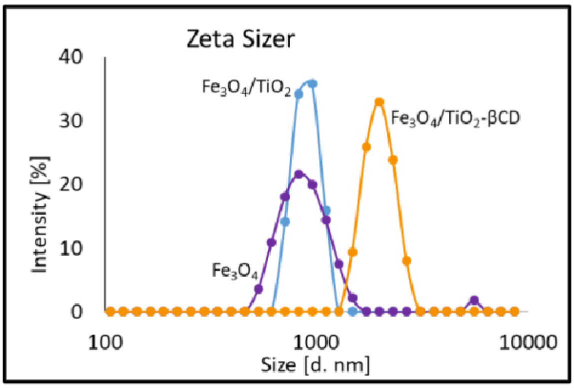


Figure 4. Hydrodynamic size of Fe_3O_4, Fe_3O_4/TiO_2 and Fe_3O_4/TiO_2-βCD.

With increases in hydrodynamic size, the formation of the photocatalytic complex is checked.

ZETA POTENTIAL

The surface load for Fe_3O_4 was -12.13 ± 0.32 mV, later this value varied when the material was covered with TiO_2 to 16.87 ±0.90 mV, which is indicative of the existence of the TiO_2 layer, this value represents greater stability. Finally, the surface load of the photocatalytic complex formed Fe_3O_4/TiO_2-βCD registered a value of -19.95 ± 0.92 mV, which indicates

(a) (b) (c) (d)

Figure 3. Formation of the Fe_3O_4/TiO_2-βCD complex: (a) Balloon flask containing fresh Fe_3O_4/TiO_2 particles, (b) Magnetic separation process, (c) Balloon flask with Fe_3O_4/TiO_2 particles **βCD, (d**) Vial with washed particles and vial with phenolphthalein used for colorimetric response.

that with the βCD layer the photocatalytic complex is much more stable (Joseph and Singhvi, 2019). In Fig. 5, the graphs of the surface loads obtained by zeta potential are presented.

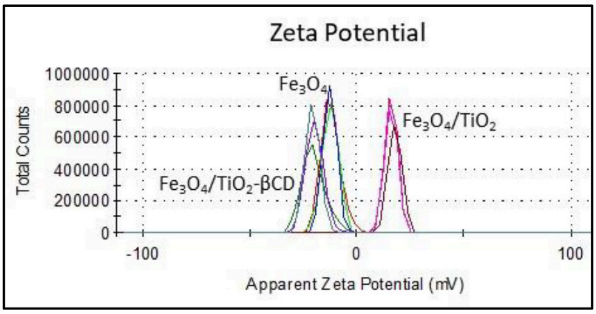


Figure 5. Fe_3O_4, Fe_3O_4/TiO_2 and Fe_3O_4/TiO_2-βCD surface loads.

With the results obtained, the formation of the layers to form the photocatalytic complex Fe_3O_4/TiO_2-βCD is again confirmed.

UV-Vis SPECTROPHOTOMETRY

UV-Vis spectrophotometry was used to obtain the reflectance spectra (Figure 6) of the material in each of the stages of obtaining the photocatalytic complex, which allowed to establish the wavelength values where the characteristic reflectance maxima were found. After analyzing these results, it was found that from Fe_3O_4 particles, a TiO_2 layer was formed and finally the βCD layer, to obtain the photocatalytic complex Fe_3O_4/TiO_2-βCD.

For the reflectance spectrum of Fe_3O_4 (brown line in Fig. 6) a characteristic peak at 900 nm can be identified with a reflectance percentage of 48.2108 ± 0.258% value that is within the range reported in the literature (750-900 nm) (Cobos Cruz et al., 2008; Anamika,).

For pure TiO_2 (orange line in Fig. 6), the results showed characteristic absorption bands at 204 and 233 nm with reflectance percentages of 47.917 ± 0.368% and 51.656 ± 0.351% respectively, values found in the ultraviolet spectrum, which is where TiO_2 presents the greatest absorption of light (Al-Mamun et al., 2019). Praveen and collaborators reported that at 235 nm TiO_2 has a characteristic peak in the reflectance spectrum (Praveen et al., 2014). In addition, the analyzed TiO_2 showed the typical reflectance edge in the range of 340-400 nm (Kralchevska et al., 2012; Linh, Tuan y Dzung, 2014; Nyamukamba et al., 2017).

For the Fe_3O_4/TiO_2 complex, the spectrum (purple line in Fig. 6) showed characteristic absorption bands at 239 and 200 nm with reflectances of 45.467 ± 0.814% and 37.754 ± 0.816% respectively. We can see the difference in the Fe_3O_4 spectrum compared to the Fe_3O_4/TiO_2 complex, since the absorption bands are related to the presence of TiO_2 on the surface of Fe_3O_4, which confirms the formation of the TiO_2 layer. The decrease in reflectance between Fe_3O_4 and Fe_3O_4/TiO_2, according to Cornell and Schwertmann, is attributed to a decrease in particle size (Cornell and Schwertmann, 2003).

Finally, the Fe_3O_4/TiO_2-βCD complex presented a peak at 244 nm with a reflectance of 60.025 ± 0.648% (green line in Fig. 6) suggesting a slight shift of the typical TiO_2 peak. In addition, at 207 nm (with a reflectance of 55.687 ± 0.516%) there is a change of slope, which is attributable to the presence of βCD in the structure of the material, this based on the spectrum of the CMCD obtained previously (light pink line in Fig. 6). This confirms the formation of the βCD layer on the Fe_3O_4/TiO_2 complex.

PREPARATION AND ASSEMBLY OF EXPERIMENTS

The experiments were carried out in triplicate in Bach reactors, which contained 36 mL of the dye solution at [120 mg/L] at pH 2, the addition of the oxidizing agent (H_2O_2) and the photocatalyst complex.

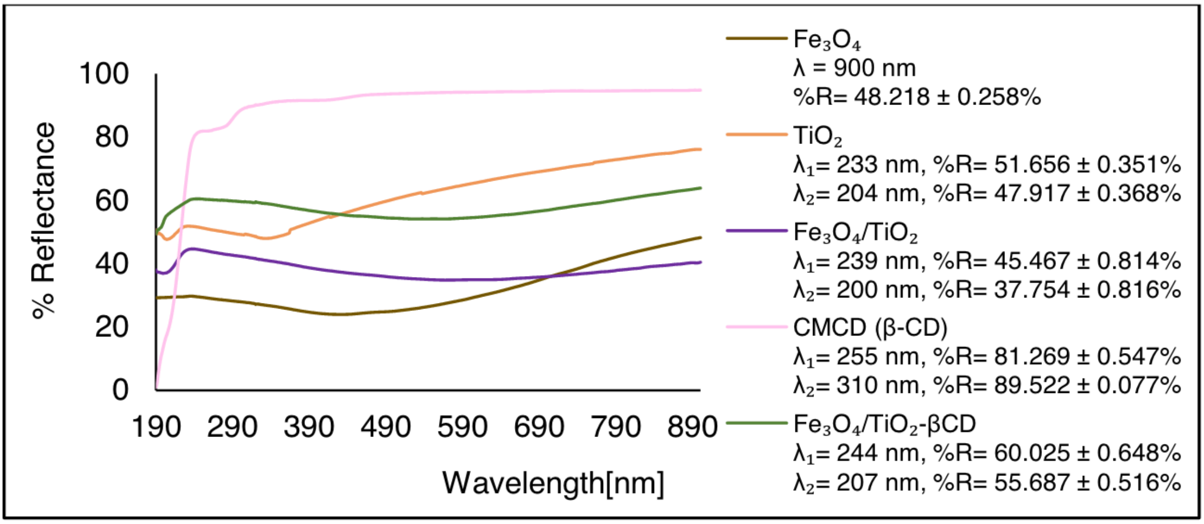


Figure 6. Fe_3O_4, Fe_3O_4/TiO_2 and Fe_3O_4/TiO_2 reflectance spectra.

Once the reactors are prepared to the conditions required in each assessment, these were stabilized for 30 minutes in an orbital agitator under dark conditions and then placed on a clear surface and exposed directly to sunlight for 180 minutes. The experiments were carried out between 11:00 and 15:00 hours during the spring-summer period (S-S) in the UAM-Azc installations in Mexico City.

The reduction of the maximum absorbance in the color of the effluent was followed by UV-Vis, 1 mL of the effluent under treatment was taken every 30 minutes and placed in an Eppendorf tube of 1.5 mL, subsequently placed in a magnetic separator for 1 minute to concentrate the photocatalysts complex, 300 µL of the supernatant of each sample was placed on a ELISA plate for endpoint measurements at 484 nm wavelength. The EPOCH2 equipment was used to determine the absorbance.

INFLUENCE OF CATALYST CONCENTRATION ON THE PHOTODEGRADATION OF ORANGE DYE II WHEN USING FE_3O_4 AND FE_3O_4/TIO_2 AND FE_3O_4/TIO_2-βCD COMPLEXES

The influence of the concentration of the photocatalysts used on the degradation of orange dye II was investigated. Fig. 7 shows the results obtained when evaluating concentrations of 50 and 100 mg/L of Fe_3O_4 and Fe_3O_4/TiO_2 and Fe_3O_4/TiO_2-βCD complexes at pH 2 in the presence of the oxidizing agent (H_2O_2).

It was found that there is no significant variation between the degradation percentages obtained when 50 or 100 mg/L photocatalyst is used, because the maximum degradation values occurred in the same time interval. For the Fe_3O_4/TiO_2-βCD complex, maximum degradation occurred within 90 minutes. The results are summarized in Table 1.

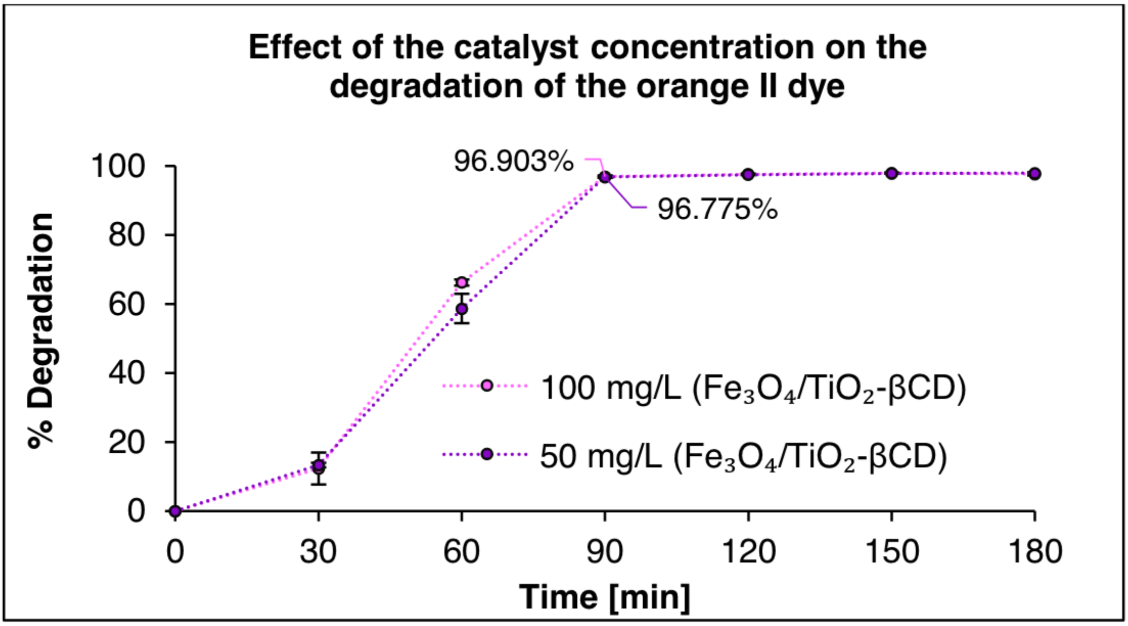


Figure 7. Effect of catalyst concentration on the degradation of orange dye II, (Assessment at pH 2 in the presence of H_2O_2).

	% Degradation				
	Concentration [mg/L]	30 minutes	60 minutes	90 minutes	120 minutes
Fe_3O_4/TiO_2-βCD	**50**	13.327 ± 0.652	**58.699 ± 4.243**	**96.775 ± 0.164**	97.476 ± 0.090
	100	12.355 ± 4.615	**66.262 ± 0.885**	**96.903 ± 0.337**	97.608 ± 0.161

Table 1. Percentage of degradation at 30, 60, 90 and 120 minutes

From the results obtained, a slight effect can be seen which had the increase in the concentration of the photocatalysts. Experiments with 100 mg/L of Fe_3O_4/TiO_2-βCD showed greater degradation at 60 minutes (see Figure 7) of exposure than experiments with 50 mg/L, at 90 minutes the degradation was very similar for both concentrations, at 120 minutes the increase was minimal.

This behavior can be explained by the fact that the higher mass of photocatalysts leads to a greater availability of active sites, so the number of dye molecules adsorbed on the surface of these photocatalysts also increases (Pitchaimuthu et al., 2014). However, in both cases the maximum percentage of degradation at 50 and 100 mg/L occurred at the same time, 90 minutes.

From the above results, it is concluded that 50 mg/L is the concentration that allows the greatest degradation of the orange dye II by using the Fe_3O_4/TiO_2-βCD complex in 90 minutes with natural solar radiation.

CONCLUSION

This work has shown that from a paramagnetic base (Fe_3O_4) layers of TiO_2 and βCD have been formed, thus forming the Fe_3O_4/TiO_2-βCD complex. It was evaluated as a photocatalyst agent for the degradation of the orange textile dye II. Where, the results show that, with sunlight naturally, it is sufficient to be able to degrade a textile dye with an efficiency of approximately 96 % in 90 min. Reducing the use of lamps that after their useful life are converted into a waste, as well as electricity consumption, where pollutants from electricity generation are indirectly reduced, such as greenhouse gases. So the complex that has been developed and tested, is a novel photocatalytic process with minimal waste generation taking advantage of natural sunlight.

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