

Photodegradation of Herbicide Dicamba with TiO₂ Immobilized on HZSM-11 Zeolite

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ABSTRACT: Photodegradation of dicamba, an ionizable herbicide, using TiO₂ supported on HZSM-11 zeolite was investigated. Four photocatalysts with different weight percentages (wt%) of TiO₂ were evaluated: 3%, 10%, 30% and 50%. The effects of the catalyst concentration, the initial pH value and the repeatability of the photocatalytic activity after multiple cycles of reuse were also evaluated. Results showed complete degradation of dicamba within 120 min with the TiO₂/HZSM-11 (30 wt%) catalyst. Also, this catalyst is stable (no detectable leaching was observed), can be easily removed from treated solutions and it is reusable for at least nine consecutive cycles. An XRD analysis indicated that the TiO₂/HZSM-11(30%) catalyst remained unchanged until the ninth cycle, when it was compared with a new catalyst. The results indicated that the addition of H₂O₂ to the solution did not affect the catalyst structure. These are important advantages over unsupported TiO₂, making it a good photocatalyst for the treatment of water courses polluted with dicamba.

Key words: Dicamba, Zeolite, Supported catalyst, Photodegradation, Remediation

INTRODUCTION

Herbicides are the most commonly applied pesticides in agroecosystems. Among them, the herbicide dicamba (3,6-dichloro-2-methoxybenzoic acid) is being applied more extensively by farmers because of weeds resistant to other herbicides, including glyphosate (Gleason *et al.*, 2011). Also, the recent development of crops with resistance to dicamba indicates that this herbicide will be widely used in agricultural practices (Bohnenblust *et al.*, 2013) and, therefore, might contaminate water courses. Dicamba might be toxic to fishes (Ruiz de Arcautea *et al.*, 2014; Zhu *et al.*, 2014) and humans (Moon and Chun, 2014).

A photocatalytic degradation process is one of the most effective methods for removing aquatic contaminants (Saratale *et al.*, 2014). TiO₂ is the most widely used photocatalyst, but it remains in suspension after the reaction has been completed, requiring costly special filtration equipment to remove it. In addition, if TiO₂ is released into natural water courses, it might be toxic to aquatic organisms (Li *et al.*, 2014), and cause serious damage to human cells (Shukla *et al.*, 2013; Makumire *et al.*, 2014). An alternative is the use of TiO₂ immobilized on a porous material such as zeolite. This

support facilitates the removal of TiO₂ from treated solutions. Moreover, these materials have channels, pores and cavities of regular size, and the capacity to adsorb polar molecules (Grieco and Ramarao, 2013), increasing the concentration of these molecules around supported TiO₂. It is important to note that HZSM-11 zeolite has a good stability, so much mechanical, chemical and thermal, which allows to preserve the structure of the zeolite both when generating the catalyst as after measurements of catalytic activity. In a previous report (Gómez *et al.*, 2013) this catalyst proved effective to degrade the insecticide Dichlorvos, a non-ionizable compound, under UV-irradiation.

It is known that materials supported on silica or alumina have lower surface areas and smaller particle size than zeolites. Whereby, they are more difficult to recover from the reaction medium and they have a lower adsorption of the compounds which could provide a lower catalytic activity than zeolites (Chen *et al.*, 2004).

In this study, the photocatalytic activity of TiO₂ supported on HZSM-11 zeolite was evaluated with respect to the degradation of dicamba, an ionizable

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herbicide, under conditions similar to solar radiation. The effects of the wt% of TiO₂ supported on HZSM-11, catalyst concentration, initial pH value and the repeatability of the photocatalytic activity after multiple cycles of reuse were investigated. The main goal of this research is to develop an adequate and efficient method for the degradation of dicamba in aqueous media, thereby expanding the number of target contaminants that can be degraded by this catalyst.

MATERIALS & METHODS

HZSM-11 zeolite was prepared using the following reactants: sodium aluminate (NaAlO₂, Johnson Matthey Electronics), tetrabutylammonium hydroxide (TBAOH, Fluka), silicic anhydride (Fluka) and distilled water. Titanium (IV) isopropoxide was purchased from Aldrich and used as received. Ethanol (Cicarelli) was used. P-25 and dicamba were kindly supplied by Degussa and Atanor, Rio Tercero, Córdoba, Argentina, respectively.

Four catalysts with theoretical TiO₂ concentrations of 3, 10, 30 and 50 wt% on HZSM-11 zeolite, were synthesized and characterized in a previous work (Gómez *et al.*, 2013). The samples were characterized by X-Rays Diffraction (XRD), Fourier Transform Infrared Spectrometry (FTIR), Brunauer, Emmett, and Teller (BET), Scanning Electron Microscopy (SEM), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), and Diffuse Reflectance Spectroscopy (DRS) methods. The catalysts were labeled TiO₂/HZSM-11(3%), TiO₂/HZSM-11(10%), TiO₂/HZSM-11(30%) and TiO₂/HZSM-11(50%), respectively. Commercial TiO₂ (P25 Degussa) was also used for comparison purposes.

All experiments were performed in triplicate in a water-jacketed borosilicate glass reactor (Fig. 1)

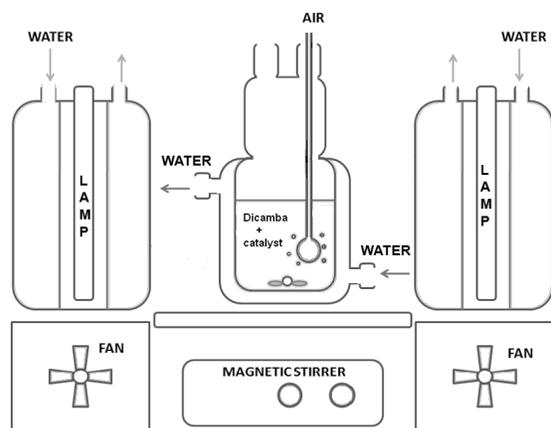


Fig. 1. Experimental photocatalytic reactor

irradiated with two water/air cooled Philips Master HPI-T Plus 400-W lamps, with an emission interval of 350-650 nm, according to the manufacturer's specifications. The emission spectrum of these lamps is very similar to the emission spectrum of sunlight at sea level.

Photocatalytic activity measurements were conducted on the catalysts at different concentrations: 0.5, 1 and 2 mg mL⁻¹. For this purpose, an aqueous solution of dicamba (1 x 10⁻⁴ M), containing the photocatalyst in suspension, was allowed to equilibrate in the dark for 30 minutes with mechanical stirring and without air bubbling. Subsequently, this mixture was irradiated for 4 h under air bubbling. Aliquots were withdrawn at specific time intervals and analyzed after filtration with a Millipore membrane (0.45 μm) to remove catalyst particles. The starting aliquot corresponds to the time at which the lamps were turned on.

The aliquots were then analyzed using Waters 1525 HPLC equipment with an Agilent Zorbax Eclipse XDB-C18 5 μm column and a UV-visible photodiode array detector operating at 190-600 nm. A mixture of methyl alcohol (66% v/v) and water (33% v/v) was used as mobile phase at a flow rate of 0.75 mL min⁻¹. Twenty-five μL of each aliquot were injected and analyzed at a wavelength of 207 nm. Direct photolysis was also studied by irradiating a dicamba solution for 4 h in the absence of the photocatalyst.

In addition, an adsorption experiment of dicamba was carried out at room temperature (25 °C). For this purpose, an aqueous solution 1 x 10⁻⁴ M of this herbicide, containing the photocatalyst in suspension, was kept in the dark for 24 h with mechanical stirring and air bubbling. Aliquots were withdrawn at specific time intervals and analyzed as described above.

The conservation of the photocatalyst activity was determined by the percentage of degradation of dicamba after irradiation, and was calculated as follows for every cycle:

$$\text{Degradation percentage} = (1 - C / C_0) \times 100$$

where C is the dicamba concentration in the solution after 2 h of irradiation, and C₀ is the initial concentration (1 x 10⁻⁴ M).

RESULTS & DISCUSSION

The crystalline structure of the zeolitic supports and the supported catalysts was studied using SEM (Fig. 2). According to the SEM images the zeolite matrix presents prismatic-like crystals. The surface morphology of the TiO₂/HZSM-11(30%) catalyst shows the prismatic crystals characteristic of HZSM-11 zeolite and TiO₂ spherical nanoparticles (size in the range 200-400 nm) and clusters attached to the zeolite surface.

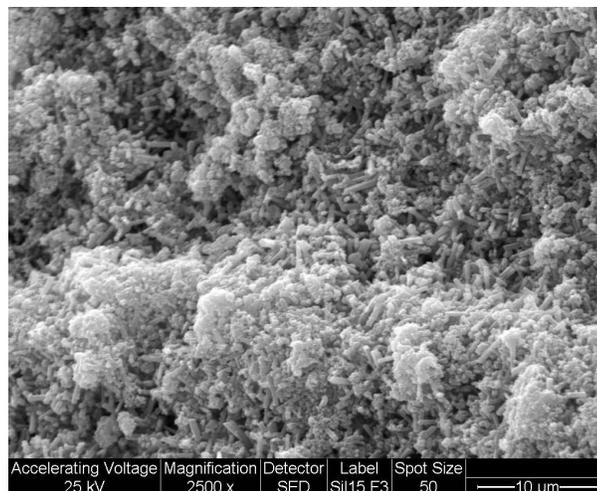


Fig. 2. SEM image of $\text{TiO}_2/\text{HZSM-11}$ (30%) sample. Note that the zeolite matrix presents prismatic-like crystals with TiO_2 particles attached to the zeolitic surface.

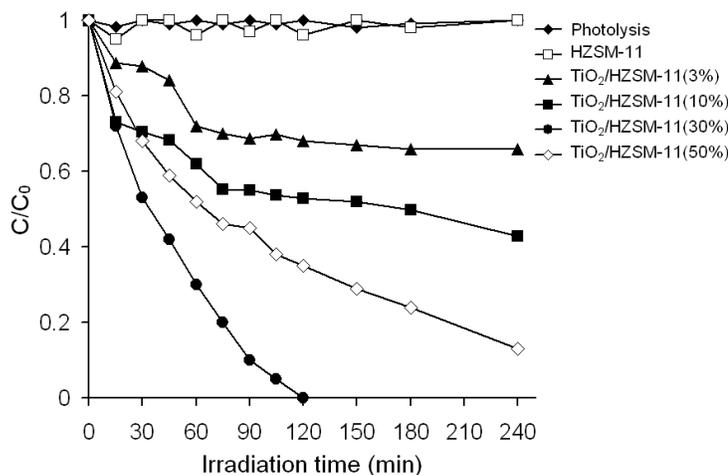


Fig. 3. Photolysis and photocatalytic decomposition of dicamba on HZSM-11 zeolite, $\text{TiO}_2/\text{HZSM-11}$ (3%), $\text{TiO}_2/\text{HZSM-11}$ (10%), $\text{TiO}_2/\text{HZSM-11}$ (30%) and $\text{TiO}_2/\text{HZSM-11}$ (50%) catalysts

The average crystallite size of TiO_2 particles on the zeolite matrix was estimated using XRD data and the Scherrer equation. The crystal sizes were 12.04 nm, 18.86 nm and 22.98 nm for $\text{TiO}_2/\text{HZSM-11}$ (10%), $\text{TiO}_2/\text{HZSM-11}$ (30%) and $\text{TiO}_2/\text{HZSM-11}$ (50%) catalysts, respectively. Note that the particle size rising with the increasing load of TiO_2 , probably due to the aggregation of the TiO_2 particles on the surface of the HZSM-11 zeolite. The surface area of the synthesized catalysts was determined by using the Brunauer-Emmett-Teller method. The adsorption-desorption isotherms of $\text{TiO}_2/\text{HZSM-11}$ samples exhibit characteristics similar to those of HZSM-11. According to IUPAC classification, they are Type I isotherms, characteristic of microporous solids having relatively small external surfaces (Sing *et al.*, 1985). Also, the surface area of $\text{TiO}_2/\text{HZSM-11}$ (3%) has similar characteristics to $\text{TiO}_2/\text{HZSM-11}$ (10%).

With an increase in TiO_2 loading, a linear decrease in the surface area of the samples can be observed, as compared with the zeolite: 382, 370, 365, 309 and 255 m^2/g for HZSM-11 zeolite and $\text{TiO}_2/\text{HZSM-11}$ (3%), $\text{TiO}_2/\text{HZSM-11}$ (10%), $\text{TiO}_2/\text{HZSM-11}$ (30%) and $\text{TiO}_2/\text{HZSM-11}$ (50%) samples, respectively. It could be possibly due to the deposit of TiO_2 particles on the HZSM-11 surface, thus, blocking the pores. Ti, Si and Al content of $\text{TiO}_2/\text{HZSM-11}$ catalysts were determined by ICP-OES. The Ti amount increased when TiO_2 loading increased, varying from 1.243 ($\text{TiO}_2/\text{HZSM-11}$ (3%)) to 27.200 ($\text{TiO}_2/\text{HZSM-11}$ (50%)) wt %, which is in good agreement with theoretical values. Si and Al content decreases proportionally with the increasing amount of Ti content.

Fig. 3 shows the photocatalytic decomposition of dicamba on $\text{TiO}_2/\text{HZSM-11}$ catalysts (1 mg mL^{-1} in all

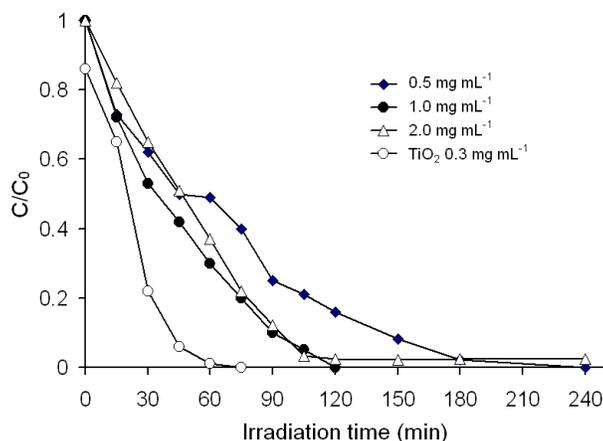


Fig. 4. Effect of the amount of $\text{TiO}_2/\text{HZSM-11(30\%)}$ and TiO_2 catalysts on the photocatalytic decomposition of dicamba

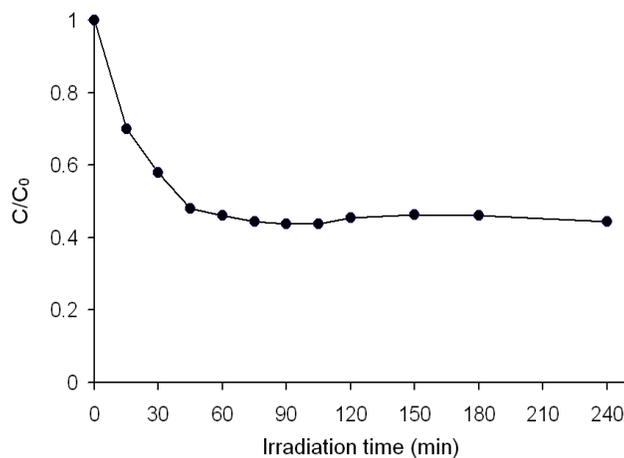


Fig. 5. Leaching study: Photocatalytic decomposition of dicamba on $\text{TiO}_2/\text{HZSM-11(30\%)}$

reactions). It did not photolyse and did not decompose with HZSM-11 zeolite; showing that the zeolite is a very adequate support. Dicamba is not adsorbed by this zeolite (pore size 5.3 \AA , Dey *et al.*, 2012) because this herbicide has a higher molecular diameter (7.19 \AA), which does not facilitate their entry into the zeolitic matrix.

The degradation rate of dicamba increased with TiO_2 loading, except for the $\text{TiO}_2/\text{HZSM-11(50\%)}$ catalyst. The degradation rate was enhanced due to the increase of the catalytic surface with catalyst loading, but as the continuous agglomeration of these particles on the zeolitic matrix became significant, photocatalytic activity decreased because of its lower catalytic surface. $\text{TiO}_2/\text{HZSM-11(30\%)}$ was the most efficient catalyst, as dicamba was completely degraded after 2 h of irradiation. It was therefore chosen for the following experiments.

A series of experiments were carried out to find the optimum amount of catalyst by varying the

concentration of $\text{TiO}_2/\text{HZSM-11(30\%)}$ from 0.5 mg mL^{-1} to 2 mg mL^{-1} (Fig. 4). Photodegradation of dicamba increases with the amount of $\text{TiO}_2/\text{HZSM-11(30\%)}$ up to 1 mg mL^{-1} , but above this concentration the degradation rate does not increase further. This is because as the concentration of the photocatalyst increases, the number of active sites increases as well, resulting in an improvement of the photocatalysis rate. However, when 2 mg mL^{-1} were added, this rate remained unchanged, probably due to the scattering of a fraction of incident radiation as a result of the higher amount of particles present in the solution, an effect previously observed by other authors (Ahmed *et al.*, 2011; Alkaim *et al.*, 2013). Starting from a certain concentration of $\text{TiO}_2/\text{HZSM-11(30\%)}$, the dicamba solution becomes opaque due to the suspended particles, preventing irradiation of active sites. The optimum amount of TiO_2 catalyst can take values from 0.07 g L^{-1} to 12 g L^{-1} (Ahmed *et al.*, 2011), depending on light intensity, wavelength, oxidizing agents, kind of contaminant, among other factors. In our work, the

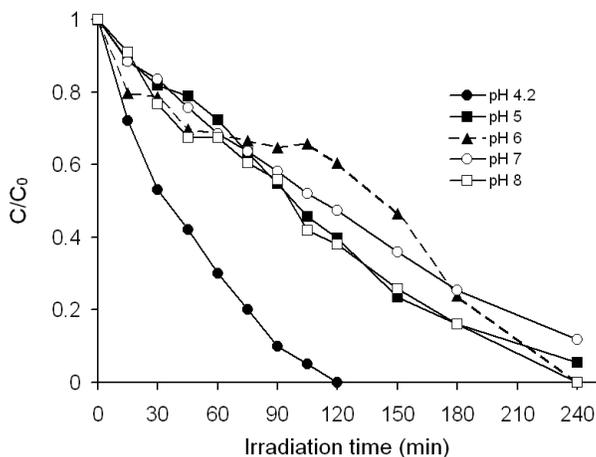


Fig. 6. Effect of initial pH on the degradation rate of dicamba. At pH values higher than 4.2 the photocatalytic activity of TiO₂/HZSM-11(30%) catalyst decreased

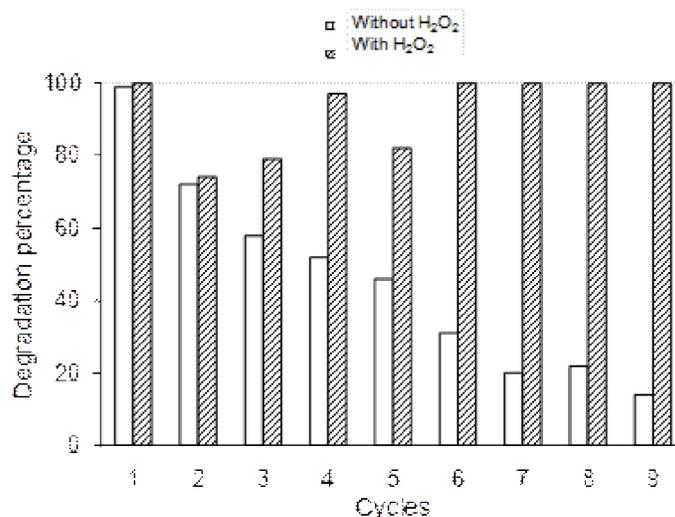


Fig. 7. Activity study: Photocatalysis of dicamba in different cycles, with and without addition of H₂O₂. [Dicamba] = 1 x 10⁻⁴ M; TiO₂/HZSM-11(30%) = 1 mg mL⁻¹. [H₂O₂] = 1 x 10⁻² M (inside the reactor)

optimum amount of TiO₂/HZSM-11(30%) catalyst was 1 mg mL⁻¹, which corresponds to 0.3 g L⁻¹ of TiO₂.

Photocatalysis was faster when unsupported TiO₂ was used at a concentration of 0.3 mg mL⁻¹. This difference between TiO₂ and TiO₂/HZSM-11 may be due the scattering of incident radiation induced by HZSM-11 zeolite. This does not occur in solutions with unsupported TiO₂. However, although unsupported TiO₂ is a better photocatalyst in these reactions, it cannot be recovered easily. Expensive and laborious methods are required to separate the catalyst from the solution (Honda, 2014); thus, it is not easy to use unsupported TiO₂ to decontaminate large volumes of water such as lakes or rivers. In contrast, the TiO₂/HZSM-11(30%) catalyst can be easily recovered from the reaction medium by filtration. On the other hand,

the spontaneous agglomeration of unsupported TiO₂ particles, when dispersed in aqueous media, may cause a rapid decrease in specific surface area, decreasing the photocatalytic activity (Li *et al.*, 2010).

No dicamba degradation byproducts were observed in any of the reactions studied. When this herbicide is photodegraded on TiO₂, chlorinated intermediates mineralize immediately as they are formed, and therefore do not accumulate in the reaction medium (Fabbri *et al.*, 2007). A rigorous proof of catalyst stability can be obtained by filtering the catalyst at the reaction temperature before completion of the reaction, and then testing the filtrate for catalytic activity (Pirkanniemi and Sillanpaa, 2002). In order to check the stability of the TiO₂/HZSM-11(30%) catalyst, a solution of dicamba 1 x 10⁻⁴ M containing 1 mg mL⁻¹ of

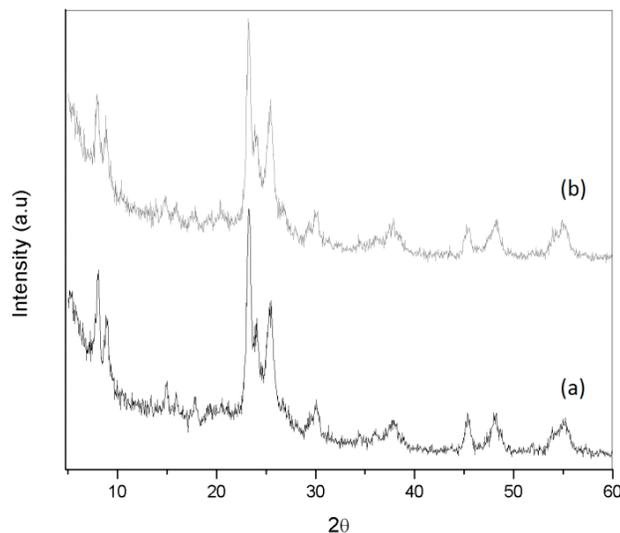


Fig. 8: XRD analysis of TiO₂/HZM-11 (30%) new catalyst (a) and used catalyst before nine cycles (b).

the photocatalyst was irradiated for 1 h (Fig. 5). Subsequently, TiO₂/HZSM-11(30%) was removed from the solution by filtration, and the remaining solution was irradiated for 3 h more. After the first hour, the dicamba concentration decreased to 46% of its original value, remaining constant for 3 h thereafter. These results would indicate that TiO₂ does not become detached from the zeolite matrix. There would be then no detectable leaching of the catalyst in the reaction media. The TiO₂/H-ZSM- 11 (30%) catalyst is thus a very stable structure, remaining unchanged throughout the reaction.

The effect of pH on photocatalytic degradation was studied by varying the initial pH of the dicamba solution (equal to 4.2) and keeping all other experimental conditions constant. Different reactions were carried out with initial pH in the range of 5–8, adjusted with sodium hydroxide (Fig. 6). The dicamba degradation rate was higher at pH 4.2 than at other pH values. The pH of a solution is an important variable for photocatalytic reactions in aqueous phase; it influences the adsorption and dissociation of the substrate, the catalyst surface charge, the oxidation potential of the valence band and other physicochemical properties of the system (Alkaim *et al.*, 2013). In addition, the concentration of OH⁻ anions (they generate OH• radicals when reacting with positive holes) near TiO₂ particles depends on this factor.

The point of zero charge of the TiO₂/HZSM-11(30%) catalyst, determined by the pH drift method (Bessekhouad *et al.*, 2004) was 4.8, corresponding to anatase phase of TiO₂ (Carbajo *et al.*, 2014). At a pH value of 4.2, the TiO₂ surface was positively charged and there was electrostatic attraction between the

catalyst surface and the anion of dicamba (pKa equal to 1.90, therefore carboxylate anion: protonated acid ratio is 200:1 at this pH), enhancing the photodegradation rate. At pH values higher than 4.8, the concentration of OH• radicals on the catalyst surface increases with the concentration of OH⁻ anions, but this fact decreases the degradation rate of dicamba because the TiO₂ surface becomes negatively charged and repels dicamba anions.

The reuse potential of a photocatalyst is one of the most important parameters for determining, from an economic point of view, the exploitation potential of a material in practical systems for water treatment (Hamdi *et al.*, 2013). The photodegradation of dicamba with the TiO₂/HZSM-11(30%) catalyst was carried out in several cycles in order to evaluate the conservation of the catalytic activity. A solution of dicamba with TiO₂/HZSM-11 (30%) was irradiated for 2.5 h; the catalyst was then recovered by filtration and reused immediately, without any treatment, using a new solution of dicamba.

The photocatalytic activity of TiO₂/HZSM-11(30%) decreased continuously until the ninth cycle (Fig. 7; white bars), which may be due to the continuous agglomeration of chloride anions on the TiO₂ surface. This fact influences on the degradation rate in two ways: it reduces the positive charge of TiO₂ (Sontakke *et al.*, 2011) and therefore, the coulombic attraction between dicamba anions and the catalyst decreases, and eliminates OH• radicals.

Chloride anions on the TiO₂ surface may scavenge OH• radicals (Yang *et al.*, 2014; Grebel *et al.*, 2010) and positive holes (h⁺, Wu *et al.*, 2009), generating halogen radicals like ClOH[•], Cl[•] and Cl₂^{•-}. The reactivity of these radicals is lower compared to

h^+ and OH^\bullet (Yang *et al.*, 2014; Saha *et al.*, 2012); thus, the observed retardation of the degradation rate of dicamba was still thought to be due only to the strong adsorption of chloride anions on the TiO_2 surface. As indicated before (Fabbri *et al.*, 2007), dicamba degradation intermediates are degraded while they are produced. Thus, they are not involved in the decreasing rate of degradation of dicamba. Also, at the end of first cycle the chloride anion concentration inside the reactor is about 2×10^{-4} M. At this chloride amount, the photocatalytic activity of TiO_2 decreases (Sontakke *et al.*, 2011). This decrease becomes more important with the increase of chloride anions in subsequent cycles.

A new series of cycles was carried out to recover catalyst activity. In this case, H_2O_2 was added to the reactor at the end of each cycle, keeping it under stirring for 30 min without irradiation (to prevent generation of OH^\bullet radicals by UV light). The catalyst was then recovered by filtration and allowed to dry at 75 °C for 24 h, before the following cycle. This procedure was repeated until the ninth cycle was completed (samples corresponding to every cycle were taken prior to the addition of H_2O_2). The catalyst activity was successfully recovered, as can be seen in Fig. 7 (gray bars). The degradation percentage of dicamba was above 70% in all cycles. Based on the reduction potentials, it is possible that chloride anions on the TiO_2 surface were oxidized to chlorine by H_2O_2 , thereby activating the catalyst surface. The addition of H_2O_2 was effective for the recovery of catalyst activity.

An XRD analysis indicated that the TiO_2 /HZSM-11(30%) catalyst remained unchanged until the ninth cycle, when it was compared with a new catalyst (Fig. 8). This analysis indicated that the addition of H_2O_2 to the solution did not affect the catalyst structure; therefore, this catalyst can be used in more than nine cycles.

CONCLUSIONS

We evaluated the photocatalytic degradation of dicamba with four TiO_2 /HZSM-11 catalysts. TiO_2 loading is one of the most important factors to be considered, because the optimal photocatalytic surface depends on it.

TiO_2 /HZSM-11(30%) was the most effective catalyst for completely degrading this herbicide in a short time. In these conditions, this catalyst is very stable, can be easily removed from the solution and it is reusable, even in the presence of inhibitory amounts of chloride anions. These are very important advantages of TiO_2 /HZSM-11(30%) over unsupported TiO_2 , making it a good photocatalyst for the treatment of polluted waterways. Furthermore, this catalyst could be effective under solar irradiation, saving electrical energy.

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