Cypermethrin elimination using Fe-TiO₂ nanoparticles supported on coconut palm spathe in a solar flat plate photoreactor

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Abstract
In this research, the photocatalytic degradation of cypermethrin using iron-titanium dioxide (Fe-TiO₂) nanoparticles supported in a biomaterial was evaluated. The nanoparticles of TiO₂ were synthesized by the green chemistry method assisted by ultrasound and doped by chemical impregnation using Fe³⁺:Ti molar ratios of 0, 0.05, 0.075 and 0.1 to make efficient use of direct sunlight (λ > 310 nm). All nanoparticles were immobilized on the surface of coconut spathe (Cocos nucifera). The degradation was carried out at room temperature and natural pH in a flat plate solar reactor, on which the composite material was subjected. The concentration of cypermethrin was determined after 12,000 J m⁻²/C₀ of accumulated radiation from gas chromatography–mass spectrometry and the resulting material was characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Fourier-transform infrared spectroscopy, ultraviolet–visible diffuse reflectance spectroscopy, and Brunauer-Emmett-Teller (BET) surface area. The best results were achieved with the use of Evonik TiO₂ P-25, Fe:Ti = 0 and Fe:Ti = 0.05 in suspension, with percentages of degradation of cypermethrin of 99.84%, 99.62%, and 100%, respectively. However, the materials supported on the biomaterial of coconut allowed to reach degradation percentages higher than 80%, with the advantage that it minimizes operating costs, as they are not necessarily filtering or centrifuging processes to separate the catalyst.

Keywords
cypermethrin, green chemistry, photocatalysis, sunlight, flat plate

Introduction
A current shift in the paradigm of the intensification of pest control in agriculture has increased the demand for pesticides because these have become fundamental tools in the productivity of the agro-industrial sector.¹–⁶ This industry produces close to 150 million tons of wastewater during the year worldwide,⁷ mainly by the use of herbicides, fungicides, and insecticides, approximately 3.3 × 10⁶ tons per year worldwide, of which 0.42 × 10⁶ tons per year are consumed in Europe (data 2010–2014 of FAOSTAT).⁸ These wastewaters show very different characteristics because of the variety of pesticides (herbicides, insecticides, fungicides, rodenticides, nematicides, microbicides, and regulators of plant and insect growth) that have been identified in concentrations of up to 500 mg L⁻¹.⁷,⁹ The excessive amount of pesticide residues in the soil, surface water, and groundwater causes serious contamination of soil and water; due to their high toxicity and persistence, these residues have been declared as priority pollutants by the Environmental Protection Agency of the United States.¹⁰–¹² On the other
hand, European legislation for drinking water sets a limit of 0.1 μg L⁻¹ for a single active ingredient of pesticide and 0.5 μg L⁻¹ for the sum of all the individual active substances detected.⁷ In Colombia, Resolution No. 2115 of June 22, 2007 establishes that the maximum permissible limit value for the active ingredients of pesticides of toxicological category II is 0.1 mg L⁻¹.¹⁴ Cypermethrin (Class II, moderately dangerous) causes human health problems related to immunosuppression, hormonal alteration, diminished intelligence, reproductive anomalies, and cancer. In the studies focused on these problems, only 0.1% of the pesticide used reaches the target pest and the remaining 99.9% scatter in the environment through routes such as runoff and erosion, leaching, drainage, and discharges of pesticide production plants.¹⁵ In wastewater treatment plants, biological treatment does not eliminate toxic, polar, or nonbiodegradable contaminants, although it is fostered as the best accessible technology. To comply with strict environmental laws, significant research studies are being conducted to develop better and more affordable wastewater treatment schemes, and improvements in processes that can degrade all biorecalcitrant organic pollutants, minimizing their accumulation.¹⁶ Advanced oxidation processes (AOPs) are characterized by the “in situ” production of hydroxyl radicals (OH•), which are capable of oxidizing and mineralizing any organic molecule, producing CO₂, H₂O, and inorganic ions. Due to the reactivity of the hydroxyl radicals, its attack is nonselective, which is useful for the treatment of wastewater containing different pollutants. AOPs can be executed with solar irradiation since the sun provides photons with the required wavelength for these processes.⁹,¹⁶,¹⁷–¹⁹

Heterogeneous photocatalysis is an advanced oxidation technology for the degradation of persevering organic pollutants, such as pesticides, which produces by-products that are more biodegradable than the original compounds. Titanium dioxide (TiO₂) is a standard photocatalyst used for this process when applying ultraviolet/ultraviolet–visible (UV/UV-vis) spectroscopy. Commercial TiO₂ is manufactured by the traditional sulfate process or high-temperature chloride process; the sulfate process involves digesting ilmenite or titania slag with concentrated sulfuric acid to produce titanium sulfate which is hydrolyzed to precipitate a hydrous titanium oxide compound and calcined at 650–1000°C to form either anatase or rutile-type TiO₂.²⁰ On the other hand, emerging technologies such as green chemistry aim to reduce the use of high toxicity reagents and achieve products with high performance and low environmental impact.²¹ A further procedure to expand the photo-response of TiO₂ in the visible light region of the spectrum is the doping of this material with nonmetallic elements, such as N, C, B, P and F, with noble metals such as Au and transition metals such as Cr, Fe, Ni, V, Mn, and Cu.²⁵–³⁰ In the photocatalytic degradation of chlorpyrifos, a composite material of CoFe₂O₄–TiO₂/reduced graphene was used in a batch reactor under UV radiation, reaching a degradation efficiency of 95% for an initial concentration of 5 mg L⁻¹, pH 5.8, a catalyst dose of 0.6 g L⁻¹, and 60 min of reaction.¹⁶,³¹,³² In a similar study, the batch degradation of atrazine was evaluated using B-TiO₂ nanomaterials, reaching efficiencies close to 85% in the photocatalytic process.³³ Additionally, heterogeneous photocatalysis has been integrated with other AOPs such as ozonation. The O₃/UV/TiO₂ treatment has been proposed for the elimination of cypermethrin, malathion, and dichlorvos, through which a degradation percentage of 83% was obtained for cypermethrin.⁹,³⁴ Also, a wide variety of common pesticides such as bromoxynil, diuron, α-phenylphenol, 2-methyl-4-chlorophenoxyacetic acid, and terbuthylazine have been mineralized through heterogeneous photocatalysis using B-TiO₂ and Cs-TiO₂ catalysts, which exhibit degradation efficiencies greater than 75% for these pollutants.³⁵,³⁶

In the present research, the photocatalytic degradation of cypermethrin was evaluated using Fe-TiO₂ nanoparticles in slurry and supported on coconut palm spathe (Cocos nucifera) in a flat plate solar reactor (FPSR) for an initial cypermethrin content of 50 mg L⁻¹. The TiO₂ nanoparticles were synthesized following the method of green chemistry assisted by ultrasound using an aqueous extract of lemongrass (Cymbopogon citratus), obtained after Soxhlet extraction and modified with Fe³⁺ atoms using chemical impregnation, while the immobilization of the nanoparticles on coconut palm spathe was carried out through the doctor blade technique. The concentration of cypermethrin was determined after 12,000 J m⁻² of accumulated radiation from gas chromatography–mass spectrometry (GC-MS), the powder materials were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), ultraviolet–visible diffuse reflectance spectroscopy (UV-vis-DRS), and BET surface area, while composite materials (coconut palm spathe/catalyst) were analyzed through scanning electron microscopy (SEM).

Materials and methods

Materials

Fresh lemongrass plant leaves (C. citratus) were collected from Cartagena, Colombia. Titanium(IV) isopropoxide (C₃H₇O₂Ti) solution (95%) and Iron(III) chloride hexahydrate (98% purity) were purchased from Alfa Aesar® (Ward Hill, MA, USA) and Panreac (Castellar del Vallès, Barcelona, Spain), respectively. All reactions were carried out using American Chemical Society (ACS) Reagent chemicals.

Plant extract and green synthesis of Fe-TiO₂ nanoparticles

Lemongrass aqueous extract and TiO₂ nanoparticles using green chemistry were obtained through a previously
reported procedure. The lemongrass leaves were washed with tap water. Then, they were dried for 6 h in an air circulation oven at 60°C (Esco Isotherm® OFA 32-8, Changi South, Singapore, Singapore) and crushed with a manual mill. The dried and crushed biomass (100 g) was placed in cloth bags and subjected to a solvent extraction process using a Soxhlet extractor for 6 h in approximately 600 mL of distilled water. The extract was cooled down to 4°C so that it could later be used to synthesize TiO$_2$ nanoparticles. In a typical experiment, the reaction was carried out in a 250 mL beaker, which was introduced in an ultrasound processor (WiseClean WUC-A06 H, Acinterlab (Miami, Florida, USA) 60 Hz). Then, 20 mL of the precursor agent (C$_{12}$H$_{28}$O$_4$Ti) was added along with 100 mL of the aqueous extract of lemongrass, which was contained in a burette, at a rate of 1 mL s$^{-1}$; additionally, the reaction lasted approximately 30 min with constant agitation, making use of a stirring rod. The nanoparticles were washed with 70 vol% ethanol and then with distilled water, using separation by centrifugation (Universal Centrifuge PLC-012E, GEMMY INDUSTRIAL CORP., Taipei, Taiwan) for 15 min at 5000 r min$^{-1}$. The synthesized TiO$_2$ nanoparticles were calcined at 550°C for 3 h in a Thermo Scientific FB1415M-1450 W-50/60 Hz muffle. For wet impregnation, 1 g of TiO$_2$ and the amount of FeCl$_3$·6H$_2$O were weighed to obtain Fe$_3$O$_4$:Ti molar ratios of 0.05, 0.075, and 0.1 and dissolved in 20 mL of double distilled water with constant magnetic stirring for 1 h at 500 r min$^{-1}$. Then, the precipitate was washed with distilled water and separated by centrifugation for 15 min at 5000 r min$^{-1}$; this process was repeated three times. Next, the precipitate was calcined at 350°C for 3 h, and finally, the catalyst was sieved in a 300 mesh.

**Immobilization of Fe-TiO$_2$ nanoparticles on coconut palm spathe**

The immobilization of the nanoparticles on the coconut palm spathe was carried out through the doctor blade technique using a water-based emulsion composed of styrene copolymer and 50% solids acrylic ester (RECOL® CRYL, Bogotá, Cundinamarca, Colombia). For this, the coconut spathe sample ($10 \times 10$ cm$^2$) was placed on a flat surface. Then, 4 g of emulsion was used to create a thin film on which 0.15 g of nanopowder was uniformly deposited to ensure that most of the nanomaterial remained on the surface of the composite. Finally, it was homogenized using a metal spatula.

**Characterization**

The samples were studied by XRD using a Panalytical X’Pert Pro Alpha1 instrument Malvern Panalytical (Madrid, Spain), which is equipped with a primary fast X’Celerator detector operating at 45 kV and 40 mA, and fitted with a primary curved Ge 111 monochromator, to obtain Cu K$_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å). Data were collected at 20 between 10° and 90°, with a step size of 0.04° s$^{-1}$. The morphology of the powder samples of bare and Fe-TiO$_2$ was studied in a transmission electron microscope (Tecnai F20 Super Twin TMP; FEI (Hillsboro, Oregon, USA)). UV-vis absorption studies of diffuse reflectance (UV-Vis-DRS) of the photocatalysts were carried out in UV-vis diffuse reflectance spectrophotometer (Thermo Scientific Evolution-600, Waltham, MA, USA), with BaSO$_4$ as reference and taking a scanning speed of 240 nm min$^{-1}$. The micrographs of the composite materials were taken in SEM FEI Inspet TM S50. FTIR spectroscopy was done in an IRAffinity-1 FTIR spectrophotometer (Shimadzu Kyoto, Japan) in the spectral range of 400–4000 cm$^{-1}$. The spectra of the samples were collected by the KBr pellet technique. The sensibility of the apparatus was 4 cm$^{-1}$. The specific surface area ( BET method) was measured by nitrogen (N$_2$) adsorption analysis at −196°C using a Micromeritics ASAP 2020 (Norcross, GA, USA) surface area and porosity analyzer. Before N$_2$ adsorption, the samples were outgassed at 300°C for 2 h in vacuum. A 0.1 g of the catalyst sample was used.

**Solar photocatalysis experiment**

A photocatalysis experiment was executed in a lab-scale pilot plant in Cartagena, Colombia (latitude 10° 25′30″ N, longitude 15° 32′25″ W) using natural sunlight irradiation during July–September 2018. Radiation levels were measured with a portable photoradiometer (Delta Ohm HD 2102, Padova, Veneto, Italy) with LP-UVB (300–600 nm) probe. The solar lab-scale pilot used in this experiment is based on FPSR technology (Figure 1). This small prototype consists of one photo reactor module (100 cm$^2$), where the water flows directly from a tube to the flat plate and finally to the reservoir tank (1 L), and a centrifugal pump (12 V DC, 0.7A, 1/2-inch suction/discharge diameter and 8 L min$^{-1}$ maximum flow). Storage tank, flowmeter (Arduino flow sensor by effect hall YF-S401, working voltage: DC 5–24V, flow rate range: 0.3–6 L min$^{-1}$), pipes (1/4-inch), and fittings completed the installation. In photocatalysis assay, 250 mL of solution (50 mg L$^{-1}$ of cypermethrin) was prepared; this will be exposed to sunlight in the flat plate photocatalytic reactor without (photolysis test) and with addition of a catalyzed (powder and composite) until it reaches a cumulative solar radiation value of 12,000 J m$^{-2}$. For the molecular adsorption test, 250 mL (50 mg L$^{-1}$) was placed in contact with the synthesized composite or 0.15 g of Fe-TiO$_2$ (Fe:Ti = 0). The solution was maintained in constant recirculation at 1.3 L min$^{-1}$ in a closed wooden box, taking samples at the beginning and after 120 min, separating the solution by centrifugation when this is required.

Cypermethrin concentration in aqueous solution was determined by GC-MS. Gas chromatographic analysis was carried out on an Agilent 7820A gas chromatography...
equipped with an HP-5 MS capillary gas chromatographic column (30 m × 0.25 mm ID × 0.25 μm) and a 5975-mass spectrometry. Helium was used as the carrier gas in a constant flow of 53.3 mL min⁻¹ at an input temperature of 250°C. The temperature program of the oven was set as follows: initial temperature at 80°C for 3 min; then ramped at 20°C min⁻¹ to 130°C and 30°C min⁻¹ to 190°C, held for 10 min; then ramped at 40°C min⁻¹ to 280°C, held for 7 min. On the other hand, chromatographic data were analyzed using the ChemStation software (Agilent, Santa Clara, California, USA).

Results and discussion

Characterization

XRD. XRD patterns of synthesized TiO₂ nanoparticles using the leaves extract of lemongrass (C. citratus) and Fe-doped TiO₂ are depicted in Figure 2. The nine distinct peaks at 2θ = 25.34°, 38.05°, 48.02°, 54.28°, 55.03°, 62.83°, 69.14°, 70.19°, and 75.40°, which correspond to (101), (103), (200), (111), (204), (116), (220), and (107) in lattice planes of the tetragonal phase (anatase) of TiO₂ nanoparticles according to the database of Joint Committee on Powder Diffraction Standards (JCPDS) file no. 89-4202.40,47 Besides, none of the prepared samples (pure and Fe-doped TiO₂) showed characteristic peaks of the rutile phase, while in Evonik (Essen, Germany) P-25 three peaks were identified at 27.51, 36.20, and 41.37, which are associated with (110), (101), and (111) (JCPDS card no. 21-1276), respectively.48 Also, the most intense and defined peak corresponds to the plane (101) of the anatase phase, indicating the predominant orientation and crystalline nature of the samples. The average crystalline size of TiO₂ nanoparticles was calculated using equation
(Debye–Scherrer equation) for the plane (101) of the anatase phase

\[ D = \frac{K\lambda}{\beta\cos\theta} \]  

where \( \lambda \) is the wavelength of X-ray radiation (Cu Ka = 0.15406 nm), \( K \) is a constant taken as 0.89, \( \beta \) is the line width at half maximum height of peak, and \( \theta \) is the diffracting angle. 49 Table 1 shows the results obtained for the average size of the nanoparticles prepared using the ultrasound-assisted green chemistry and wet impregnation process; also, values achieved in other recent research are reported. Iron (Fe, 0.69 Å) can replace titanium (Ti, 0.61 Å) in the TiO2 matrix due to the similarity of its atomic radii and a slight increase in the size of the nanocrystals could be observed as the doping concentration increased.50–52

**FTIR spectroscopy.** FTIR spectra were also registered between the wavenumber of 400 cm\(^{-1}\) and 4000 cm\(^{-1}\) for all samples. The FTIR spectrum of all these samples is shown in Figure 3, showing nearly similar patterns between them. The functional groups of the commercial catalyst (Evonik P-25) prepared TiO2 and Fe-TiO2 were determined using FTIR. The synthesized TiO2 and Fe-TiO2 absorption band at 3400 cm\(^{-1}\) can be assigned to the vibration of OH groups including the Ti–OH group. The band at 1620 cm\(^{-1}\) corresponds to the Fe-TiO2 bond and H–O–H bending vibration of adsorbed water.17 The absorption peak between 400 cm\(^{-1}\) and 690 cm\(^{-1}\) corresponds to the Ti–O–Ti bond vibration and the symmetrical vibration of Fe–O–Fe bonds, for the case of doped nanomaterials. All four synthesized materials have a high intensity of Ti–O–Ti bond, including the reference material (P-25).55

**TEM.** The microstructure and morphology of undoped and Fe-doped TiO2 nanoparticles were observed by TEM. Figure 4(a) and (b) shows the TEM images of the undoped TiO2 and Fe-doped TiO2, respectively. It could be found that the shape of all the nanoparticles is generally spherical and quite similar to each other with size varying from 13.73 ± 1.69 nm to 15.60 ± 1.95 nm which are in close with the XRD result.

**Surface area and porosity analysis.** N\(_2\) physical adsorption/desorption studies were carried out to determine the surface area and the pore distribution of the synthesized TiO2 and Fe-TiO2 samples. The isotherms and their relative Barret–Joyner–Halender (BJH) pore size distributions gathered from the isotherm’s adsorption branch of the catalysts are shown in Figures 5 and 6, respectively.

In Figure 5, it was observed that the prepared TiO2 and Fe-TiO2 possess mesoporous surface as the isotherms are of type IV and with typical H3 hysteresis loop according to the International Union of Pure and Applied Chemistry (IUPAC) convention; it indicates that TiO2 sample contain nonrigid aggregates of plate-like or slit-shaped pores with a contribution of micropores and mesopores.56–59 Furthermore, Figure 6 shows broad pore size distributions, ranging from 1.7 nm to 280 nm, further confirming the existence of micropores and mesopores.56–59 Additionally, from BET data, the particle size, \( D \) (nm), was estimated using equation (2),60 assuming a spherical shape for particles, where \( S_{BET} \) refers to BET surface area (m\(^2\) g) and \( \rho \) refers to density of samples (g cm\(^{-3}\)) and \( V_{pore} \) is single point adsorption total pore volume of pores less than 2069.006 Å radius at \( P/P_0 = 0.995 \). Table 2 summarizes the results obtained by equation (2)

\[ D = \frac{6000(S_{BET} \times \rho)^{-1}}{V_{pore}} \]  

### Table 1. Particle sizes obtained by Debye–Scherrer equation.

| Sample   | \( D \) (nm) | Reference               | Synthesis method                        |
|----------|---------------|-------------------------|----------------------------------------|
| Fe:Ti = 0| 9.059         | 13 (Goutam et al.49)    | Green chemistry (Jatropha curcas L.)    |
| Fe:Ti = 0.05| 9.988         | 8.2 (Ali et al.53)      | Sol–gel                                |
| Fe:Ti = 0.075| 9.793         | 10–20 (Sood et al.17)  | Ultrasound-assisted hydrothermal        |
| Fe:Ti = 0.1 | 9.574         | 13.5 (Vargas et al.54)  | Sol–gel combined with solvothermal      |

Fe: iron; Ti: titanium.
UV-Vis-DRS. The optical properties of TiO$_2$ and Fe-TiO$_2$ were separately detected by ultraviolet–visible diffuse reflection spectrometer. According to Figure 7, the absorption edge of the Fe-TiO$_2$ in comparison to undoped TiO$_2$ is extended greatly toward the visible light. The absorption edge is more extended to the visible light with the increasing of the Fe concentration, which is induced was attributed

Figure 4. TEM images of (a) undoped and (b) Fe-doped TiO$_2$ (Fe:Ti = 0.1) nanoparticles. Fe: iron; TiO$_2$: titanium dioxide; TEM: transmission electron microscopy.

Table 2. Textural properties of pure TiO$_2$ and Fe-TiO$_2$ nanoparticles.

| sample       | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_{pore}$ (cm$^3$ g$^{-1}$) | $D$ (nm) |
|--------------|-----------------------------|-------------------------------|----------|
| Fe:Ti = 0    | 64.442                      | 0.261                         | 21.031   |
| Fe:Ti = 0.05 | 60.499                      | 0.282                         | 23.445   |
| Fe:Ti = 0.075| 70.566                      | 0.319                         | 20.100   |
| Fe:Ti = 0.1  | 66.661                      | 0.262                         | 21.278   |

Fe: iron; TiO$_2$: titanium dioxide.

Figure 5. Nitrogen adsorption–desorption isotherms of bare TiO$_2$ and Fe-TiO$_2$. Fe: iron; TiO$_2$: titanium dioxide.

Figure 6. Cumulative pore volume from BJH adsorption isotherm. BJH: Barret–Joyner–Halender.

Figure 7. Typical UV-vis spectra and Tauc plot analysis (inset) of bare TiO$_2$ and Fe-TiO$_2$ and band gap energy. Fe: iron; TiO$_2$: titanium dioxide; UV-vis: ultraviolet–visible.

**UV-Vis-DRS.** The optical properties of TiO$_2$ and Fe-TiO$_2$ were separately detected by ultraviolet–visible diffuse reflection spectrometer. According to Figure 7, the absorption edge of the Fe-TiO$_2$ in comparison to undoped TiO$_2$ is extended greatly toward the visible light. The absorption edge is more extended to the visible light with the increasing of the Fe concentration, which is induced was attributed.
to the electron transition from Fe3d orbitals to the TiO2 conduction band (CB). Doping Fe3+ causes structural defects of crystal lattice to introduce impurity or defect energy level and induces the local states below the CB edge, then results in this redshift and narrows the band gap. Doping of the Fe ions in the TiO2 introduces new energy levels (Fe3+/Fe4+) of the transition Fe ions into the band gap of the TiO2. The direct band gap energy ($E_g$) was calculated using the following Tauc plot equation (equation (3)), which is derived assuming a direct transition ($n = 0.5$) between the edge of the valence band and conduction band.

$$ (a\hbar \nu)^{1/n} = A(h\nu - E_g) $$

where $h\nu$ is the photon energy, $a$ is the absorption coefficient, and $A$ is an energy-dependent constant and known as the band tailing parameter. Another constant is $n$, which is
known as power factor of the transition mode of the materials. Therefore, the graph $(\alpha h\nu)^2$ versus $h\nu$ is shown in Figure 7 (inset).

**SEM.** Figure 8 shows the microscopy of coconut palm spathe and coated by the doctor blade technique. Samples prepared with water-based emulsion composed of styrene copolymer and 50% solids acrylic ester (Figure 8(c) to (e) and (f)) present a coarse nonhomogeneous layer of TiO$_2$ or Fe-TiO$_2$ and some cracks are visible, similar to that reported by Mejía et al.$^{63}$

**Photocatalytic activity and mechanism**

Results obtained for the photocatalytic degradation of cypermethrin using nanomaterials suspended and immobilized are shown in Figure 9 and the GC-MS analysis for the slurry Fe:Ti = 0.05 sample is illustrated in Figure 10. The best results were achieved in slurry with the use of TiO$_2$ Evonik P-25, Fe:Ti = 0 and Fe:Ti = 0.05, with rates of degradation of cypermethrin of 99.84%, 99.62%, and 100%, respectively. However, the molar ratios higher than Fe:Ti (Fe:Ti = 0.075 and Fe:Ti = 0.1) had a negative effect on the percentage degradation, like what was reported recently by Moradi et al.$^{64}$ In this study, the authors evaluated the photocatalytic degradation of methyl orange (20 mg L$^{-1}$) using TiO$_2$ doped with different concentrations of Fe$^{3+}$ (0.25, 0.5, 1, 5, and 10 Fe:Ti mol% ratio). These authors found that it is only possible to achieve degradation percentages lower than 5% with the use of catalysts doped with high concentrations of Fe$^{3+}$ (5–10 Fe:Ti mol% ratio), which is attributed to the formation of layers composed of iron oxide, with photocatalytic reactions generating pollution on the surface of the catalyst particles, which decreases the available active sites, where they occur.$^{64}$ For this reason, the authors proposed an acid treatment with HCl (pH 2 solution) to remove impurities that cause inhibition of the photocatalytic activity, achieving a significant improvement in the percentage of degradation.

On the other hand, the phenomenon of inhibition caused by high concentrations of the dopant has also been explained by other authors. Ali et al.$^{53}$ studied the photocatalytic activity of TiO$_2$ doped with Fe$^{3+}$ ions for the elimination of methylene blue (10 mg L$^{-1}$), finding high concentrations of dopant (5, 7, and 10 Fe:Ti mol% ratio) produces accumulation on the surface of the catalyst, which reduces the depth of light penetration. Besides, such saturation covers part of the surface of the photosensitive, thus reducing the number of surface active sites for the effective degradation of organic molecules.$^{53}$

The generalized mechanism for degradation of cypermethrin is shown in Figure 11. Photocatalytic degradation is initiated by electron/hole pairs, and the recombination of these carrier species decreases the photocatalytic efficiency of TiO$_2$. Fe$^{3+}$ ions can act as trap for photo-generated carriers (equations (4) to (8)). However, when the doping agent concentration is very high, Fe$^{3+}$ ions become recombination centers for electron/hole pairs, resulting in reduced photocatalytic activity (equations (9) to (13)).$^{25,64}$ From Figure 9, it can be seen that Fe:Ti = 0.05 (molar ratio) is the optimal Fe$^{3+}$ doping content for the degradation of the cypermethrin under visible light irradiation. When the Fe:Ti molar ratio was higher than 0.05 (Fe:Ti = 0.075 and 0.1), the photocatalytic activity decreased. It means that the Fe ions will become recombination centers for high doping levels.$^{25}$

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow h^+ + e^- \\
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+} \\
\text{Fe}^{2+} + \text{O}_2(\text{abs}) & \rightarrow \text{Fe}^{3+} + \text{O}_2 \\
\text{Fe}^{2+} + \text{Ti}^{4+} & \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+} \\
\text{Fe}^{3+} + h^+_{\text{P}} & \rightarrow \text{Fe}^{4+} \\
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+} \\
\text{Fe}^{2+} + h^+_{\text{P}} & \rightarrow \text{Fe}^{3+} \\
\text{Fe}^{3+} + h^+_{\text{P}} & \rightarrow \text{Fe}^{4+} \\
\text{Fe}^{4+} + e^- & \rightarrow \text{Fe}^{3+} \\
\text{Fe}^{2+} + \text{OH}^- & \rightarrow \text{Fe}^{3+} + \text{OH}^- 
\end{align*}
\]
spectroscopy (EIS), intensity-modulated photocurrent spectroscopy, and Mott–Schottky analysis. In a current research, Chakhari et al. studied the electrochemical properties of Fe-TiO₂ nanorods deposited on fluorine-doped SnO₂ conductive glass for application as photoanodic materials. The Fe³⁺ concentration was varied between 0 mM and 10 mM during material synthesis, and electrochemical properties were determined by experiments in PECs using Ag/AgCl as a working electrode under illumination, and EIS in open circuit in dark and under illumination with an AC perturbation of 10 mV. Results showed that high Fe concentrations decrease photocurrent density as a result of the increase in the recombination rate because photo-generated electron or hole trapping sites will disappear, and more oxygen vacancies act as recombination centers; on the other hand, the EIS (Nyquist plots) for TiO₂ and Fe-TiO₂ under illumination revealed a significant increase in impedance due to a poor charge transfer for materials with excess of doping.

Based on the results shown in Figure 9, it can be inferred that the immobilization of nanoparticles on the spathe of coconut palm biomaterial generates a decrease in the percentages of elimination of cypermethrin, although it is possible to achieve efficiencies of degradation close to 85% for reference Evonik P-25, Fe:Ti = 0 and Fe:Ti = 0.05, while the doping made with high molar ratios of Fe:Ti (Fe:Ti = 0.075 and Fe:Ti = 0.1) only allowed to achieve efficiencies of 67% and 48%, respectively, due to above
reasons. Also, there is evidence of the appearance of a yellowish coloration, which is attributed to nonselective degradation of the resin and the biological material used for the immobilization of the powder materials by the hydroxyl radicals generated (OH\textsuperscript{•}).\textsuperscript{75}

There is also a clear decrease in the efficiency of degradation of the supported systems in comparison to the evaluated in suspension (slurry). Recent studies support the low-efficiency for immobilized catalysts, which is associated with a decrease in the surface area exposed to the solution. For example, Cerrato et al.\textsuperscript{76} studied the immobilization of TiO\textsubscript{2} on glass materials for the degradation of Ibuprofen under UV-C radiation, finding that the application in suspension allows to achieve the best results for the degradation of the studied drug.

The cypermethrin elimination or degradation percentages were determined using equation (14). The results showed values lower than 5\% and 10\% for the photolysis and dark adsorption tests, respectively, which correspond to commonly published in research related to targets of molecular adsorption and photolysis of organic compounds, such as pesticides, dyes, and pharmaceuticals, among others.\textsuperscript{55,76,77}

\begin{equation}
\eta = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (14)
\end{equation}

where \(C_0\) represents the initial concentration of cypermethrin in the sample (50 mg L\(^{-1}\)) and \(C_t\) is the concentration at the end of the treatment.

Conclusions

The immobilization of nanoparticles on the spathe of coconut palm biomaterial generates a decrease in the percentages of elimination of cypermethrin, although it is possible to achieve efficiencies of degradation close to 85\% for reference Evonik P-25, Fe:Ti = 0 and Fe:Ti = 0.05, while the doping made with high molar ratios of Fe:Ti (Fe:Ti = 0.075 and Fe:Ti = 0.1) only allowed to achieve efficiencies of 67\% and 48\%, respectively. However, the immobilization of nanoparticles on coconut palm-based biomaterial using the resin applied in this study brings two important advantages from an economic and environmental point of view, that is, it eliminates operating costs associated with the separation of the material after the treatment when applied in suspension, and also prevents potential contamination of the effluent treated by TiO\textsubscript{2} or Fe-TiO\textsubscript{2} nanoparticles, which could impact negatively on the aquatic ecosystems and human health.

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