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Magnetic TiO_2/Fe_3O_4-Chitosan Beads: A Highly Efficient and Reusable Catalyst for Photo-Electro-Fenton Process

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Abstract: Heterogeneous photo-electro-Fenton process is an attractive technology for the removal of recalcitrant pollutants. To better exploit the presence of an irradiation source, a bifunctional catalyst with TiO_2 nanoparticles embedded into an iron–chitosan matrix was developed. The catalytic activity of the catalyst was improved by the optimization of the loaded TiO_2 content. The prepared composite catalysts based on TiO_2, Fe_3O_4 and chitosan were called TiO_2/Fe_3O_4-CS beads. The best catalyst with an optimal ratio TiO_2/Fe = 2 exhibited a high efficiency in the degradation and mineralization of chlordimeform (CDM) insecticide. Under the optimum conditions (concentration of catalyst equal to 1 g L\(^{-1}\) and applied current intensity equal to 70 mA), a real effluent doped with 30 mg L\(^{-1}\) of CDM was efficiently treated, leading to 80.8 ± 1.9% TOC reduction after 6 h of treatment, with total removal of CDM after only 1 h. The generated carboxylic acids and minerals were identified and quantified. Furthermore, the stability and reusability of the developed catalyst was examined, and an insignificant reduction in catalytic activity was noticed for four consecutive cycles of the photo-electro-Fenton process. Analyses using SEM, XRD and VSM showed a good stability of the physicochemical properties of the catalyst after use.

Keywords: photo-electro-Fenton process; chlordimeform; wastewater treatment; bifunctional catalyst

1. Introduction

In recent decades, the extensive use of pesticides to improve agricultural production has led to an increased risk of water pollution. In fact, these pollutants can be classified as persistent and extremely toxic organic substances. The ability of these harmful pollutants to easily bioaccumulate even at very low concentrations represents a serious issue that can cause problems for the environment, human health and living organisms [1]. Consequently, the removal of pesticides from water and wastewater has become a great global challenge.

In recent years, electrochemical advanced oxidation processes (EAOPs) have been considered an option for the removal of toxic and persistent organic micropollutants from wastewater [2–4]. One of the most powerful and attractive techniques among EAOPs is the electro-Fenton (EF) process, whereby hydrogen peroxide (H_2O_2) is generated at a cathode by O_2 reduction (Equation (1)), and a ferrous ion or iron oxide catalyst is added to the effluent [5]. The EF process is very effective in the mineralization of organic pollutants due to the production of strongly oxidizing hydroxyl radicals through the Fenton reaction (Equation (2)) [6]. However, this technology is limited by a few factors, such as the rapid accumulation of Fe(III) ions and the possibility of their complexation with hydroxyl ions and oxidation products during treatment [7].

\[
\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2
\]  

(1)
\[ H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \cdot OH \] (2)

The presence of UV irradiation has two specific aims: the regeneration of Fe(II) ions and the degradation of the formed complexes until their mineralization due to an additional production of \( \cdot OH \) [8]. This process is called the photo-electro-Fenton (PEF) process, and it leads to great performance in the mineralization of organic pollutants [9,10].

However, the application of UV irradiation could increase the operational cost, but it can be justified by the use of a photocatalyst, such as TiO\(_2\), to increase its economic cost effectiveness. The application of a ferromagnetic-TiO\(_2\) composite material is widely used for photocatalysis due to its efficiency and magnetic properties [11,12].

In fact, in a heterogeneous system, many solid catalysts containing iron, such as Fe, Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\) and FeOOH, were successfully used for the treatment of recalcitrant organic pollutants in water [13–17]. Among iron oxides, the immense popularity of Fe\(_3\)O\(_4\) as a catalyst originates from its broad application potential due to high saturation magnetization, easy handling, relatively low cost, non-toxicity and environmentally friendly character [18,19]. Titanium oxide (TiO\(_2\)) has also shown widespread photocatalytic application in the field of wastewater treatment due to its unrivalled properties of non-toxicity, easy UV activation, chemical stability and availability [20]. Despite all these outstanding properties, TiO\(_2\) deployment for photocatalytic application has witnessed drawbacks due to its large energy band gap of about 3.2 eV [20,21]. In addition, one of the problems hindering TiO\(_2\) use is its agglomeration in aqueous solution, which requires a post-filtration treatment [21]. In order to overcome the problem of the band gap of TiO\(_2\), several studies revealed that the presence of Fe\(_3\)O\(_4\) enhances the photocatalytic activity of TiO\(_2\) by decreasing the charge carrier recombination, with a band gap of the composite material around 2.5 eV. This is caused by the generated Z-scheme on the composite TiO\(_2\)/Fe\(_3\)O\(_4\) where the recombination between holes and electrons on TiO\(_2\) is restrained by the addition of another valence band (Fe\(_3\)O\(_4\)). Indeed, Fe-species have been reported as an outstanding alternative for creating Z-scheme photocatalytic heterojunction systems [22]. Moreover, this modified TiO\(_2\) nanoparticle can be separated from water by means of an external magnetic field [11,23]. However, the use of magnetic separation is complicated in real water applications. Therefore, the use of a catalytic support, such as chitosan, for both metal oxides (Fe\(_3\)O\(_4\) and TiO\(_2\)) not only avoids the agglomeration issue, but it also facilitates catalyst recovery, protects ferroparticles from oxidation and extends their storage life [24].

Therefore, in the present study, we innovatively synthesized the TiO\(_2\)/Fe\(_3\)O\(_4\)-CS catalytic beads through a green co-precipitation method in only one step. The co-precipitation method involves the dispersal of a mixture of chitosan and metals into an alkaline solution to form nanoparticles strongly bound to chitosan with attractive catalytic and magnetic properties for easy catalyst recovery and reuse [24–28]. TiO\(_2\)/Fe\(_3\)O\(_4\)-CS was used as a novel nano-structured heterogeneous catalyst for the oxidation of CDM insecticide by an efficient cyclic PEF process; therefore, Fe(II), within the structure of Fe\(_3\)O\(_4\), can activate the Fenton system [29], and TiO\(_2\) acts as a photocatalyst to better exploit the use of UV irradiation. In the PEF system, an electrochemical reactor was used for the electrogeneration of H\(_2\)O\(_2\), and the catalyst was added to a second photocatalytic reactor. The effects of operational parameters were studied, such as the TiO\(_2\) loading in the beads, catalyst dosage and the current intensity applied. Under optimal conditions, aqueous wastewater doped with 30 mg L\(^{-1}\) of CDM was treated. The carboxylic acids and inorganic ions generated during the treatment process were identified and quantified. Finally, the electric energy consumed was estimated, and the stability of the best catalyst in terms of CDM and TOC removal efficiencies was studied.

2. Results
2.1. Optimization of Operational Parameters
2.1.1. Performance Comparison of Several Processes for the Removal of CDM

Initially, some control experiments were performed. To begin with, the adsorption assays of the developed catalytic beads showed no CDM adsorption after 4 h of treat-
ment on the synthesized catalytic beads (data not shown). Then, the low efficiencies of photoelectrolysis–H₂O₂ (electrogenerated H₂O₂ + UV-LED) and photocatalysis (1 g of TiO₂/Fe₃O₄-CS catalyst + UV-LED) systems revealed, respectively, 70.6 ± 5.3% and 13.2 ± 4.4% of CDM removal yield after 1 h of electrolysis (Figure 1) along with only 18.2 ± 3.3% and 4.4 ± 1.6% of TOC abatement after 4 h of treatment (Table 1). However, the PEF process running at I = 50 mA and pH₄ = 3, in the presence of 1 g L⁻¹ TiO₂/Fe₃O₄-CS, exhibited higher efficiency, with total degradation of CDM after only 1 h and TOC abatement equal to 69.6 ± 2.7% after 4 h of treatment (Table 1).

![Figure 1. Performance comparison of several processes and effect of the addition of TiO₂ to magnetic chitosan beads: (a,d) % removal of CDM; (b) –Ln (C/C0) vs. time; (c) [H₂O₂] vs. time: I = 50 mA in the presence of 1 g L⁻¹ of catalyst and at pH = 3.](image)

2.1.2. Influence of TiO₂ in Magnetic Chitosan Beads

As found previously in the PEF system, the composite catalyst TiO₂/Fe₃O₄-CS showed higher catalytic activity, with total degradation of CDM after only 1 h and TOC abatement of around 70% after 4 h of treatment. However, in the presence of Fe₃O₄-CS catalytic beads, only 87.9 ± 3.1% CDM removal yield and TOC abatement was achieved, not exceeding 33.9 ± 4.1%. The higher photocatalytic activity of TiO₂/Fe₃O₄-CS beads could be attributed to the acceleration of electron mobility in the Fe³⁺/²⁺/TiO₂ system [12,30] and the synergistic combination of PEF with photocatalysis. It is widely reported that the combination of TiO₂ and Fe₃O₄, with their different band gaps, can suppress the electron–hole recombination, enhancing the photocatalytic activity, and thus, the PEF process efficiency, thanks to the generation of the Z-scheme [11,22,30–32]. Moreover, the degradation of CDM by the PEF process was found to follow a pseudo-first-order kinetic (Figure 1b), which is probably related to the steady ⋅OH concentration throughout the treatment process [33,34]. To evaluate the catalytic decomposition of the oxidant, the concentration of H₂O₂ was monitored during treatment with and without the developed catalysts, and the results are presented in Figure 1c. In the absence of the catalyst and UV-LED lamp, the accumulated amount of H₂O₂ after 4 h of electrolysis was estimated
at 64.4 ± 0.5 mg L⁻¹. In the presence of UV-LED irradiation, the concentration of H₂O₂ decreased to 53.8 ± 0.9 mg L⁻¹, which means that the amount of H₂O₂ decomposed by photolysis after 4 h of electrolysis was around 16.6%. As expected, by adding the Fe₃O₄-CS and TiO₂/Fe₃O₄-CS catalytic beads to the (H₂O₂ + UV-LED) system, the concentration of the oxidant decreased significantly to 39.9 ± 1.1 mg L⁻¹ and 29 ± 0.8 mg L⁻¹, respectively, indicating that approximately 38% and 55% of the H₂O₂ amount was decomposed. These findings were in agreement with our previous results, and they confirmed the best catalytic activity of TiO₂/Fe₃O₄-CS beads because an increase in the decomposition rate of H₂O₂ is related to an increase in the production yield of •OH radicals [35]. Therefore, it is clear that the incorporation of TiO₂ into magnetic CS beads favors an effective usage of H₂O₂, allowing great improvement to the PEF process efficiency.

Table 1. Summary table of mineralization rates.

| Parameter                                      | Assay                                | Rate of TOC Removal after 4 h of Treatment |
|------------------------------------------------|--------------------------------------|-------------------------------------------|
| Performance comparison of several processes     | TiO₂/Fe₃O₄-CS(2) + UV-LED            | 4.4 ± 1.6                                 |
|                                                | H₂O₂ + UV-LED (Without catalyst)    | 18.2 ± 3.3                                |
| Influence of TiO₂ in magnetic chitosan beads    | TiO₂/Fe₃O₄-CS(2) + H₂O₂ + UV-LED     | 69.6 ± 2.7                                |
|                                                | Fe₃O₄-CS + H₂O₂ + UV-LED            | 33.9 ± 4.1                                |
| Effect of TiO₂ loading content into magnetic chitosan beads | Molar ratio TiO₂/Fe = 1            | 38.2 ± 3.5                                |
|                                                | Molar ratio TiO₂/Fe = 2             | 69.6 ± 2.7                                |
|                                                | Molar ratio TiO₂/Fe = 3             | 54.2 ± 5.6                                |
|                                                | Catalytic beads of TiO₂             | 24.5 ± 1.9                                |
|                                                | 0.25 g L⁻¹                          | 40.9 ± 4.1                                |
|                                                | 0.5 g L⁻¹                           | 60.8 ± 3.2                                |
| Effect of catalyst dosage                      | 1 g L⁻¹                             | 69.6 ± 2.7                                |
|                                                | 1.5 g L⁻¹                           | 70.2 ± 1.7                                |
|                                                | 2 g L⁻¹                             | 58.2 ± 6.2                                |
|                                                | 50 mA                               | 68.6 ± 4.9                                |
| Effect of current intensity                    | 70 mA                               | 76.9 ± 3.7                                |
|                                                | 100 mA                              | 77.7 ± 1.2                                |

2.1.3. Effect of TiO₂ Loading Content into Chitosan Beads

In order to increase the catalytic activity of TiO₂/Fe₃O₄-CS beads, the effect of TiO₂ content in the catalyst was studied. For this purpose, the molar ratio TiO₂/Fe was varied during the preparation of the catalyst from 1 to 3 (to facilitate a designation of the developed catalysts, the molar ratio values between the brackets were added to TiO₂/Fe₃O₄-CS). The results showed that a molar ratio equal to 2 (TiO₂/Fe₃O₄-CS(2)) was optimal, leading to total degradation of CDM after 1 h (Figure 1d) and TOC removal yield of around 70% after 4 h of treatment (Table 1), against 38.2 ± 3.5% and 54.2 ± 5.6%, respectively, for the molar ratios TiO₂/Fe = 1 and 3. On the other hand, the comparison of the photocatalytic activities of TiO₂/Fe₃O₄-CS(2) and TiO₂-CS (Figure 1d) showed a remarkable difference in their catalytic performance, which was greater for the composite catalyst. In fact, the CDM degradation rate did not exceed 35% after 1 h of treatment using TiO₂-CS beads, with low TOC abatement estimated at 24.5 ± 1.9% after 4 h of treatment. Therefore, it is obvious that the Fe(II) ions in TiO₂/Fe₃O₄-CS catalytic beads notably improve their catalytic performance by the Fenton reaction with H₂O₂, so that •OH radicals are produced. Numerous studies have reported the high photocatalytic activity of the mixture of TiO₂/Fe₃O₄ compared to pure TiO₂, and they explained this improvement by the fast photogenerated electron transfer between Fe₃O₄ and TiO₂, which can effectively reduce electron/hole recombination [12,33,36,37].

To sum up, a molar ratio TiO₂/Fe = 2 is optimal both for the removal of the pollutant and its mineralization. In fact, varying the molar ratio from 1 to 2, the photocatalytic activity of the catalytic beads increased through the increase in TiO₂ active sites. The improvement in pollutant degradation and mineralization by the increase in TiO₂ load in
the iron catalysts has already been reported by many research studies, and it is related to the enhancement of the electron transfer reducing electron–hole recombination \cite{32,38}. For a molar ratio TiO$_2$/Fe = 3, the catalytic performance of the system decreased due to the decrease in active iron sites in favor of the photocatalytic sites of TiO$_2$, which has a wide band gap energy, causing a rapid recombination of the electron–hole pairs \cite{39}. It is well known that the fast recombination of charge carriers significantly lowers the photocatalytic performance \cite{24,40}. Thus, a TiO$_2$/Fe molar ratio equal to 2 was optimal for the preparation of TiO$_2$/Fe$_3$O$_4$-CS beads, and the catalyst TiO$_2$/Fe$_3$O$_4$-CS(2) was selected thereafter.

The photodegradation of pesticides using TiO$_2$/Fe$_3$O$_4$-based materials as catalysts has been poorly reported. Compared to the efficiency of TiO$_2$/Fe$_3$O$_4$ composite catalysts listed in Table 2, TiO$_2$/Fe$_3$O$_4$-CS showed good catalytic activity. Nevertheless, the reactor set-up, such as the irradiation source, can greatly affect the overall efficiency of the process \cite{41}.

Table 2. The comparison of photodegradation efficiency of TiO$_2$/Fe$_3$O$_4$-CS catalytic beads with other TiO$_2$/Fe$_3$O$_4$-based materials against different pesticides.

| Catalysts                              | Pesticides     | Degradation Efficiency (%) | Refs.    |
|----------------------------------------|----------------|---------------------------|----------|
| Fe$_3$O$_4$-TiO$_2$/reduced graphene oxide | Atrazine       | 99% within 40 min          | \cite{42} |
| N-doped TiO$_2$@SiO$_2$@Fe$_3$O$_4$ nanocomposite | Paraquat       | 98.7% within 180 min       | \cite{43} |
| Bare 3D-TiO$_2$/magnetic biochar dots   | Diazinon       | 98.5% within 30 min        | \cite{44} |
| TiO$_2$/Fe$_3$O$_4$-CS                 | Chlordimeform  | 100% removal within 60 min | Present work |

2.1.4. Effect of Catalyst Dosage

Catalyst dosage was another parameter affecting the heterogeneous Fenton reaction \cite{45}. The effect of catalyst dosage on the degradation of CDM by the PEF process was studied by applying a current intensity of 50 mA at pH$_{\text{initial}}$ = 3. It is clear from Figure 2a that the increase in TiO$_2$/Fe$_3$O$_4$-CS(2) catalytic beads from 0.25 g L$^{-1}$ to 1 g L$^{-1}$ increased the rate of CDM removal, and an almost total degradation was obtained for all assays after 1 h of treatment, with an improvement in TOC abatement, respectively, from 40.9 ± 4.1% to 69.6 ± 2.7% (Table 1). For a concentration equal to 1.5 g L$^{-1}$, there was a trivial enhancement in CDM and TOC removal efficiencies. However, the removal yields of CDM and TOC were decreased for a high concentration equal to 2 g L$^{-1}$. Indeed, an increase in the concentration of catalytic beads in solution can inhibit the penetration of light into the photocatalytic reactor \cite{46,47}. Additionally, an increase in the active catalytic sites can cause secondary reactions with •OH radicals, thus producing less reactive oxidizing species (Equation (3)), which can reduce the efficiency of the process for the mineralization of organic pollutants \cite{25}.

\[
\text{Fe}^{2+} + \bullet\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-
\] (3)

2.1.5. Effect of the Current Intensity

The current intensity applied is a key parameter in the electrochemical Fenton technologies because it is the driving force for the reduction in oxygen, leading to the generation of H$_2$O$_2$ at the cathode, and it affects the regeneration of Fe(II) \cite{48}. In order to study the effect of the current intensity applied on CDM degradation and its mineralization by the PEF process, several experiments were carried out using different current intensities in the range from 50 mA to 100 mA in the presence of 1 g of TiO$_2$/Fe$_3$O$_4$-CS(2) and at initial acid pH (Figure 2b). The results showed that an increase in the current intensity from 50 mA to 70 mA leads to total degradation of the pollutant after only 1 h, with almost 10% improvement in TOC abatement (Table 1). This finding can be mainly attributed to the fast production of H$_2$O$_2$ at a higher current and the fast regeneration of Fe(II) enhancing the production of •OH radicals \cite{49}. 
2.1.5. Effect of the Current Intensity

The current intensity was a key parameter in the electrochemical Fenton process. Several studies have shown the degradation of CS in the presence of an irradiation source and intensities in the range from 50 mA to 100 mA in solution 

As seen in Figure 2b and Table 1, no further increase in the removal efficiencies was observed for the current intensity applied beyond 70 mA. This behavior can indicate that parasitic reactions, such as the four-electron reduction in O2 with H2O formation, as well as the decomposition and hydrogenation of H2O2, would take place when the current increased beyond a certain value [49-52]. On the other hand, working at higher current intensities can generate a degradation of our organic catalytic support “CS”. In fact, several studies have shown the degradation of CS in the presence of an irradiation source and high concentrations of H2O2 [53,54]. An optimal current intensity equal to 70 mA, which ensured high treatment efficiency and good catalyst stability, was therefore established for the upcoming experiments.

To confirm the role of •OH radicals in the mineralization of the organic pollutant, isopropanol was used as a •OH scavenger. The degradation of CDM was totally inhibited in the presence of isopropanol. Thus, •OH should be the main active species for the degradation of CDM by the PEF process.

2.2. Treatment of Wastewater Doped with Chlordimeform by Photo-Electro-Fenton Process

To evaluate the applicability of the PEF process using TiO2/Fe3O4-CS(2) as a catalyst for the removal of CDM in a more complex matrix than ultrapure water, an experiment was carried out on secondary treated wastewater kindly given by the municipal wastewater treatment plant in the northwest of Spain, whose physiochemical characteristics are summarized in Table 3.

Table 3. Physicochemical properties of the collected wastewater.

| Parameter                        | Value |
|----------------------------------|-------|
| Total organic carbon TOC (mg L⁻¹) | 52.7  |
| Chemical oxygen demand DCO (mg L⁻¹) | 35    |
| Biological oxygen demand BOD₅ (mg L⁻¹) | 2     |
| Conductivity (mS cm⁻¹)            | 3.33  |
| pH                               | 7.31  |
| Turbidity (mg L⁻¹)                | 12    |

Under optimal experimental conditions ([CDM] = 30 mg L⁻¹, [TiO2/Fe3O4-CS(2)] = 1 g L⁻¹, and I = 70 mA), total degradation of CDM was achieved after 1 h, and TOC abatement reached 50.6 ± 5.1% after 1 h of electrolysis; then, it increased slowly to attain 80.8 ± 1.9% after 6 h of treatment (Figure 3b).

Furthermore, a slight decrease in the efficiency of the system was noticed compared to previous results when ultrapure water was used as the matrix (Figure 2b). This finding
can be explained, according to zazouli et al. [55], by the presence of organic matter and inorganic anions in wastewater. In fact, the anions (X⁻) can react with the •OH to produce X• radicals, which are less reactive.

In addition to the aqueous matrix influence, it should be noted that EEC is another big concern, which should be considered for sustainable development [56]. The results showed that global EEC was low compared to some literature values on the treatment of real wastewater by electrochemical processes [57–59] around 1.7 kWh m⁻³ and 1.4 kWh m⁻³, respectively, for real wastewater and ultrapure water matrices. However, it should be noted that the difference (≃0.3 kWh m⁻³) is probably due to the presence of degradable compounds in the treated wastewater matrix, whose oxidation requires a little more energy.

2.3. Evaluation of Organic Acids and Minerals Produced during Treatment

Studies of organic pollutants’ mineralization by advanced oxidation processes show that oxidation by •OH radicals leads to the formation of carboxylic acids [60, 61]. To better assess the oxidative capacity of our PEF process, an analysis of carboxylic acids was performed in order to identify and quantify them during treatment. The evolution of the identified acids during the mineralization of CDM is presented in Figure 3c. All the acids produced reached their maximum concentrations after around 2 h. Then, they decreased to a zero value after 6 h of treatment, indicating the deep mineralization of all detected acids. The concentration of oxalic acid during the treatment process was low (almost zero), which can be explained by the high reactivity of oxalic acid with Fe(III) and the formation of Fe(III)–oxalate complexes that are easily photolyzed in the presence of UV light and H₂O₂ oxidant [62]. However, the other acids detected were malonic, succinic, formic and glycolic acids, appearing at the beginning of treatment. These results showed the effectiveness of our PEF process in removing the aliphatic compounds known for their resistance to oxidation.

![Graphs showing removal of CDM, TOC, and carboxylic acids vs. time](image)

Figure 3. Treatment of a real effluent: (a) % removal of CDM; (b) % removal of TOC; (c) [carboxylic acids] vs. time (d) [ions] vs. time: I = 70 mA in the presence of 1 g L⁻¹ of TiO₂/Fe₃O₄-CS(2) and at pH_{initial} = 3.

On the other hand, considering the CDM molecule is composed of a chlorine atom and two nitrogen atoms, its treatment by an advanced oxidation process leads to the production of minerals. The evolution of these ions was monitored by ion chromatography. The ob-
tained results (Figure 3d) showed that the chloride ions reached a maximum concentration of 6.22 mg L\(^{-1}\) after 1 h; this concentration presented the total amount initially present in the parent molecule. This finding was in agreement with several studies, which have shown that the release of chloride ions is rapid using a BDD anode and that the dechlorination of aromatic compounds occurs before the opening reaction of the aromatic cycle \[63–65\].

Then, the concentration of chloride ions decreased to approximately half (3.05 mg L\(^{-1}\)) after 6 h of treatment, which was in agreement with the results found by Mhemdi et al. \[64\] who studied the effect of the anode material (platinum and BDD) on the evolution of chlorides during the mineralization of 2-chlorobenzoic acid by an electrochemical oxidation process. The results showed that, for platinum, the concentration of chloride ions reached a maximum after 2 h and then remained constant. Using the BDD anode, a different behavior of chloride ions was observed. They accumulated rapidly after 1 h; then, their concentration decreased due to their oxidation to chlorine (Cl\(_2\)), which transformed into hypochlorite ions HClO\(^-\) by hydrolysis. Consequently, the decrease in the accumulated chloride concentration during treatment could be explained by the oxidizing power of the BDD anode and the synthesized catalysts, causing the transformation of Cl\(^-\) ions into Cl\(_2\).

Furthermore, the concentration of nitrate ions (NO\(_3^-\)) after 6 h was estimated at 0.68 mg L\(^{-1}\). However, the accumulated concentration of ammonium ions (NH\(_4^+\)) was high, and it was around 4.75 mg L\(^{-1}\). The accumulated concentrations of nitrate and ammonium ions after 6 h of treatment represent approximately 90% of the amount of nitrogen initially contained in the molecule of CDM. Consequently, one can confirm that CDM is mineralized during PEF application.

2.4. Stability of the Catalyst

2.4.1. Catalytic Stability

The recycling and reusability of a heterogeneous catalyst are important parameters for economic and environmental considerations \[66\]. The TOC abatement obtained using the same TiO\(_2\)/Fe\(_3\)O\(_4\)-CS(2) beads for four consecutive runs is depicted in Figure 4. After each run, the catalyst was washed with distilled water and dried at ambient temperature. The results showed that TOC removal remained almost constant for four cycles of reuse. The slight decrease (\(\approx 6.7\%\)) observed in the fourth cycle could be attributed to the modification of the physicochemical properties of the catalyst’s surface by the effect of UV-LED irradiation and the presence of H\(_2\)O\(_2\) as an oxidant. In addition, possible leaching of Fe ions in the reaction medium was checked. The leached amount of Fe after each run did not exceed 1.7 mg L\(^{-1}\), corresponding to 0.5% of the initial metal content in catalytic beads. These results revealed an excellent structural stability of the catalytic beads and minimal leaching of iron according to the environmental standards demanded by the European Union (<2 mg L\(^{-1}\)) \[67\].

2.4.2. Characterization of Catalyst before and after Use

SEM Analysis

The SEM images of TiO\(_2\)/Fe\(_3\)O\(_4\)-CS(2) beads before and after use are illustrated in Figure 5. As shown, the surface of the beads is smooth, indicating that iron and TiO\(_2\) are attached to CS. The use of high magnification highlighted the observation of TiO\(_2\) nanoparticles on the surface of the beads. The comparison of images in Figure 5a,b showed that, after four consecutive cycles, the surface of the beads was slightly damaged by oxidizing conditions and UV-LED irradiation, which explained the leaching of the metal.
XRD Analysis

In order to determine the crystalline structure of the TiO$_2$/Fe$_3$O$_4$-CS(2) beads, an XRD analysis was performed. In the XRD patterns (Figure 6a), the peak positions at 2Theta = 30.14°, 35.59°, 43.47°, 53.87°, 57.41° and 62.65° corresponded, respectively, to the Miller indices of (220), (311), (400), (422), (511) and (440) of the crystalline structure of Fe$_3$O$_4$, and the peak positions at 2Theta = 25.29°, 37.78°, 38.59°, 48.01°, 55.03°, 68.74°, 70.25°, 75.01°, 82.62° could be attributed to the diffraction planes of (110), (101), (004), (220), (105), (400), (220), (215) and (312) of the crystalline structure of TiO$_2$. The obtained peaks are well matched with standard data [ICPDS-ICDD card N°:00-019-0629 for the Fe$_3$O$_4$ magnetite and 00-021-1272 for the TiO$_2$ anatase.}
XRD Analysis

In order to determine the crystalline structure of the TiO\(_2\)/Fe\(_3\)O\(_4\)-CS(2) beads. In fact, indexing the pattern exhibited the crystal structure of the TiO\(_2\) anatase (ICDD 00-021-1272). However, the peak positions at 2Theta = 30.14°, 35.59°, 43.47°, 48.01°, 55.03°, 57.41° and 62.65° corresponded, respectively, to the Miller indices of (220), (311), (400), (421), (422) (511) and (440) of the crystalline structure of maghemite Fe\(_3\)O\(_4\) (ICDD 00-039-1346) instead of magnetite Fe\(_3\)O\(_4\). Fe\(_3\)O\(_4\) had the same spinel structure as magnetite, but it only contained iron in the trivalent Fe(III) state [68], which indicated the oxidation of Fe\(_3\)O\(_4\). Furthermore, using the Debye–Scherer equation, the grain size of TiO\(_2\) was estimated at 64.5 nm, while the size of Fe\(_3\)O\(_4\) was around 11.6 nm, indicating that the beads exhibit superparamagnetic behavior [69].

Magnetic Properties Analysis

The magnetization curve of the TiO\(_2\)/Fe\(_3\)O\(_4\)-CS(2) beads revealed a saturation intensity equal to 11.40 emu/g (Figure 6b). This low value is due to the presence of non-magnetic materials (CS and TiO\(_2\)) [70]. The magnetization intensity of the beads used was almost the same, and it was estimated at 10.48 emu g\(^{-1}\), which means that the beads have a good stability of the magnetic properties after four consecutive cycles.

3. Materials and Methods

3.1. Chemical Products

All chemicals were of analytical–laboratory grade and applied without further purification. Chlordimeform, chitosan, sodium hydroxide, ferrous sulfate iron (II), iron (III) chloride, titanium oxide and potassium titanium oxide oxalate dehydrate were purchased from Sigma-Aldrich (Madrid, Spain). Acetic acid, sulfuric acid and nitric acid were supplied by Analar Normapur (Radnor, PA, USA). Acetonitrile (HPLC-grade) was purchased...
from Fisher Scientific (Loughborough, UK). Ultrapure water obtained through reverse osmosis technology (Basic 360) was utilized throughout all the experiments.

3.2. Preparation of TiO$_2$/Fe$_3$O$_4$-Chitosan Magnetic Beads

An eco-friendly, low-cost and simple approach was used to synthesize the composite catalysts. Magnetic TiO$_2$/Fe$_3$O$_4$-CS beads were prepared via a precipitation method using sodium hydroxide (1 M) as a precipitating agent. First, 2% CS gel solution was prepared by dissolving 1 g of CS in acetic acid (1%) under stirring at room temperature. After the total dissolution of CS flakes, 5 mmol of iron salts at a molar ratio Fe$^{3+}$:Fe$^{2+}$ = 2:1 was added. Then, the TiO$_2$ nanoparticles were blended in the iron salts–CS gel solution. The amount of TiO$_2$ varied from 5 mmol, 10 mmol to 15 mmol, which corresponds, respectively, to the molar ratios TiO$_2$/Fe equal to 1, 2 and 3. By adding TiO$_2$, the color of the solution changed from orange to white, as shown in Figure 7A. Then, the mixture was dropped through a syringe into the hardening sodium hydroxide solution to create spherical CS gel beads. The beads were washed several times with deionizer water to remove any residual alkali and dried in an oven at 50 °C.

![Figure 7. (A) Chitosan gel/Fe$_3$O$_4$ solutions. (B) Wet chitosan beads at a molar ratio TiO$_2$/Fe: (1) 0; (2) 1; (3) 2 and (4) 3. (C) Superparamagnetic behavior of the TiO$_2$-CS beads at a molar ratio TiO$_2$/Fe = 2.](image)

As seen in Figure 7B, the obtained beads are black for those containing iron only, and they take on a greenish coloration in the presence of TiO$_2$. All the prepared beads exhibited magnetic behavior in the presence of an external magnetic field (Figure 7C). The TiO$_2$-CS beads were prepared following the same alkaline co-precipitation method without addition of iron salts.

3.3. CDM Removal Assays

The PEF process of CDM degradation was performed in a cyclic mode, as shown in Figure 8. The process was composed of two reactors connected in series, allowing the treatment of (400 mL, 30 mgL$^{-1}$) CDM solution. A recirculation flow (200 mL min$^{-1}$) was set using a pump to connect the two reactors.
3.3. CDM Removal Assays

The PEF process of CDM degradation was performed. In the first reactor, a solution of CDM was added previously as a support electrolyte at a concentration of 0.01 M, and the pH was adjusted to 3 using sulfuric acid solution. Air bubbling was maintained 15 min before the start of the reaction and through the treatment in order to saturate the medium with oxygen.

The second reactor is a cylindrical glass cell. A low-consumption UV-LED lamp (365 nm, 40 W, 550 lumens) from Luckylight electronics was placed above it, emitting at a wavelength equal to 365 nm. The catalyst was added into the photocatalytic reactor to promote its activation and avoid its electrochemical degradation, especially in the presence of a powerful oxidizing BDD anode in the first reactor.

To highlight the contribution of (photo)electrolysis + H₂O₂ and photocatalysis processes to the degradation of CDM, assays were conducted, respectively, without catalytic beads and in the absence of a current. Likewise, to evaluate the adsorption process contribution, another assay was conducted in the absence of UV irradiation and a current.

3.4. Analytical Methods

3.4.1. Determination of CDM Concentration

During experiments, the samples were collected and filtered prior to analysis through a 0.45 µm pore-size cellulose acetate membrane. CDM was quantified by HPLC (Agilent 1260 equipped with UV detector) with a C18 reverse-phase (4.6 mm × 250 mm, 5 µm; Agilent) column. The diode array detector was set at a fixed wavelength equal to 240 nm. The eluent was water/acetonitrile (60/40), with a flow rate of 1 mL min⁻¹.

3.4.2. Determination of Carboxylic Acids Concentrations

To identify and quantify the carboxylic acids generated during electrolysis, an HPLC was used with a diode array detector fixed at 206 nm. A Rezex™ ROA-Organic Acid H⁺ (8%) (300 × 7.8 mm, i.e., 8 µm) column was used and placed in an oven at 60 °C. The eluent was 0.005 N H₂SO₄ solution pumped at a flow rate of 0.5 mL min⁻¹. The

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**Figure 8.** Cyclic electro-photocatalytic reactors: (I) electrochemical reactor: (1) power supply, (2) carbon felt electrode, (3) BDD electrode, (4) air supply, (5) magnetic stirrer, (6) peristaltic pump; (II) photocatalytic reactor: (5) magnetic stirrer, (7) UV-LED lamp, (8) catalytic beads.

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identification of carboxylic acids was based on a comparison of the retention times with those of pure standards.

3.4.3. Determination of Ions Concentrations

The ions generated were quantitatively followed by an ion chromatography system Dionex ICS-3000. The separation of ions was performed by a Metrosep A Supp 5 column (4.0 × 250 mm). The eluent was 3.2 mmol L⁻¹ Na₂CO₃ and 1 mmol L⁻¹ NaHCO₃ at a flow rate of 0.7 mL min⁻¹. The limit of quantification (LOQ) of all chromatographic methods was 0.1 mg L⁻¹.

3.4.4. Total Organic Carbon Measurements

The total organic carbon (TOC) was measured via catalytic high-temperature combustion by multi N/C 3100 equipment (Analytic Jena, Germany) coupled with a non-dispersive infrared detector. The percentage removal of TOC was calculated using the following equation:

\[
\text{% removal of TOC} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100 \tag{4}
\]

with TOC₀ and TOCₜ representing the initial TOC and that at instant t.

3.4.5. Determination of Fe Concentration

The Fe concentration was determined by Inductively Coupled Plasma ICP (model: Optima 4300 DV Perkin Elmer Instruments). To obtain a metal solution from the heterogeneous catalyst, an acid digestion method was carried out using a concentrated nitric acid solution with the beads and placed on an autoclave at 121°C (Danish standard DS250).

3.4.6. Determination of H₂O₂ Concentration

The concentration of H₂O₂ was determined by a colorimetric method using a (Thermo Electron Corporation Helios) spectrophotometer because a titanium oxalate complexing agent can react with H₂O₂, producing a yellow peroxy–titanium complex, which absorbs at \( \lambda_{\text{max}} = 400 \text{ nm} \) [71].

3.4.7. Characterization of the Synthesized Catalysts

The surface morphology of the catalytic beads was observed using a scanning electron microscope (JEOL JSM-6700F). The crystalline structure of the obtained catalysts was determined by X-Ray Diffraction (XRD, X’Pert PRO MPD). Finally, the Physical Properties Measurement System equipment (PPMS Ever Cool-II 9T) with a Vibrating Sample Magnetometer (VSM) at 298 K was used to explore the magnetic properties of the catalysts.

3.5. Specific Energy Consumption

The electric energy consumption (EEC) per unit volume of treated solution (kWh m⁻³) was calculated according to the following equation [72]:

\[
\text{EEC} \left( \text{kWh m}^{-3} \right) = \frac{I \times E \times t}{V} \tag{5}
\]

where I is the current applied (A), E is the average cell voltage (V), t is the electrolysis time (h), and V is the solution volume (L or m³).

4. Conclusions

In summary, magnetic TiO₂/Fe₃O₄-CS beads were synthesized following an easy in situ co-precipitation approach. The molar ratio TiO₂/Fe was studied, and the enhanced catalytic activity of TiO₂/Fe₃O₄-CS, with a molar ratio equal to 2, was probably due to the reduced recombination of charge carriers on the surface of the catalyst.

The performance of the PEF process using TiO₂/Fe₃O₄-CS(2) as a photocatalyst for the treatment of real wastewater doped with CDM insecticide was evaluated under optimal conditions.
experimental conditions. Complete CDM removal was attained in 1 h, and more than 80% TOC abatement was achieved after 6 h of treatment, with simple carboxylic acids as the main by-product.

The catalytic activity of TiO$_2$/Fe$_3$O$_4$-CS(2) was satisfactorily validated in four consecutive cycles, and a slight decrease was obtained between the first and the fourth runs. Post-reaction catalyst characterization showed a high stability of magnetic properties despite the oxidation of Fe$_3$O$_4$ to Fe$_2$O$_3$, which is known for its good catalytic activity, sometimes similar to Fe$_3$O$_4$. Thus, the slight decrease in the catalytic activity could be attributed to the leaching of metals caused by the effect of the oxidizing conditions and UV-LED irradiation on catalytic beads.

This study offered a simple approach for constructing an eco-friendly, simple recovery and efficient bifunctional catalyst for advanced oxidation processes for treating recalcitrant organic pollutants in wastewater.

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