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Enhanced Photocatalytic Kinetics Using HDTMA Coated TiO$_2$-Smectite Composite for the Oxidation of Diclofenac under Solar Light

Imen Fellah [1,2], **Ridha Djellabi** [3,4,*] , **Hédi Ben Amor** [1], **Noureddine Hamdi** [2,5] , **Marcela Frias Ordonez** [4] and **Claudia L. Bianchi** [4,*]

1. Engineering School (ENIG), RL Processes, Energetic and Environment and ElectricSystems (PEESE), University of Gabes, Gabes 6072, Tunisia
2. Laboratory of Composite Materials and Clay Minerals, National Center for Research in Materials Sciences (CNRSM), Soliman 8020, Tunisia
3. Department of Chemical Engineering, Universitat Rovira i Virgili, 43007 Tarragona, Spain
4. Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milano, Italy
5. Higher Institute of Sciences and Techniques of Waters, University of Gabes, Gabes 6072, Tunisia
* Correspondence: ridha.djellabi@yahoo.com (R.D.); claudia.bianchi@unimi.it (C.L.B.)

Abstract: Slow kinetics is one of the capital issues of photocatalytic technology because of its heterogeneous nature, which involves multi-step processes. Herein, we show that the simple modification of the sol-gel-based TiO$_2$-smectite composite by hexadecyltrimethylammonium bromide (HDTMA) significantly boosts adsorption and photocatalytic efficient sol-gel-based light towards the removal of diclofenac from water. Three photocatalysts were prepared, including TiO$_2$, TiO$_2$-smectite, and HDTMA-TiO$_2$-smectite. The materials were characterized to understand the surface interaction and crystal characteristics. In terms of photoactivity, it was found that the addition of HDTMA to TiO$_2$-smectite improved the removal rate by twice. HDTMA changes the functional groups to TiO$_2$-smectite composite allowing enhanced adsorption and photoactivity through the so-called Adsorb and Shuttle process. The recycling tests show that HDTMA-TiO$_2$-smectite can be used up to four times with good performance. This modification approach could intensify the removal of pollutants from water instead of using complicated and costly techniques.

1. Introduction

Water pollution by pharmaceutical compounds, widely used in human and veterinary medicine, is a capital environmental issue due to these compounds' massive use and discharge [1,2]. At a large scale, several approaches are applied to physically break down these compounds into CO$_2$ and mineral salts. However, process intensification is always needed to fit with the requirement of nowadays companies following mostly these factors: the fast removal of pollutants, the selectivity in some cases, the low cost of the treatment, including the materials design and operating needed conditions, and the sustainability of the process [3]. Therefore, the research community is asked to develop materials that can be used at a large scale as an alternative to existing ones. Photocatalytic technology has been employed at the lab scale for more than 40 years for environmental remediation and energy production [4–6]. This process is based on the excitation of a photocatalyst with light energy equal to or greater than the band gap of the photocatalyst [7]. Immediately, a redox system of e$^-$/h$^+$ on the conduction and valence band takes place. The first step in photocatalysis is light absorption which requires enough light energy with enough intensity. Photocatalysis is mainly designed for solar light applications [8,9]. Because of this, much focus on the intensification of light absorption was reported using approaches such as doping [10,11],

photosensitizing [12,13], and so on. TiO_2 has been the most used photocatalyst for water treatment due to its photonic performance under UV light. However, to boost its activity in the visible range, a lot of surface and structure modifications have been reported, such as doping [10,14], heterostructures, e.g., TiO_2/Ag_3PO_4 [15], polymer sensitizing [16,17], a combination of carbon materials [18] and so on.

Once the photocatalyst receives optimum energy, a maximum excitation occurs depending on working conditions. However, photoexcitation is only a step in a complicated process. The separation of e^-/h^+ is directly associated with the photocatalytic rate. Naturally, the oxidation of water molecules by positive holes or/and the reduction of oxygen by photogenerated electrons partially limit the recombination of charges. Material modification could decrease the recombination charges by building heterojunction systems [19,20], allowing the interfacial transfer of electrons and holes. Even though the separation of charges is maximized, the photocatalytic rate is mainly based on the interaction of the pollutants in water with these separated charges and produced reactive oxygen species (ROS). The physical interaction is the first step before the photocatalytic oxidation of organic pollutants. Since the produced ROS remain fixed mostly on the surface of the photocatalyst, and their lifetime is accounted for a few nanoseconds, a photocatalyst with enhanced adsorption might lead to a better photocatalytic rate. Using a naked photocatalyst, if huge adsorption occurs, the surface will be blocked from light, and less excitation rate occurs. However, coating semiconductors nanoparticles on the surface of highly adsorptive materials is a perfect solution to make the Adsorb and Shuttle Process into action [21–23]. The adsorptive area can concentrate the pollutant species around the photoactive area to be oxidized continuously and systematically. In our recent study [24], an enhanced Adsorb and Shuttle Process was obtained through the hybridization of $BiPO_4$ and Montmorillonite, followed by HTDMA coating.

The visible light response was enhanced due to interface interactions between $BiPO_4$ and HTDMA. This study aims to develop TiO_2 based composite with excellent adsorption ability and photocatalytic activity under solar light via a simple green approach. No studies have investigated the role of HTDMA in improving the photoactivity of TiO_2 under solar light. Herein, sol-gel as-prepared TiO_2-smectite was modified by HTDMA to enhance the photocatalytic removal of diclofenac sodium from the water. Diclofenac sodium is an analgesic drug with a large annual consumption (940 tons/year). It is a common pharmaceutical water contaminant with high hydrophobicity and stability. Although TiO_2 is not a visible light-responsive photocatalyst, it was used in this study to perform a solar light-based photocatalytic reaction as its hybridization with smectite and HDTMA would improve its photoactivity under solar light. The photocatalytic activity of three materials was comparatively studied, including TiO_2, TiO_2-smectite, and HDTMA-TiO_2-smectite.

2. Results and Discussion

2.1. Characterization

XRD spectra of TiO_2, Smectite-TiO_2, and HDTMA@Smectite-TiO_2 are shown in Figure 1a. Diffraction peaks were produced at 25.3, 37.8, 48.0, 53.9, 55.0, 62.7, and 75.0°, indicating the anatase phase of TiO_2 crystals [25]. Smectite XRD pattern shows two strong d(001) (Smectite) d(001) Kaolinite basal spacing reflections at around d_{001} = 14.35° and d_{001} = 7.16°, respectively [26]. Nevertheless, no d(001) peak can see after the coating of TiO_2 on the surface of the smectite. The structure of Smectite-TiO_2 is named "delaminated," confirming the insertion of TiO_2 in the interlayer of smectite and on the surface of smectite. After the hybridization of Smectite-TiO_2 with HDTMA, a slight increase in TiO_2 diffraction peaks has been found. This can be explained by the surface interactions of Smectite-TiO_2 with HDTMA. FTIR spectra of different samples are presented in Figure 1b. The spectrum of bare smectite shows bands at 526.40 and 1036, 93 cm^{-1}, corresponding to Si-O-Al and Si-O-Si stretching peaks, respectively [26]. The absorption band at 1656 cm^{-1} (H-O-H) may be related to the presence of adsorbed water. The band at 1430 cm^{-1} is due to calcite vibration [27]. The bands at 3633 and 3410 cm^{-1} are associated with the –OH stretching

vibration of adsorbed water and Si-O surface, respectively. Regarding bare TiO_2, broadband approximately at 400 to 800 cm^{-1} is due to the characteristic vibrations of Ti-O bonds of titanium dioxide crystal lattice [13]. The peak at 1640 cm^{-1} is assigned to the vibration of the O-H bond. The large band at 3330 cm^{-1} is due to the physically adsorbed water molecules. The broad and intense band at 3330 cm^{-1} is associated with the physic-absorbed water in the solid [28]. For the Smectite-TiO_2, the characteristic band of Ti-O appears at 400 to 800 cm^{-1}. FTIR confirmed the fixation of HTDMA in HDTMA@Smectie-TiO_2, wherein two peaks at around 2936 and 2871 cm^{-1} appeared due to the presence of CH_2 and CH_3, respectively [29].
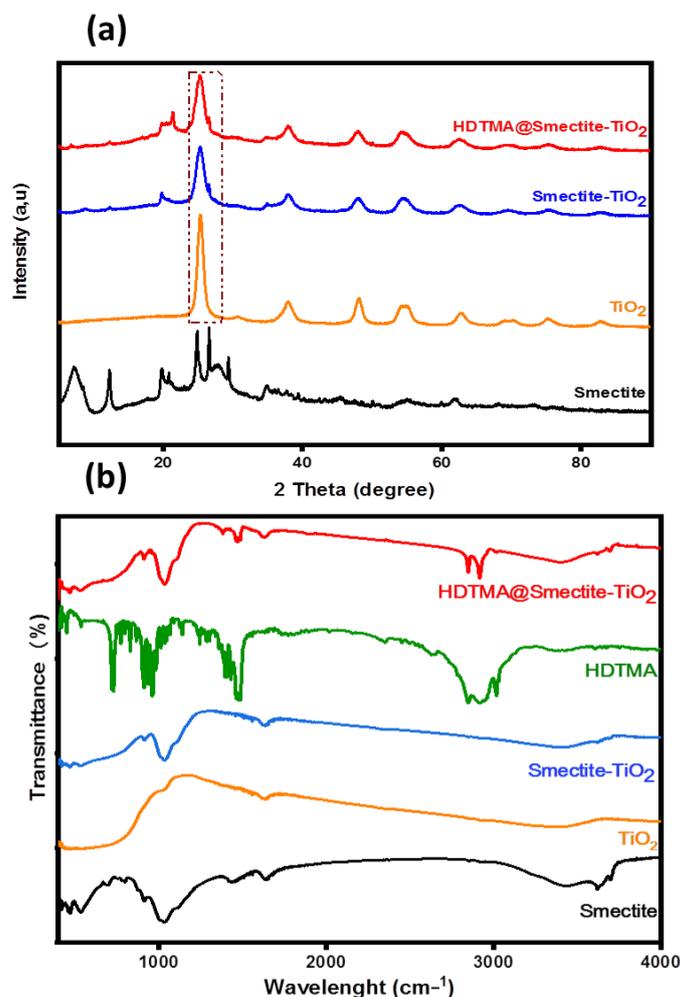
Figure 1. (**a**) XRD patterns of Smectite, TiO_2, Smectite-TiO_2, and HDTMA@Smectite-TiO_2. (**b**) FTIR spectra of Smectite, TiO_2, Smectite-TiO_2, HDTMA, HDTMA@Smectite-TiO_2 samples.

The results of the survey XPS analysis carried out on TiO_2, Smectite-TiO_2, and the HDTMA@SmectiteTiO$_2$ samples are presented in Figure 2a. Spectra of Ti2p (Figure 2b) in different photocatalysts display spin-orbit peaks due to Ti(2p3/2) and Ti(2p1/2) having a slitting value of around 5.7 eV, confirming the generation of the anatase phase. The binding energies are found at ~458.6 eV and ~464.1 eV for Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively. In terms of Smectite-TiO_2 and the HDTMA@Smecite-TiO_2, the positions of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ are slightly shifted due to the interactions between TiO_2 and smectite' elements or/and HDTMA, which may influence the electronic state of the Ti element in the TiO_2 lattice. The HDTMA@Smecite-TiO_2 spectrum shows a significant decrease in the intensity of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks because of the dilution effect. O1s spectrum of TiO_2 displays one peak located at a binding energy of around 530.2 eV, which is due to Ti-O-Ti units in the TiO_2 lattice. This peak is positively shifted in the cases of Smectite-TiO_2 and HDTMA@Smecite-

TiO$_2$ spectra as a result of surface interactions. The peak of C1s in TiO$_2$ and Smectite-TiO$_2$ might be due to the contamination. The peak of C1s in HDTMA@Smecite-TiO$_2$ is considerably intense and large, which confirms the fixation of HDTMA.
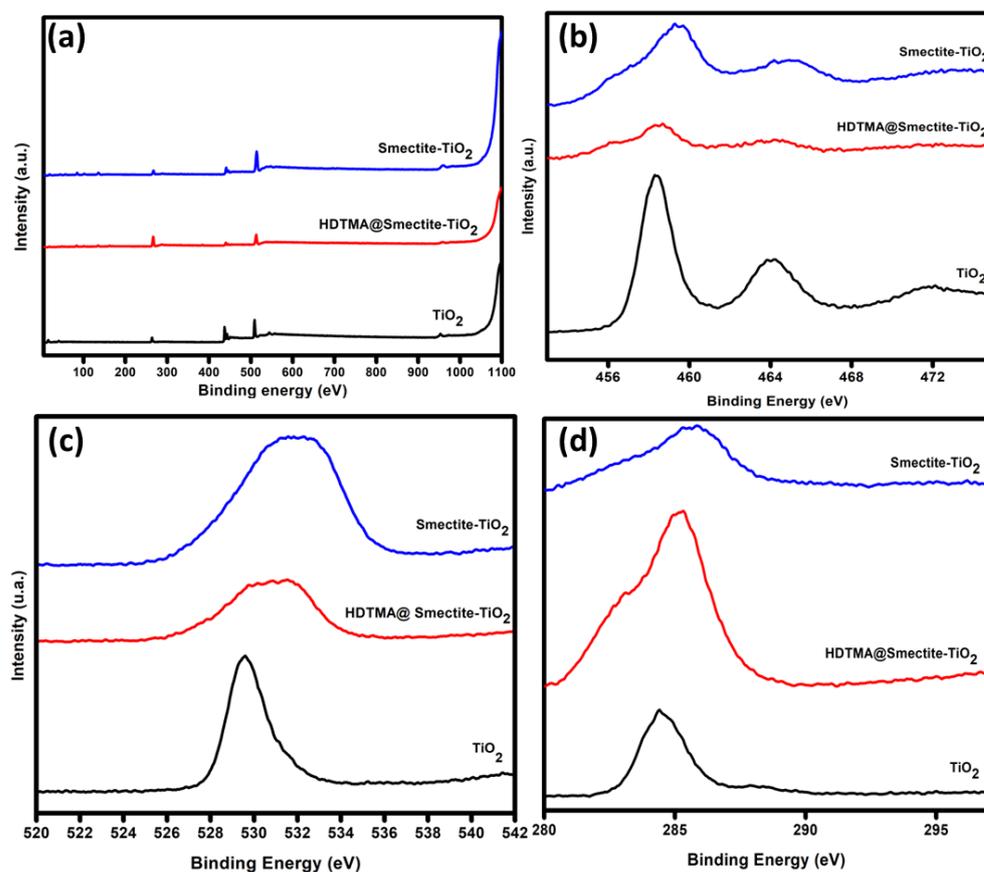

Figure 2. (**a**) XPS survey spectra of TiO$_2$, Smectite-TiO$_2$, and HDTMA@Smectite-TiO$_2$ samples. (**b**) Ti2p high-resolution profiles. (**c**) O1s high-resolution profiles. (**d**) 1Cs high-resolution profiles.

2.2. Photocatalytic Activity

2.2.1. Control Experiments

The adsorption and solar light-driven photocatalytic performances of TiO$_2$, Smectite-TiO$_2$, and HDTMA@Smectite-TiO$_2$ were studied comparatively, and the results are shown in Figure 3. It can be deduced that the coating of Smectite by TiO$_2$ led to improve adsorption capacity compared to naked TiO$_2$, which is an advantage in promoting photocatalytic activity. Under solar irradiation, TiO$_2$ showed a slight photoactivity activity, while the removal rate by Smectite-TiO$_2$ was slightly enhanced. The combination of photocatalytic nanoparticles and adsorbing materials puts the Adsorb & Shuttle Process into action, wherein the smectite promotes the fixation of diclofenac molecules on the surface near the photoactive TiO$_2$, creating a successful adsorb and photooxidation cycle under solar light [22]. In addition, adsorbed molecules could be oxidized by direct positive holes, in addition to ROSs. To improve further the Adsorb & Shuttle Process, HDTMA was hybridized with Smectite-TiO$_2$, and its function is to accelerate the adsorption several times, and thus the photooxidation of diclofenac molecules. HDTMA@Smectite-TiO$_2$ showed excellent adsorption and photocatalytic oxidation within a lesser 15 min; more than 70% of diclofenac was removed under solar light. In conventional photocatalysis, the slaw kinetics of redox reaction has been reported widely, limiting the competition of photocatalytic technology with existing technologies. HDMTA is very significant in improving the kinetics of photocatalytic oxidation of organic pollutants. It can fix organic molecules through cation-exchange reactions and enhance the hydrophobicity of the photocatalyst.
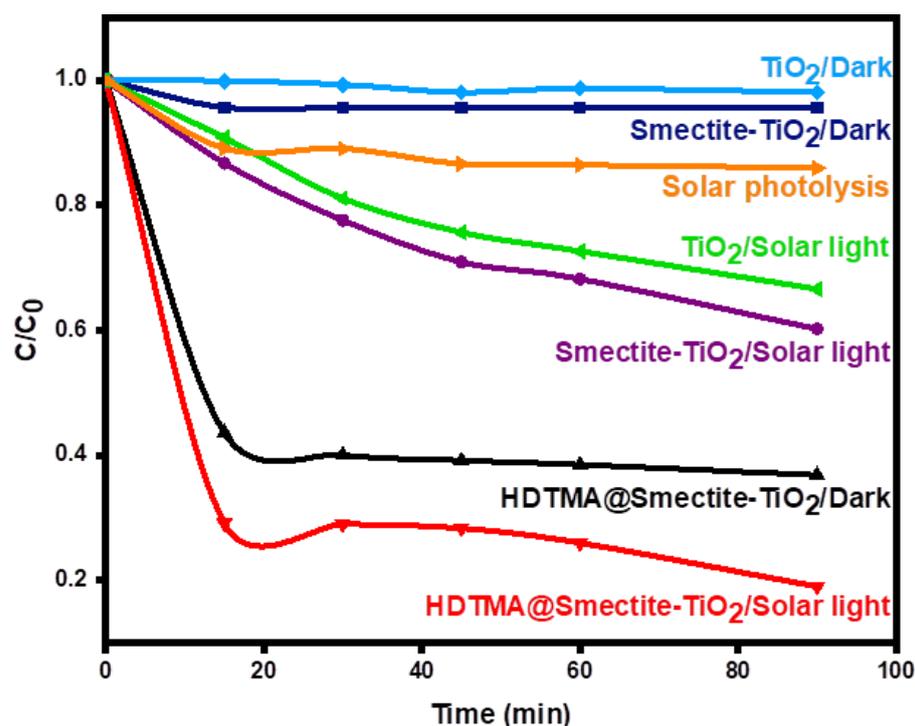
Figure 3. Adsorption, photolysis, and photocatalytic oxidation of diclofenac under solar irradiation by TiO$_2$, Smectite-TiO$_2$, and HDTMA@Smectite-TiO$_2$. [Photocatalyst]: 0.5 g/L, [Diclofenac]: 100 ppm.
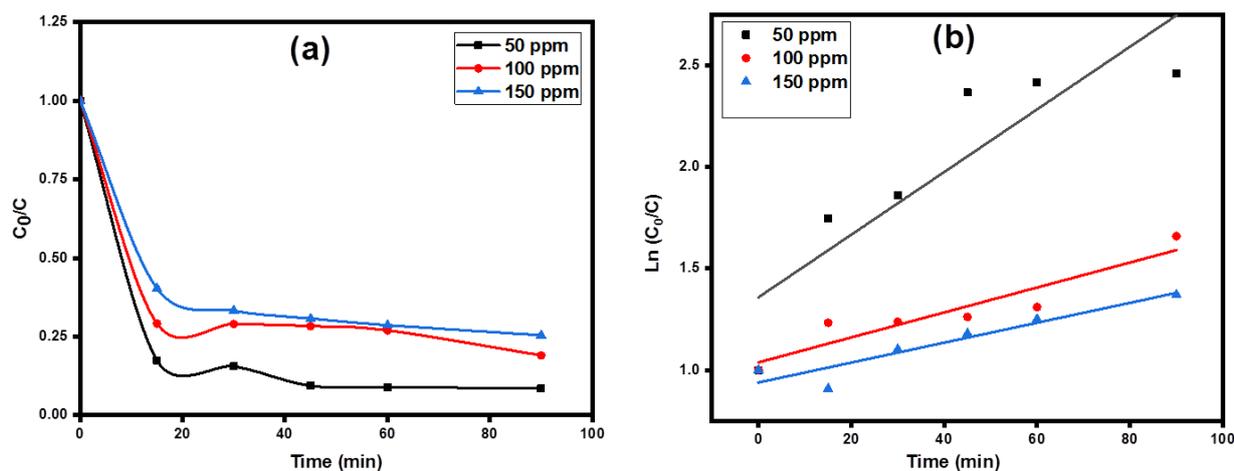
2.2.2. Effect of Photocatalyst Mass

To further prove the role of HDTMA, adsorption and photocatalytic tests were carried out using Smectite-TiO$_2$ and HDTMA@Smectite-TiO$_2$ at different photocatalyst masses (Figure 4). In terms of Smectite-TiO$_2$, it can be noticed that photocatalytic oxidation is more predominant than the adsorption process; thus, the photocatalytic rate increases with the photocatalyst mass increase. However, in the case of HDTMA@Smectite-TiO$_2$, both the adsorption process and photocatalytic oxidation were promoted, wherein the photodegradation rate reached about 95% at the mass of 1g/L. This is mainly due to Adsorb and Shuttle Process, wherein the molecule of diclofenac was adsorbed better on the surface of HDTMA@ Smectite-TiO$_2$ than the Smectite-TiO$_2$.
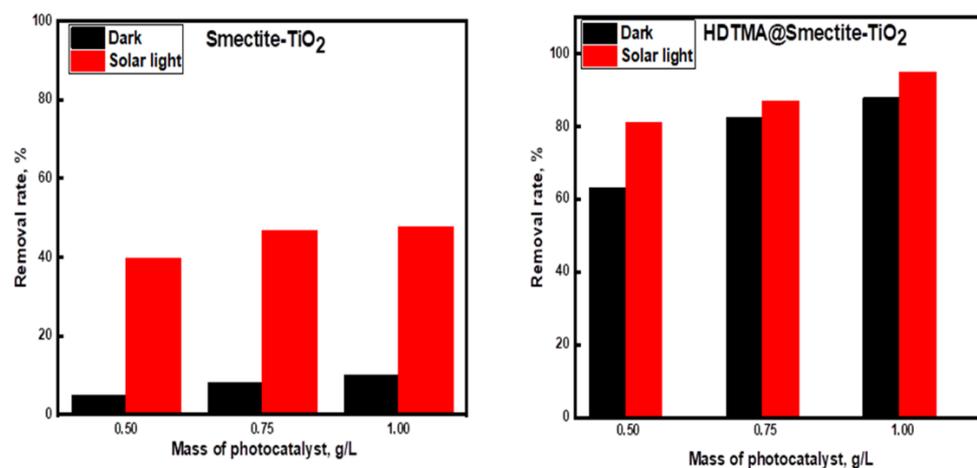
Figure 4. Effect of photocatalyst mass (Smectite-TiO$_2$ and HDTMA@Smectite-TiO$_2$) on the removal of diclofenac by adsorption and photocatalytic activity under solar light, [diclofenac]: 100 ppm, contact time 90 min.

2.2.3. Effect of Initial Concentrations and Kinetics

The effect of diclofenac concentration was studied at 50, 100, and 150 ppm. Figure 5a shows that the more the diclofenac concentration increases, the more photocatalytic oxidation decrease. The adsorption/oxidation of diclofenac is adsorbing sites, and ROS yield depends on it. Therefore, the higher concentration would limit the fixation of more diclofenac molecules and ROS oxidation at a given photocatalyst mass. Moreover, a high yield of diclofenac molecules could absorb light irradiation (screen effect). To determine the degradation rate of the kinetic reaction, the pseudo-first-order model (PFO) has been investigated because of its extensive use in studies on the degradation of various pharmaceutical compounds.

Figure 5. (**a**): Effect of diclofenac concentration on its photocatalytic activity under solar light using HDTMA@Smectite-TiO$_2$. [Photocatalyst]: 0.5 g/L (0.02 ∗ 40), contact time 90 min, (**b**) Linear plot of the kinetic data based on the parameters in Equation (2).

The PFO was fitted by the following Equation (1):

$$Ln\frac{C_0}{C} = K * t \qquad (1)$$

where *K* is the rate constant (min^{-1}) of the PFO reaction.

Figure 5b shows a linear plot of the kinetic data at different concentrations. As can be seen, the reaction rate constant was inversely proportional to the concentration values tested. 0.0154, 0.0064, and 0.0049 min^{-1} for 50, 100, and 150 ppm, respectively. This decrease of reaction rate constant with the increase of the concentrations is the result of inhibition of the action of active hydroxyl radicals due to the rise of intermediate products in the reaction at high concentrations.

2.2.4. Recycling Tests

Recycling tests using HDTMA@Smectite-TiO$_2$ were performed four times, and the results are shown in Figure 6a. After each use, the photocatalyst was washed with acetone and water. After four tests, the material was characterized by FTIR (Figure 6b). The tests showed a decrease in the photocatalytic rate for some reason. First, the accumulation of by-products on the surface of the photocatalyst might decrease the adsorption ability; even though acetone was used to clean the surface, it might not be enough to remove all by-products [30]. In addition, the loss of photocatalyst during the recycling would also be an issue, reducing the mass/volume ratio. However, the capital issue here is the loss of some quantity of HDTMA after the fourth use, as seen in FTIR spectra. Peaks representing CH$_2$ and CH$_3$ decreased significantly. Herein, it would be recommended to find better fixation approaches to coat photocatalysts by HDTMA rather than the microwave. For

example, the ultrasonic-assisted coating would be applied to prepare HDTMA-coated photocatalysts [31].
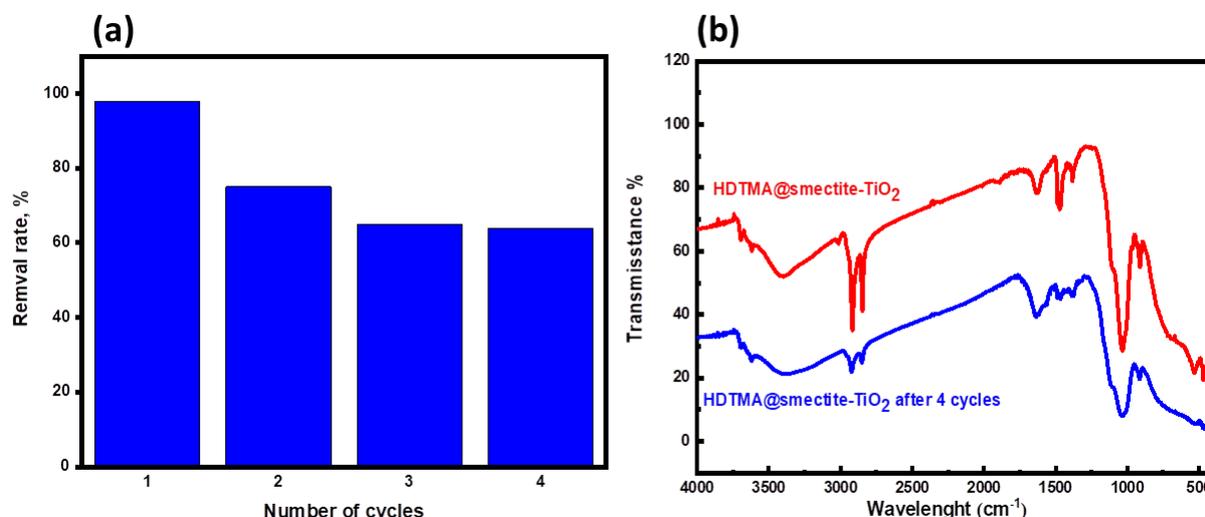
Figure 6. (**a**) Recyclability of HDTMA@Smectite-TiO$_2$ for four photocatalytic cycles. (**b**) FTIR spectra of HDTMA@SmectiteTiO$_2$ of samples before and after photodegradation.

3. Materials and Methods

3.1. Synthesis of Photocatalysts

Gray smectite derived from Djebel Aidoudi El Hamma- Gabes (Tunisia) was used as support material. The cation exchange capacity (CEC) of row smectite was 64.28 meq/100 g. The synthesis of Smectite-TiO$_2$ was performed by impregnation with Titanium(IV) n-butoxide according to the following process: 1g of smectite was dispersed in 20 mL of deionized water and sonicated for 20 min. Then, 7.12 mL of Titanium(IV) n-butoxide was dissolved in 20 mL of ethanol. The mixture was added dropwise into the suspension of smectite and still aging under vigorous stirring at 80°C for 4 h. The photocatalyst suspension was washed properly with deionized water, and then it was dried overnight at 120 °C. The obtained Smectite-TiO$_2$ was ground and calcined at 400 °C for 2 h. HDTMA@Smectite-TiO$_2$ was prepared by mixing Smectite-TiO$_2$ in HDTMA solution, followed by microwave treatment, and then dried overnight at 120°C. Bare TiO$_2$ is prepared by sol-gel using Titanium(IV) n-butoxide precursor.

3.2. Characterization of Materials

The as-prepared materials were characterized by Fourier transforms infrared spectroscopy analyses (FT-IR) analysis on the as-prepared samples using a Bruker Vertex 70 spectrophotometer (Bruker, Billerica, MA, USA). Spectra of XRD were recorded on a PANalytical X'PERT-PRO (Malvern, UK) diffractometer with monochromatic CuKα radiation (λ = 1.54056 Å). X-ray photoelectron spectroscopy spectra were obtained using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al Kα radiation (1486.6 eV). 1s level hydrocarbon-contaminant carbon was taken as the internal reference at 284.6 eV. For each sample, survey analyses in the whole range of the X-ray spectrum have been performed in order to determine the surface elemental composition. Similarly, high-resolution scans around C 1s, O 1s, and Ti 2p were acquired for the determination of the chemical environment surrounding every species.

3.3. Photocatalytic Test

Photocatalytic tests were performed under solar light simulator (35 W.m^{-2}, ULTRA VITALUX 300 W-OSRAM, OSRAM, Munich, Germany) irradiations. Tests were carried out as follows: 0.02 g of photocatalyst and 40 mL of diclofenac solution at 100 mg/L were stirred under solar light for 90 min. The adsorption tests were carried out under the same

conditions without solar irradiation. Samples for analysis were taken at different intervals, the suspension was removed, and the concentration of diclofenac was determined at 276 nm using a UV-vis spectrophotometer.

The removal rate of the diclofenac was calculated using the following equation (Equation (2)):

$$\text{Removal } (\%) = \frac{C_0 - C_e}{C_0} \tag{2}$$

where C_0 and C_e (mg/L) are the initial and at time t and at the equilibrium, the aqueous DFC concentrations

4. Conclusions

In the present work, we showed the results of the combination of HDTMA and Smectite-TiO_2 to enhance the kinetics of adsorption and photocatalytic oxidation of diclofenac under solar light significantly. The combination of TiO_2 with smectite and HDTMA led to shift Ti(2p3/2) and Ti(2p1/2) peaks, confirming the chemical interaction. On top of the role of HDTMA to increase the adsorption, the interactions with TiO_2 would improve the visible light response. Smectite-TiO_2 showed better photocatalytic activity compared to bare TiO_2. On the other hand, both the adsorption and photocatalytic oxidation rates were doubled after the coating of HDTMA on the surface of Smectite-TiO_2, along with a very fast mass transfer and kinetics. The recycling tests showed that the photocatalytic oxidation decreased by around 30% after the fourth use, which is due to the accumulation of by-products on the surface. In addition, FTIR analysis shows that the characteristic peaks of HDTMA were decreased, suggesting the partial degradation of HDTMA on the surface of the photocatalyst.

Compared to reported studies on the intensification of the photocatalytic process, the approaches of photocatalyst modification by HDTMA would be interesting because of the high efficiency, simplicity (HDTMA can be coated in a few min by microwave), and low cost. However, based on the material's recycling results, a better approach to enhance the fixation of HDTMA is much recommended to make the material more recyclable. I.F, H.B.A., H.B., R.D., M.F.O., C.L.B.

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