Photocatalytic Destruction of Caffeine on Sepiolite-Supported TiO$_2$ Nanocomposite

Başak Savun-Hekimoğlu $^{1,*}$, Zeynep Eren $^2$ and Nilsun H. Ince $^3$

$^1$ Institute of Marine Sciences and Management, Istanbul University, Istanbul 34134, Turkey
$^2$ Department of Environmental Engineering, Atatürk University, Erzurum 25030, Turkey; zeren@atauni.edu.tr
$^3$ Institute of Environmental Sciences, Boğaziçi University, Istanbul 34342, Turkey; ince@boun.edu.tr

* Correspondence: basak.savun@istanbul.edu.tr

Received: 19 November 2020; Accepted: 9 December 2020; Published: 10 December 2020

Abstract: The study is about the degradation of a common pharmaceutical and personal care product (PPCP) caffeine by photocatalysis under UV–visible light using pristine TiO$_2$ (P-25) and a lab-made nanocomposite of sepiolite–TiO$_2$. It was found that the dark adsorption of caffeine on P-25 was insignificant, but considerably high on the nanocomposite, owing to the high porosity and unique structure of sepiolite. The degradation of the compound in the presence of P-25 and Sep–TiO$_2$ followed the pseudo-first order and exponential decay kinetics, with a rate constant of 0.12 min$^{-1}$ and 0.50 min$^{-1}$, respectively. The efficiency of both catalysts for carbon mineralization was better at acidic pH, but that of the nanocomposite was significantly higher at all pH than that of the unmodified P-25 (36.1 against 9.6% at pH 6.0). The loading of TiO$_2$ on sepiolite was an important factor in the activity of the catalyst, as the maximum activity was observed at a loading ratio of 12.5 mmol per g sepiolite, which decreased at higher ratios of the semiconductor to sepiolite. Exposure of the treated samples to high-frequency ultrasound at pH 6 was found to enhance the degree of mineralization to 65.1 and 52.1% in the presence of the nanocomposite and P-25, respectively. The outcome was attributed to the unique properties of ultrasound for the cleaning of solid surfaces, for enhancing the mass transfer of solutes to heterogeneous interfaces, and for generation of excess hydroxyl radicals. Finally, the nanocomposite was found to be considerably stable, as it was easily recovered and used four times without a significant loss in activity.

Keywords: photocatalysis; sepiolite; caffeine; PPCPs; ultrasound; TiO$_2$

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are used for personal health, cosmetics and agribusiness, thus comprising of thousands of organic compounds. Caffeine is one of the most common PPCPs as it is an ingredient of coffee, tea, chocolate, cocoa and beverages, and widely used in the production of the prescription medicine and personal care products [1]. Being a highly soluble compound, caffeine is rapidly discharged (via wash water and excretion) into sewage treatment facilities with low biodegradability. As such, it is frequently detected in effluents of wastewater treatment operations, soil, groundwater systems and fresh water bodies, [2], where it exhibits toxic effects to aquatic organisms, and imposes a health threat to humans (hyperactivity and cardiovascular diseases) if the water is reclaimed and used in water supply systems [3].

The most effective methods of eliminating caffeine from water are adsorption [4,5], advanced biological treatment [6] and advanced oxidation processes (AOPs), using ozone, UV/peroxide, Fenton’s reagent and light/TiO$_2$ [7–9]. The popularity of TiO$_2$ in heterogeneous photocatalysis is due to its high photoactivity, low cost, high chemical stability, and non-toxicity. However, photocatalysis with TiO$_2$ has serious limitations, owing to the high bandgap energy, a rapid combination of e$^{-}$h$^{+}$ pairs
and the easily corroded surface of the metal [10]. Hence, much research has focused on increasing the efficiency of TiO$_2$ via immobilizing it on transition/noble metals and/or rare earth minerals, which by inhibiting the combination of e$^-$-h$^+$ pairs and photo-corrosion of the surface lead to significant enhancements in the activity of the semiconductor in the UV–visible band [10–12].

Clay minerals are layered structures of metallic clusters existing in the form of single or multi-layer sheets [13]. Being of natural origin, they are highly sustainable and require no processing for excavation. As such, they promise cost-effective and environmentally friendly means of applications in chemical, pharmaceutical, and environmental processes. Many clay minerals have a negative charge on their surface, leading to cation exchange and adsorptive properties, and a moderate reactivity [14–16]. Moreover, the slipping of the layers relative to one another leads to the rapid dispersion and easy conversion of the particles to the nano-scale [17].

Sepiolite is a clay mineral made of a hydrated magnesium silicate, arranged as five objects of talc-type sheets separated by parallel channels. The chain structure produces needle-like particles associated with the high porosity ($\sim$0.4 cm$^3$/g) and light weight of the mineral [18]. Sepiolite is also recognized with unique hydrophilicity (due to the high density of Si–OH groups), a high specific area ($>300$ m$^2$/g) and a slightly negative charge on its surface, leading to a low-to-medium degree of cation exchange capacity [19]. The mineral has been extensively used in adsorption processes, but is rarely in the synthesis of nanocomposites of metal oxides. The latter is a promising approach to the enhancement of the catalytic activity of TiO$_2$ via the combination of adsorptive and photocatalytic properties of the substances [20]. Since heterogeneous photocatalytic reactions occur on the photocatalyst surface, the adsorption of the target contaminants is important for their degradation. Therefore, the immobilization of TiO$_2$ onto porous solids is a promising tool in the development of effective and high-quality photocatalysts. The value of the method rises from the formation of nanocomposite materials with a high specific surface area and porosity that enable reactions on and at the surface boundaries [21].

Research with clay-supported TiO$_2$ nanocomposites has demonstrated the suitability of this modification for all kinds of applications. Sepiolite is a natural inexpensive and widely available clay mineral with reactive surfaces, so that it is a very attractive support material for immobilizing TiO$_2$ nanoparticles. It has been reported that sepiolite–TiO$_2$ composites have high adsorption capacity and photoactivity relative to TiO$_2$ [22,23]. In addition, sepiolite is reported to facilitate the migration of oxygen species to and away from the surface of the immobilized catalyst [24]. Moreover, embedding TiO$_2$ nanoparticles within the structure of sepiolite has been demonstrated to prevent the formation of macroscopic aggregates of photoactive particles, protect the erosion of the semiconductor surface and decrease the band gap energy of TiO$_2$ [25]. In summary, the use of sepiolite as a support material, particularly after surface modification, brings a positive synergy to the catalytic performance of the TiO$_2$ [26,27].

The present study aims to investigate the degradation of caffeine by sonolysis and photocatalysis using particles of P-25 obtained from the market, and a nanocomposite thereof, sonolytically synthesized by the immobilization of the metal on sepiolite, which is a highly abundant clay mineral in Central Anatolia. The performance of commercial and lab-made particles was compared based on the rate of caffeine decomposition, the degree of total organic carbon (TOC) decay and the stability of the particles, regarding their recovery and reuse. Finally, the treated samples in the photoreactor were exposed to the high-frequency ultrasound as a post-treatment option to enhance the degree of carbon mineralization.

2. Materials and Methods

Caffeine was purchased from Sigma-Aldrich, with >99% purity. The structure and chemical/physical properties of the compound are as given [28,29]:
was centrifuged and the precipitate was dried at 160 °C. For the preparation of the nanocomposites, the powdered sepiolite was added and the mixture was sonicated for 30 min in the 200 kHz bath under constant temperature (20 °C). The suspension was centrifuged and the precipitate was dried at 160 °C. For the preparation of the nanocomposites, the powdered sepiolite was added and the mixture was sonicated for 30 min in the 200 kHz bath under constant temperature (20 °C). The nanoparticles formed were separated by filtration through a 0.2 µm membrane (Millipore, Omni-Pore), washed thoroughly with deionized water and dried at constant temperature (160 °C) for 12 h [30]. Before the experiments and silent adsorption tests, the nanocomposite was further treated by mixing a small sample with 20 mL water and sonicating the suspension for 3 min in a water bath (35 kHz) to enhance the particle stability against agglomeration, thus to increase the adsorption properties of the catalysts.

| Characteristic                  | TiO₂     | Sepiolite | Sepiolite/TiO₂ |
|--------------------------------|----------|-----------|----------------|
| Size (nm)                      | 30–40    | 5 µm      | 23.50–91.28 nm |
| Specific surface area (m²/g)   | 35–65    | 160.77    | 210            |

The photoreactor was made of a stainless-steel vessel containing an adjustable glass reactor equipped with a xenon lamp having a wide emission spectrum in the UV–visible band (MAX-301, 300 W; Asahi Spectra, Tokyo, Japan). The sonolytic device used for synthesizing nanoparticles of sepiolite and for immobilizing TiO₂ we used a 200 kHz ultrasonic bath-type reactor (Quava-Mini, Japan), while for the sonication of light-treated samples we employed a plate-type, with a 120 W generator connected to three piezoelectric transducers emitting at 572, 856 and 1164 kHz (Ultraschall/Meinhardt, Leipzig, Germany). The solution temperature in the reactor was maintained at 25 ± 0.5 °C by cooling water passing around it, and the power density was kept constant at 0.21 W mL⁻¹.

2.1. Batch Adsorption Tests

The dark adsorption of caffeine (10 mg L⁻¹) on P-25, sepiolite and lab-made nanocomposites thereof (Sep–TiO₂) were carried out using 0.25, 0.5 and 1.0 g L⁻¹ of the particles during 1 and 2 h mixing at pH 3 to determine and compare their adsorption capacities.

2.2. Preparation of the Catalysts

For the preparation of the sepiolite, a sepiolite suspension was made by mixing the powders with deionized water and stirring for 30 min at 40 °C and keep quiescently for 24 h. The suspension was centrifuged and the precipitate was dried at 160 °C. For the preparation of the nanocomposites, after the dispersion of the powdered sepiolite in water by mixing it, 12.5 mM TiO₂ per g sepiolite was added and the mixture was sonicated for 30 min in the 200 kHz bath under constant temperature (20 °C). The nanoparticles formed were separated by filtration through a 0.2 µm membrane (Millipore, Omni-Pore), washed thoroughly with deionized water and dried at constant temperature (160 °C) for 12 h. Before the experiments and silent adsorption tests, the nanocomposite was further treated by mixing a small sample with 20 mL water and sonicating the suspension for 3 min in a water bath (35 kHz) to enhance the particle stability against agglomeration, thus to increase the adsorption capacities of the catalysts.

2.3. Photocatalysis with TiO₂ and Sep–TiO₂ Nanocomposite

The photocatalytic degradation of caffeine was carried out at three pH levels (3.0, 6.0 and 9.0), six initial caffeine concentrations (5, 10, 15, 20, 25 and 30 mg L⁻¹) and various doses of the catalysts for 15 and 30 min. The selection of the optimum values of these parameters was based on the rate of caffeine degradation and the percentage of TOC decay.

2.4. Post-Treatment of the Samples by High-Frequency Ultrasound

The test samples treated in the photoreactor for 15 and 30 min were post treated (with and without separation of the particles) by high-frequency ultrasound for 30 and 60 min at continuous and pulse modes (one-second on/one-second off) of operation to select the optimum conditions.

**Table 1.** The textural characteristics of the catalysts.

| Characteristic                  | TiO₂     | Sepiolite | Sepiolite/TiO₂ |
|--------------------------------|----------|-----------|----------------|
| Size (nm)                      | 30–40    | 5 µm      | 23.50–91.28 nm |
| Specific surface area (m²/g)   | 35–65    | 160.77    | 210            |
2.5. Analytical

Caffeine was analyzed by a Shimadzu LC-20AT HPLC with a 20A UV–vis photo diode array detector equipped with Inertsil ODS-3V (C18) (Hypersil BDS), 250 × 4.6 mm, 5 µm particle size column using water/methanol (50/50) as the mobile phase. The concentration of total organic carbon (TOC) was determined using a Shimadzu TOC-V CSH device operated at non-purgeable mode. The oxidation byproducts were identified by AB SCIEX QTRAP® 4500 LC-MS/MS system with a Turbo V™ ion source and electron spray ionization (ESI) were operated at the negative and “multiple reaction monitoring” modes. Samples after 100-fold dilution were injected into the ESI source at a flow rate of 10 µL min⁻¹ by direct infusion through a syringe pump. The mass spectrometer was operated at 500 °C; 20 psi (curtain gas); 40 psi (nebulizer gas); 60 psi (heater gas) and +5500 V (IS positive). The EMS spectra of the samples were obtained by scanning over the m/z range 70–210 at a rate of 10,000 Da s⁻¹, a collision energy of 10 V and a decluttering potential of 70 V.

The structure, morphology and size of pristine and sepiolite-immobilized particles of TiO₂ were determined by environmental scanning electron microscope (ESEM)-Philips XL30 ESEM-FEG/EDAX.

3. Results

3.1. Characterization of the Nanocomposite

SEM images of raw sepiolite, P-25 and Sep–TiO₂ nanocomposite are presented in Figure 1. The original structure of sepiolite was highly fibrous with large voids between the loosely packed aggregates. Particles of the nanocomposite were more closely packed, and the distance between layers of sepiolite was moderately reduced. More importantly, the aggregates were smoother than that of the raw mineral, and particles of TiO₂ were uniformly distributed between the voids and the fibers.

![Figure 1](image-url)
3.2. Dark Adsorption of Caffeine on Sepiolite, Pristine TiO$_2$ (P-25) and Sep–TiO$_2$ Nanocomposite

Dark adsorption tests showed that caffeine adsorbed strongly on raw sepiolite; the degree of adsorption was directly related to the concentration of the mineral, and equilibrium was reached within 30 min, regardless of the sepiolite concentration. On the other hand, no more than 10% of caffeine was adsorbed on pristine TiO$_2$ even after 2 h contact with the maximum test concentration of the metal. The data are presented in Figure 2a. To compare the capacity of all adsorbents, fractions of caffeine removed from solution after 2 h contact with each (P-25, sepiolite, Sep–TiO$_2$) were plotted against the applied test concentrations of the adsorbents, as depicted in Figure 2b. It was found that adsorption on the nanocomposite was nearly the same as that on the raw sepiolite, despite the massive surface area of the former. This is most likely due to the mass transfer limitations to the repellent surface of TiO$_2$, which was demonstrated (in Figure 2a) as a poor adsorbent for caffeine.

![Graph](https://example.com/graph1.png)

**Figure 2.** Adsorption equilibrium of caffeine on increasing concentrations of pristine TiO$_2$ and raw sepiolite (a); comparison of pristine TiO$_2$, raw sepiolite and Sep–TiO$_2$ nanocomposite for total caffeine adsorption after 2 h contact (b). Initial caffeine concentration = 10 mg L$^{-1}$, pH = 3.0.
3.3. Photocatalysis

The reaction byproducts. LC–MS analysis of a sample withdrawn from the reactor after 15 min photocatalysis with TiO$_2$ revealed six major peaks with m/z ratios of 73, 88, 100, 115, 145 and 194. The spectral output and the predicted structures of the detected byproducts are presented in Figure 3. The results are in good agreement with the literature reporting \( \bullet \)OH-mediated degradation of caffeine by advanced oxidation with Fenton’s reagent [31]. Hence, in the presence of P-25, the major mechanism governing the degradation process was advanced oxidation with OH radicals.

![Figure 3. LC–MS/MS spectra of a sample solution of caffeine after 15 min photocatalysis with TiO$_2$ at pH 6.0.](image)

Effect of initial concentration. Monitoring the concentration of caffeine during reaction in the presence of the two catalysts (P-25 and Sep–TiO$_2$) showed that the degradation of caffeine as a function of time exhibited different kinetic patterns, as depicted in Figure 4. The rate of reaction in the former was pseudo-first order (Figure 4a) and decreased as the initial caffeine concentration was increased. Maximum degradation was observed at the lowest test concentration of the compound (5 mg L$^{-1}$), with a rate constant of 0.098 min$^{-1}$. On the other hand, the degradation in the presence of the nanocomposite followed an exponential decay pattern (Figure 4b), with an extremely high rate constant during the first 2 min. The comparison of the effect of initial caffeine concentration on carbon mineralization showed that the maximum and minimum degrees of TOC decay were obtained at an initial caffeine concentration of 15 and 30 mg L$^{-1}$, respectively, regardless of the catalyst used. However, while the maximum in the presence of pristine TiO$_2$ was 31%, that in the presence of Sep/TiO$_2$ was 41%, as depicted in Figure 4c.
Figure 4. Cont.
The enhancement in the reaction rate and the mineralization of caffeine by photocatalysis with the nanocomposite is due to a combination of several factors, such as a larger degree of adsorption, easier capture of the photo-generated electrons and holes to reduce the incidence of their combination, and excess production of hydroxyl radicals. The mechanism can be outlined as the following:

(i) Strong adsorption of the parent and daughter molecules on the surface of the nanocomposite

(ii) Formation of acidic sites (generated by the Si–OH groups on sepiolite) on the surface of the catalyst that easily capture the photo-generated holes to produce •OH.

(iii) More rapid capture of photo-generated electrons by O2 to yield superoxide radicals, which upon reaction with H2O2 produce additional •OH.

The presence of excess •OH during photocatalysis with sepiolite-supported TiO2 under UV–natural light has also been reported in the literature, upon confirmation by electron paramagnetic resonance (EPR) studies [32]. It has also been reported that the enhancement in the photocatalytic activity of sepiolite-supported TiO2 is due to formation of new energy levels closer to the conduction band and leading to the excitation of the semiconductor by visible light [33].

The analysis of the data in Figure 4b to explore the reaction kinetics in the presence of Sep–TiO2 showed that the degradation reaction was represented by the Langmuir–Hinshelwood rate model (Equation (1)), which is commonly used to model heterogeneous reaction kinetics based on the assumption that adsorption and desorption are in equilibrium [34]:

$$\frac{1}{R_0} = \frac{1}{kKc_0} + \frac{1}{k}$$  \hspace{1cm} (1)

where $R_0$ is the initial reaction rate (M min$^{-1}$), $k$ is the apparent reaction rate constant (M min$^{-1}$), $K$ is the adsorption equilibrium constant (M), and $c_0$ is the initial caffeine concentration of (M). The data are presented in Figure 5.
Figure 5. The Langmuir–Hinshelwood model fits the rate of caffeine degradation as a function of initial concentration. Operating conditions were pH = 6, Sep/TiO$_2$ = 1.0 g L$^{-1}$, loading ratio=12.5 mM TiO$_2$ per g sepiolite, t = 15 min.

Effect of pH. Time-related decay of caffeine during photocatalysis at three pH levels are presented in Figure 6 for TiO$_2$ and Sep–TiO$_2$, as a pseudo-first order rate, and a two-phase exponential decay rate, respectively. The last plot in the figure shows relative fractions of carbon mineralization as a function of pH. Note that the reactions were most rapid at pH 6.0, regardless of the type of catalyst, but more than four times faster in the presence of the nanocomposite.
Effect of TiO$_2$ loading. It is well known that the loading of TiO$_2$ on a support material is a crucial parameter on the activity of the nanocomposite generated. In general, activity increases with increasing loading of the metal up to a critical value, above which it decreases again. To test the effect of TiO$_2$ loading on the activity of the Sep–TiO$_2$ nanocomposite, we monitored the degradation of caffeine in the presence of 0.5, 1.0, 2.0 and 4.0 g TiO$_2$ g$^{-1}$ sepiolite, corresponding to 6.25, 12.5, 25.0 and 50.0 mmol TiO$_2$ per g sepiolite, respectively. The light was turned off during the first 1 min to allow the dark adsorption of caffeine on the particles of the nanocomposite; and turned on immediately thereafter for the excitation of the semiconductor. We found that the rate of caffeine degradation increased with increasing loading of TiO$_2$ up to 25 mmol per g sepiolite and decreased upon further loading. The data are presented in Figure 7. A reduced rate of decomposition above a critical loading is most likely due
to the presence of too many particles of TiO$_2$ on the clay mineral that may have reduced the rate of adsorption and the thickness of the voids between the sepiolite fibers. Note also that at the minimum loading rate (6.26 mmol per g), the reaction was slowest, not only due to insufficient concentrations of the semiconductor, but also to the shadowing induced by too many metals on the surface of the catalyst.

![Figure 7](image-url)

**Figure 7.** The effect of TiO$_2$ loading on the rate of caffeine ($C_0 = 10$ mg L$^{-1}$) degradation by photocatalysis in the presence of Sep–TiO$_2$ at pH 6.0.

3.4. Post-Treatment by Sonication

Cavitation in liquids results in extreme temperatures and pressures upon the formation, growth and violent collapse of acoustic cavity bubbles [35]. The result is high-energy chemistry via the thermolytic cleavage of gases and water vapor (entrapped in the bubbles) that generate very reactive radical species in the medium. In addition to these chemical effects, cavitation leads to unique mechanical effects, such as enhanced mass transfer to heterogeneous interfaces, the cleaning and disaggregating of solid particles and minimizing the undesired corrosion of catalyst surfaces [36]. The addition of ultrasonic cavitation to a photoreactor has also been demonstrated to enhance the migration of photo-generated holes from the valence band of TiO$_2$ towards the bulk solution, and minimize the recombination of e–h pairs by disturbing the positions of valence and conduction bands [37].

In the light of the above, we tested the impact of post-sonication by exposing 10 min photo-treated samples of caffeine to high frequency ultrasound (577 kHz) for 30 min. The samples were either filtrated to remove all solids from the solution or used without filtration to elucidate the effect of solid catalysts during sonication. Because there was almost no caffeine in the samples, we monitored only the TOC content of the solutions before and after the pulse and continuous modes of sonolysis. It was found that the operation mode made little or no difference on the degree of TOC decay, but the presence of the catalysts did, as the percentage of carbon mineralization increased to a maximum of 65.13 (from 36.09) and 52.1 (from 9.64) when sonication was applied in the presence of Sep–TiO$_2$ and TiO$_2$, respectively. The results are presented in Figure 8. The higher efficiency of sonolysis in the presence of the catalysts is due to the excess number of cavity nuclei (excess collapse events) and the likely excitation of the catalyst surfaces (particularly that of P-25) by the sonoluminescence of collapse that is made by an intense UV irradiation of 200–500 nm [38]. The mineralization observed in the filtered samples was the result of sono-generated •OH and the enriched hydrophobicity of the solution that facilitates the diffusion of solutes to the vicinity of cavitation bubbles, where the concentration of hydroxyl radicals is very high.
enriched hydrophobicity of the solution that facilitates the diffusion of solutes to the vicinity of cavitation bubbles, where the concentration of hydroxyl radicals is very high.

Figure 8. The effect of post-treatment by continuous and pulse modes of ultrasound (f = 572 kHz, pH = 6.0) on the total percentage of TOC mineralization (by photocatalysis + sonolysis).

For comparison, a set of control experiments were also conducted to evaluate the role of sonolysis alone on the degradation of caffeine. The sonication of caffeine (10 mg L\(^{-1}\)) at 577 and 856 kHz showed that there was no significant difference in terms of the applied frequencies, and nearly 60% of the compound was eliminated within 10 min contact. On the other hand, the total TOC decay after 1 h sonication was no more than 10%, regardless of the frequency.

3.5. Stability of the Nanocomposite

One of the most important features of a solid catalyst is its stability, which is defined as the ease of recovery and the loss of efficiency upon multiple use [39]. To test the stability of the nanocomposite, a 10 min-treated sample in the photoreactor was adjusted to pH 12 and kept inert for 1 h to allow desorption. The spent catalyst was recovered by filtration, washing and drying at 60 °C to make it reusable in another photocatalytic run. The procedure was repeated with the same catalyst for two additional cycles.

The results of stability experiments showed that the lab-synthesized Sep–TiO\(_2\) nanocomposite was considerably stable, with 99, 97 and 86.4% recovery, respectively, in the second, third and fourth consecutive uses of the spent catalyst. The recovery was also appreciable for carbon mineralization, as only 18% loss of activity was found at the end of the third reuse. The relative efficiency of fresh Sep–TiO\(_2\) and its recovered surface during 10 min and after 30 min reaction of caffeine under irradiation by UV/natural light is presented in Figure 9.

Finally, the stability of the catalyst was confirmed by SEM images of the spent catalyst, which showed that almost no surface damage was present in the second and third uses even after 30 min reaction and a slight damage (reduction of voids) in the last one, as depicted in Figure 10.
Figure 9. The loss of activity in spent Sep–TiO$_2$ relative to the fresh catalyst upon recovery and reuse successively in three consecutive cycles after the first. Initial conditions were $C_0 = 10$ mg L$^{-1}$, Sep–TiO$_2 = 1$ g L$^{-1}$ (12 mmol TiO$_2$ per g sepiolite), pH = 6.0.

Finally, the stability of the catalyst was confirmed by SEM images of the spent catalyst, which showed that almost no surface damage was present in the second and third uses even after 30 min reaction and a slight damage (reduction of voids) in the last one, as depicted in Figure 10.

Figure 10. SEM images of fresh and spent Sep–TiO$_2$ after 30 min reaction at pH 6.0 with caffeine under UV/natural light.
4. Conclusions

A low-cost nanocomposite synthesized by the sonolytic immobilization of anatase TiO$_2$ on a natural clay mineral sepiolite was demonstrated to be a promising option to enhance the efficiency of the photocatalytic decomposition of non-biodegradable compounds. The outcome was attributed to the high porosity and excellent adsorption properties of sepiolite, and the unique structure of the mineral that enabled the production of excess •OH on the surface of the catalyst reduced the recombination of photo-generated e–h pairs and widened the absorption spectrum of the semiconductor to absorb light at the UV–visible band. The nanocomposite was found to be considerably stable, as it was easily recovered and reused several times for the photocatalytic degradation of the test compound—caffeine. Finally, the study showed that the efficiency of the process for carbon mineralization might considerably improve via the exposure of treated samples to a high-frequency ultrasound, thus demonstrating an environmentally friendly operation for the overall degradation of caffeine.

Author Contributions: Concept—N.H.I., B.S.-H.; Design—B.S.-H.; Supervision—N.H.I.; Materials—B.S.-H.; Data Collection and Processing—B.S.-H.; Analysis—B.S.-H.; Literature Search—B.S.-H., Z.E.; Writing—B.S.-H.; Critical Reviews—B.S.-H., Z.E., N.H.I. All authors have read and agreed to the published version of the manuscript.

Funding: The study is funded partly by the Istanbul University Research Fund (BAP) through the project MAB-2019-34967 and partly by the Boğaziçi University Research Fund (BAP) through the project 18Y00P7.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Zalkeska-Radziwill, M.; Affek, K.; Rybak, J. Ecotoxicity of chosen pharmaceuticals in relation to micro-organisms risk assessment. Desalin. Water Treat. 2014, 52, 3908–3917. [CrossRef]
2. Bruton, T.; Alboloushi, A.; De La Garza, B.; Kim, B.O.; Halden, R.U. Fate of caffeine in the environment and ecotoxicological considerations. In Contaminants of Emerging Concern in the Environment: Ecological and Human Health Considerations; ACS Symposium Series; American Chemical Society: Washington, DC, USA, 2010; pp. 257–273.
3. Gardinali, P.R.; Zhao, X. Trace determination of caffeine in surface water samples by liquid chromatography—Atmospheric pressure chemical ionization—Mass spectrometry (LC-APCI-MS). Environ. Int. 2002, 28, 521–528. [CrossRef]
4. Sotelo, J.L.; Ovejero, G.; Rodríguez, A.; Álvarez, S.; Galán, J.; Garcia, J. Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon. Chem. Eng. J. 2014, 240, 443–453. [CrossRef]
5. Sotelo, J.L.; Ovejero, G.; Rodríguez, A.; Álvarez, S.; García, J. Study of natural clay adsorbent sepiolite for the removal of caffeine from aqueous solutions: Batch and fixed-bed column operation. Water Air Soil Pollut. 2013, 224, 1466. [CrossRef]
6. Kim, M.; Guerra, P.; Shah, A.; Parsa, M.; Alaee, M.; Smyth, S.A. Removal of pharmaceuticals and personal care products in a membrane bioreactor wastewater treatment plant. Water Sci. Technol. 2014, 69, 2221–2229. [CrossRef] [PubMed]
7. Miralles-Cuevas, S.; Oller, I.; Ruiz-Delgado, A.; Cabrera-Reina, A.; Cornejo-Ponce, L.; Malato, S. EDDS as complexing agent for enhancing solar advanced oxidation processes in natural water: Effect of iron species and different oxidants. J. Hazard. Mater. 2019, 372, 129–136. [CrossRef] [PubMed]
8. Ganzenko, O.; Treluy, C.; Papirio, S.; Oturan, N.; Huguenot, D.; Van Hullebusch, E.D.; Esposito, G.; Oturan, M.A. Bioelectro-Fenton: Evaluation of a combined biological advanced oxidation treatment for pharmaceutical wastewater. Environ. Sci. Pollut. Res. 2018, 25, 20283–20292. [CrossRef]
9. Shu, Z.; Singh, A.; Klameth, N.; McPhedran, K.; Chelme-Ayala, P.; Bolton, J.R.; Belosevic, M.; El Din, M.G. Application Of The UV/H$_2$O$_2$ Advanced Oxidation Process For Municipal Reuse Water: Bench-And Pilot-scale Studies. WIT Trans. Ecol. Environ. 2016, 209, 233–244.
10. Ashokkumar, M. An Overview on Semiconductor Particulate of Hydrogen Systems For. Int. J. Hydrog. Energy 1998, 23, 427–438. [CrossRef]
11. Kamat, P.V.; Meisel, D. Nanoparticles in advanced oxidation processes. Curr. Opin. Colloid Interface Sci. 2002, 7, 282–287. [CrossRef]
12. Seo, W.J.; Sung, Y.T.; Kim, S.B.; Lee, Y.B.; Choe, K.H.; Choe, S.H.; Sung, J.Y.; Kim, W.N. Effects of Ultrasound on the Synthesis and Properties of Polyurethane Foam/Clay Nanocomposites. *J. Appl. Polym. Sci.* 2006, 102, 3764–3773. [CrossRef]

13. Bergaya, F.; Lagaly, G. General introduction: Clays, clay minerals, and clay science. *Dev. Clay Sci.* 2013, 5, 1–19.

14. Coruh, S.; Geyikci, F.; Coruh, U. Removal of Cu²⁺ from copper flotation waste leachant using sepiolite: Full factorial design approach. *Acta Geodyn. Geomat.* 2013, 10, 453–458. [CrossRef]

15. Carrado, K.A.; Winans, R.E. Electrochemical performance of sepiolite-derived carbon with lithium transition metal oxide positive electrodes. *Electrochem. Carbon Mater. Proc. Int. Symp.* 2004, 2000, 162.

16. Novikova, L.; Roessner, F.; Belchinskaya, L.; AlSawalha, M.; Krupskaya, V. Study of surface acid-base properties of natural clays and zeolites by the conversion of 2-methylbut-3-yn-2-ol. *Appl. Clay Sci.* 2014, 101, 229–236. [CrossRef]

17. Reinholdt, M.X.; Hubert, F.; Faurel, M.; Tertre, E.; Razafitianamaharavo, A.; Francius, G.; Prêt, D.; Petit, S.; Béré, E.; Pelletier, M. Morphological properties of vermiculite particles in size-selected fractions obtained by sonication. *Appl. Clay Sci.* 2013, 77, 18–32. [CrossRef]

18. Sabah, E.; Turan, M. Adsorption mechanism of cationic surfactants onto acid- and heat-activated sepiolites. *Water Res.* 2002, 36, 3957–3964. [CrossRef]

19. Lemić, J.; Tomašević-Canović, M.; Djurić, M.; Stanić, T. Surface modification of sepiolite with quaternary amines. *J. Colloid Interface Sci.* 2005, 292, 11–19. [CrossRef]

20. Karamanis, D.; Ökte, A.N.; Vardoulakis, E.; Vaimakis, T. Applied Clay Science Water vapor adsorption and photocatalytic pollutant degradation with TiO₂–sepiolite nanocomposites. *Appl. Clay Sci.* 2011, 53, 181–187. [CrossRef]

21. Akkari, M.; Aranda, P.; Belver, C.; Bedia, J.; Amara, A.B.H.; Ruiz-Hitzky, E. ZnO/sepiolite heterstructured materials for solar photocatalytic degradation of pharmaceuticals in wastewater. *Appl. Clay Sci.* 2018, 156, 104–109. [CrossRef]

22. Chen, Y.; Dionysiou, D.D. Bimodal mesoporous TiO₂–P₂5 composite thick films with high photocatalytic activity and improved structural integrity. *Appl. Catal. B Environ.* 2008, 80, 147–155. [CrossRef]

23. Dvininov, E.; Popovici, E.; Pode, R.; Cochechi, L.; Barvinschi, P.; Nica, V. Synthesis and characterization of TiO₂-pillared Romanian clay and their application for azoic dyes photodegradation. *J. Hazard. Mater.* 2009, 167, 1050–1056. [CrossRef] [PubMed]

24. Suárez, S.; Yates, M.; Petre, A.L.; Martín, J.A.; Avila, P.; Blanco, J. Development of a new Rh/TiO₂–sepiolite monolithic catalyst for N₂O decomposition. *Appl. Catal. B Environ.* 2006, 64, 302–311. [CrossRef]

25. Zhang, G.; Xiong, Q.; Xu, W.; Guo, S. Synthesis of bicontinuous TiO₂ supported sepiolite fibers and their photocatalytic activity for degradation of gaseous formaldehyde. *Appl. Clay Sci.* 2014, 102, 231–237. [CrossRef]

26. Suárez, S.; Coronado, J.M.; Portela, R.; Martín, J.C.; Yates, M.; Avila, P.; Sánchez, B. On the preparation of TiO₂–sepiolite hybrid materials for the photocatalytic degradation of TCE: Influence of TiO₂ distribution in the mineralization. *Environ. Sci. Technol.* 2008, 42, 5892–5896. [CrossRef] [PubMed]

27. Shi, L.; Yang. J. Preparation of TiO₂/Sepiolite Composite and its adsorption and photo-catalysis property to simulated dye water. In 2009 *International Conference on Energy and Environment Technology*, IEEE: Piscataway, NJ, USA, 2009; Volume 3, pp. 465–468.

28. Kamaya, Y.; Fukaya, Y.; Suzuki, K. Acute toxicity of benzoic acids to the crustacean Daphnia magna. *Chemosphere* 2005, 59, 255–261. [CrossRef]

29. Hansch, C.; Leo, A. *Fundamentals and Applications in Chemistry and Biology, ACS Professional Reference Book*; American Chemical Society: Washington, DC, USA, 1995.

30. Todorova, N.; Giannakopoulou, T.; Karapati, S.; Petridis, D.; Vaimakis, T.; Trapalis, C. Applied Surface Science Composite TiO₂/clays materials for photocatalytic NOx oxidation. *Appl. Surf. Sci.* 2014, 319, 113–120. [CrossRef]

31. Dalmázzo, I.; Santos, L.S.; Lopes, R.P.; Eberlin, M.N.; Augusti, R. Advanced oxidation of caffeine in water: On-line and real-time monitoring by electrospray ionization mass spectrometry. *Environ. Sci. Technol.* 2005, 39, 5982–5988. [CrossRef]
32. Liu, R.; Wang, J.; Zhang, J.; Xie, S.; Wang, X.; Ji, Z. Honeycomb-like micro-mesoporous structure TiO\textsubscript{2}/sepiolite composite for combined chemisorption and photocatalytic elimination of formaldehyde. *Microporous Mesoporous Mater.* 2017, 248, 234–245. [CrossRef]

33. Sathishkumar, P.; Mangalaraja, R.V.; Rozas, O.; Mansilla, H.D.; Gracia-Pinilla, M.A.; Meléndrez, M.F.; Anandan, S. Sonophotocatalytic degradation of Acid Blue 113 in the presence of rare earth nanoclusters loaded TiO\textsubscript{2} nanophotocatalysts. *Sep. Purif. Technol.* 2014, 133, 407–414. [CrossRef]

34. Xiao, N.; Li, D.; Cui, G.; Li, N.; Li, Q.; Wu, G. Electrochimica Acta Adsorption behavior of triblock copolymer suppressors during the copper electrodeposition. *Electrochim. Acta* 2014, 116, 284–291. [CrossRef]

35. Ince, N.H.; Tezcanli, G.; Belen, R.; Apikyan, I. Ultrasound as a catalyzer of aqueous reaction systems: The state of the art and environmental applications. *Appl. Catal. B Environ.* 2001, 29, 167–176. [CrossRef]

36. Suslick, K.S.; Price, G.J. Applications of ultrasound to materials chemistry. *Annu. Rev. Mater. Sci.* 1999, 29, 295–326. [CrossRef]

37. Kaur, S.; Singh, V. Visible light induced sonophotocatalytic degradation of Reactive Red dye 198 using dye sensitized TiO\textsubscript{2}. *Ultrason. Sonochem.* 2007, 14, 531–537. [CrossRef] [PubMed]

38. Shimizu, N.; Ogino, C.; Dadjou, M.F.; Murata, T. Sonocatalytic degradation of methylene blue with TiO\textsubscript{2} pellets in water. *Ultrason. Sonochem.* 2007, 14, 184–190. [CrossRef] [PubMed]

39. Ziylan-Yavas, A.; Mizukoshi, Y.; Maeda, Y.; Ince, N.H. Applied Catalysis B: Environmental Supporting of pristine TiO\textsubscript{2} with noble metals to enhance the oxidation and mineralization of paracetamol by sonolysis and sonophotolysis. *Appl. Catal. B Environ.* 2015, 172–173, 7–17. [CrossRef]

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).