engineering proceedings

MDPI

Proceeding Paper

Photocatalytic Degradation and Defluorination of Per- and Poly-Fluoroalkyl Substance (PFAS) Using Biosynthesized TiO_2 Nanoparticles under UV-Visible Light †

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† Presented at the 2nd International Electronic Conference on Processes: Process Engineering—Current State and Future Trends (ECP 2023), 17–31 May 2023; Available online: https://ecp2023.sciforum.net/.

Abstract: Per- and poly-fluoroalkyl substances (PFAS) are recalcitrant chemicals with stable carbon-fluorine (C-F) bonds. These complex substances are difficult to degrade; therefore, they persist in the environment, causing potential health effects on humans. This study focused on the photocatalytic degradation and defluorination of perfluorooctane sulfonate (PFOS) in aqueous water using TiO_2 nanoparticles under UV-visible light. The biosynthesized TiO_2 catalysts at pH 8, 10, and 12 were characterized using XRD, HRTEM, and HRSEM. The XRD patterns of the respective TiO_2 nanoparticles at different synthesized pH exhibited similar anatase phases, and it was observed that the crystallite sizes decreased with increasing pH. The HRSEM and HRTEM confirmed the spherical shapes of the produced nanoparticles with the particle size distribution of 12.17 nm, 10.65 nm, and 8.81 nm for the synthesized TiO_2 nanoparticles at pH 8, 10, and 12, respectively. The photodegradation and defluorination of PFOS were performed at various initial solution pH values of 2, 4, 6, 8, 10, and 12 under UV irradiation for 150 min. The study showed 95.62 and 56.13% degradation and defluorination efficiency at pH 2. The degradation and defluorination efficiencies significantly decreased as the pH solution increased; hence the degradation increases at lower solution pH. Without UV-visible light, the photocatalysis achieved less degradation and defluorination efficiency. The photocatalysis showed that the pH solution and UV irradiation greatly influence the degradation and defluorination. Therefore, TiO_2 nanoparticles were effective for the degradation and defluorination of PFOS under UV-visible light, which could also have an influence on the treatment of other PFAS in wastewater.

Keywords: PFAS; TiO_2 nanoparticles; degradation; defluorination; wastewater

Citation: Mustapha, S.; Tijani, J.O.; Elabor, R.; Etsuyankpa, M.B.; Amigun, A.T.; Shuaib, D.T.; Sumaila, A.; Olaoye, A.J.; Abubakar, H.L.; Abdulkareem, S.A.; et al. Photocatalytic Degradation and Defluorination of Per- and Poly-Fluoroalkyl Substance (PFAS) Using Biosynthesized TiO_2 Nanoparticles under UV-Visible Light. *Eng. Proc.* **2023**, *37*, x. https://doi.org/10.3390/xxxxx

Published: 17 May 2023

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1. Introduction

PFAS, referred to per- and polyfluoroalkyl substances, is a class of chemicals that have found widespread application in consumer and industrial goods. These chemicals are made up of a fluorinated alkyl chain and a polar group, and they have qualities such as high temperatures and water resistance. Additionally, they are constituted of a polar group. The most common types of PFAS that have been found in drinking water are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). The release of PFAS into the environment can be attributed to several different sources, such as pollution from production plants, leachates from landfills, and industrial effluents. The introduction of PFAS into the environment through sources such as drinking water, foods, airborne dust, and breast milk can result in the potential for bioaccumulation and detrimental effects on living organisms [1]. The toxicological consequences of PFAS demonstrated possible adverse impacts on human health, including the production of tumors, immunotoxicity, hepatotoxicity, disturbance of the endocrine system, developmental toxicity, and neurotoxicity. As a result, the elimination of PFAS from environmental media that has been polluted is of the utmost significance. To remove PFAS from water, some different water treatment technologies, such as coagulation, sand filtration, adsorption, anion exchange, and membrane filtration, have been utilized [2].

However, these solutions are based on physical removal methods, and the PFAS that are removed still require additional degradation once they have been removed. They suffer from the same primary shortcoming as adsorption systems: they are unable to eliminate the PFAS molecules. Therefore, the most effective solution would be to devise a technology that can convert PFAS into safe species. The extremely robust C–F bond makes it possible for PFAS to be successfully dissolved by advanced oxidation conditions such as sonolysis, persulfate oxidation, electrochemical treatment, ultraviolet (UV) photolysis, and photocatalysis. However, these conditions must be met for the degradation to take place. As photocatalysts for the degradation of organic contaminants, nanoparticles have been used extensively in recent years. Verma et al. [3] conducted research to explore the effectiveness of UV-vis/$Zn_xCu_{1-x}Fe_2O_4$/oxalic acid in the breakdown of perfluorooctanoic acid (PFOA) in water. The reactive species generated from $Zn_xCu_{1-x}Fe_2O_4$ photodegraded PFOA as a result of oxidation dissociation and defluorination. The adsorption and solid-phase photodegradation of perfluorooctane sulphonate (PFOS) was investigated by Zhu et al. [4] using gallium-doped carbon-modified titanate nanotubes (Ga/TNTs@AC). The nanocomposites had faster adsorption kinetics and a higher affinity for PFOS than the activated carbon did.

Furthermore, they could break down 75.0% of the pre-sorbed PFOS and mineralize 66.2% of it within 4 h of exposure to UV light. The efficient PFOS photodegradation (decarboxylation and defluorination) by Ga/TNTs@AC was due to the oxygen vacancies, which prevented recombination of the e-/h+ couples and allowed $O_2^{\bullet -}$ formation. Under light irradiation during the reaction, the photogenerated holes of photocatalysts such as titanium(IV) oxide (TiO_2) combine with hydroxide anion to give surface adsorbed hydroxyl radicals (•OH). These hydroxyl radicals then take part in the photocatalytic breakdown of organic compounds [5]. Consequently, the TiO_2 demonstrated significantly higher photocatalytic degradation efficiencies, and the photocatalysts may also enable photodegradation. In this process, high concentrations of PFAS are adsorbed onto the photocatalytic sites and subsequently degraded under UV light.

This study was on biosynthesized TiO_2 nanoparticles and their performance for photocatalytic degradation of PFOS. The objectives were to (1) biosynthesize TiO_2 at pH 8, 10, and 12 using the sol-gel method, (2) characterization of the as-synthesized nanoparticles using XRD, HRSEM, and HRTEM, and (3) determine the effect of pH on the photodegradation of synthetic PFOS under UV-visible light irradiation.

2. Materials and Methods

Titanium tetraoxoisopropoxide (TTIP, 97%), sodium hydroxide (NaOH, 97%), hydrochloric acid (HCl, 37%), and perfluorooctane sulphonate (PFOS) were acquired from Sigma Aldrich. All chemicals were analytical grade, and all solutions were prepared using de-ionized water.

2.1. Synthesis of TiO_2 Nanoparticles

The leaves of *Albezia lebbeck* were collected, washed, and dried for the use of biosynthesis of TiO_2. 5 cm^3 of TTIP was measured into three separate 250 cm^3 beakers containing 100 cm^3 of de-ionized water were thoroughly mixed under a stirring process for 20 min at ambient temperature. 10 cm^3 of *Albezia lebbeck* leaf extract was added to each resultant solution under a continuous stirring condition for 30 min. To each of the three solutions, the pH solutions were adjusted to 8, 10, and 10, respectively, using 0.1 M NaOH and stirred at 150 rpm for 30 min. A gel formed in each of the three solutions was copiously washed with de-ionized water. The resultant products were oven-dried at 105 °C for 12 h and further calcined at 450 °C for 3 h to produce TiO_2 nanoparticles.

2.2. Characterization of TiO_2 Nanoparticles

The crystalline structure of the synthesized nanoparticles was identified using X-ray diffraction (Bruker AXS D8 Advance, X-ray diffractometer) with Cu*Kα* (*λ* = 0.154 nm) radiation at a diffraction angle between 10 and 90°. The morphology and composition of the synthesized nanoparticles were observed using high-resolution scanning electron microscopy (HRSEM, Zeiss Auriga model). The particle size analysis and size distribution of the prepared nanoparticles were investigated using high-resolution transmission electron microscopy (HRTEM, Zeiss Auriga model) operated at 200 kv.

2.3. Photodegradation of PFOS

The photocatalytic degradation of the PFOS using the as-synthesized TiO_2 was investigated at pH values of 2, 4, 6, 8, 10, and 12 by adding 0.1 HCl or NaOH solutions. The experiment was performed in a 50 cm^3 polypropylene bottle containing 200 μg/L of PFOS and adjusted at desired pH. The catalyst was added and well thoroughly mixed for 150 min. The suspension was irradiated by UV to assess the photodegradation of the PFOS. The liquid samples were collected at different time intervals to measure the final concentrations of PFOS using an Agilent 6400 series triple quadrupole liquid chromatography-mass spectrometry (LC-MS).

3. Results and Discussion

3.1. Characterization of TiO_2 Nanoparticles

Figure 1 shows XRD patterns of TiO_2 nanoparticles at different pH. It can be seen that the synthesized samples at pH 8 to 12 showed the pure anatase phase of TiO_2 with diffraction peaks at 2θ values of 25.28°, 37.80°, 48.05°, 53.89°, 55.06°, 62.69°, 70.31°, 75.03° and 82.66° with crystal planes of (101), (004), (200), (105), (211), (204), (220), (215), and (224), respectively (JCDPS No. 021-1272). The crystallite size of synthesized TiO_2 at pH 8 (14.91 nm), 12.01 nm at pH 10, and 9.15 nm at pH 12 were calculated using Debye Scherrer Equation (1);

$$D = \frac{k\lambda}{\beta \mathrm{Cos}\theta} \quad (1)$$

where k is the Scherrer constant (0.94), λ is the radiation wavelength (0.152 nm) of Cu*Kα*, β is the full width at half maximum, and θ is the Bragg angle of the orientation plane.

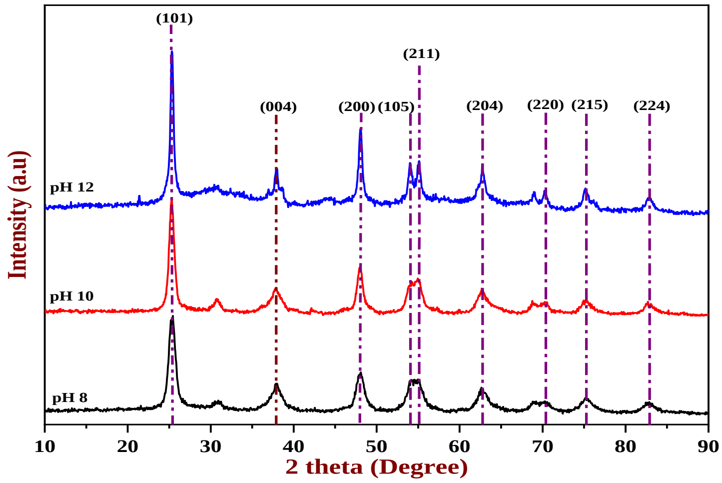

Figure 1. XRD patterns of biosynthesized TiO_2 nanoparticles at different pH values.

The HRSEM images of TiO_2 at pH 8, 10, and 12 are presented in Figure 2. The synthesized TiO_2 nanoparticles. Figure 3 presents the HRTEM images and size distribution of TiO_2 nanoparticles at different pH values. It can be concluded that the spherical shapes of TiO_2 nanoparticles prepared at pH 8, 10, and 12 have particle sizes of 12.17 nm, 10.65 nm, and 8.81 nm, respectively. The XRD and HRTEM results clearly show that the crystallite and particle sizes of the synthesized nanoparticles depend on the pH solution.

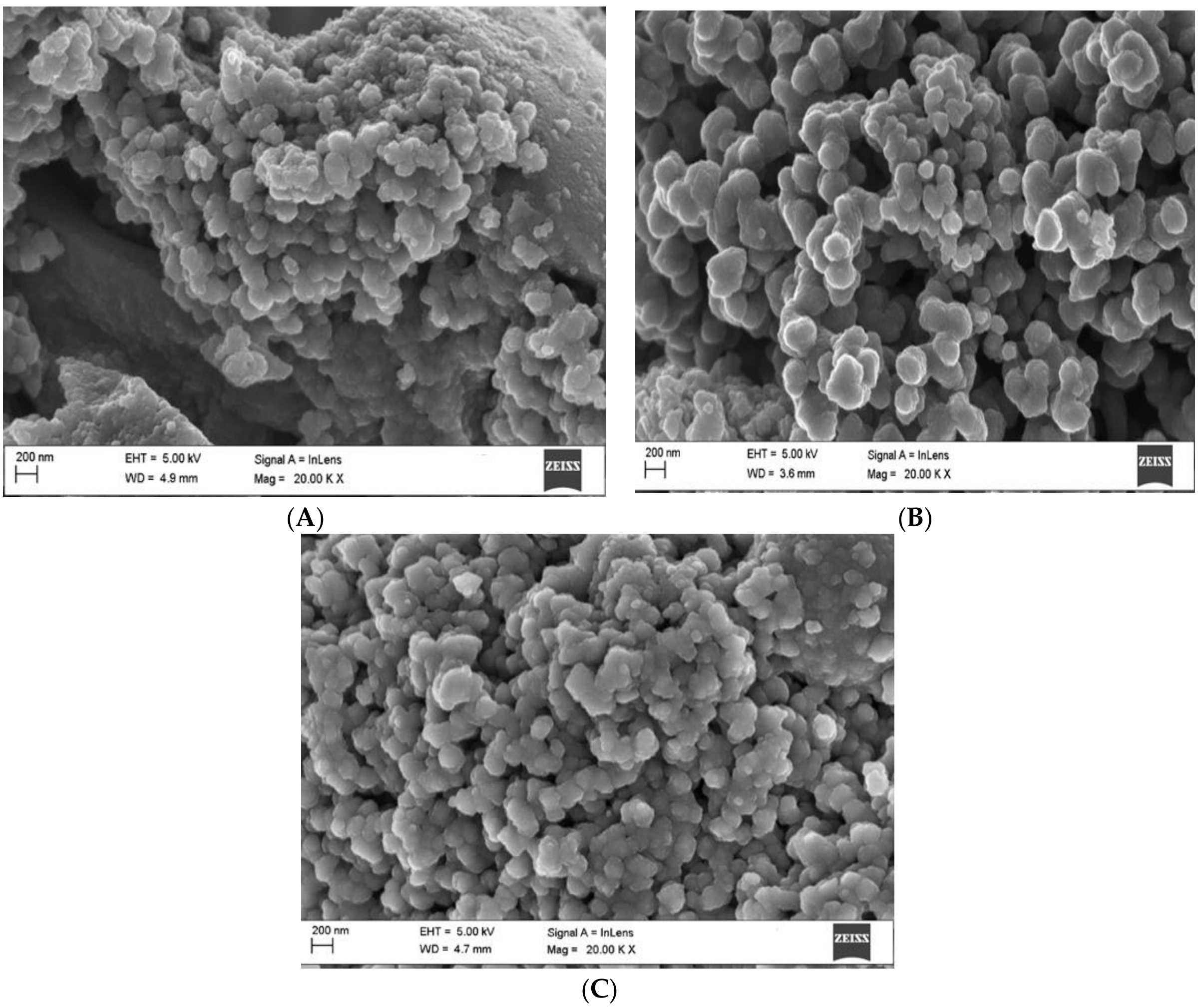

Figure 2. HRSEM image of biosynthesized TiO_2 nanoparticles at (**A**) pH 8 (**B**) pH 10 (**C**) 12.

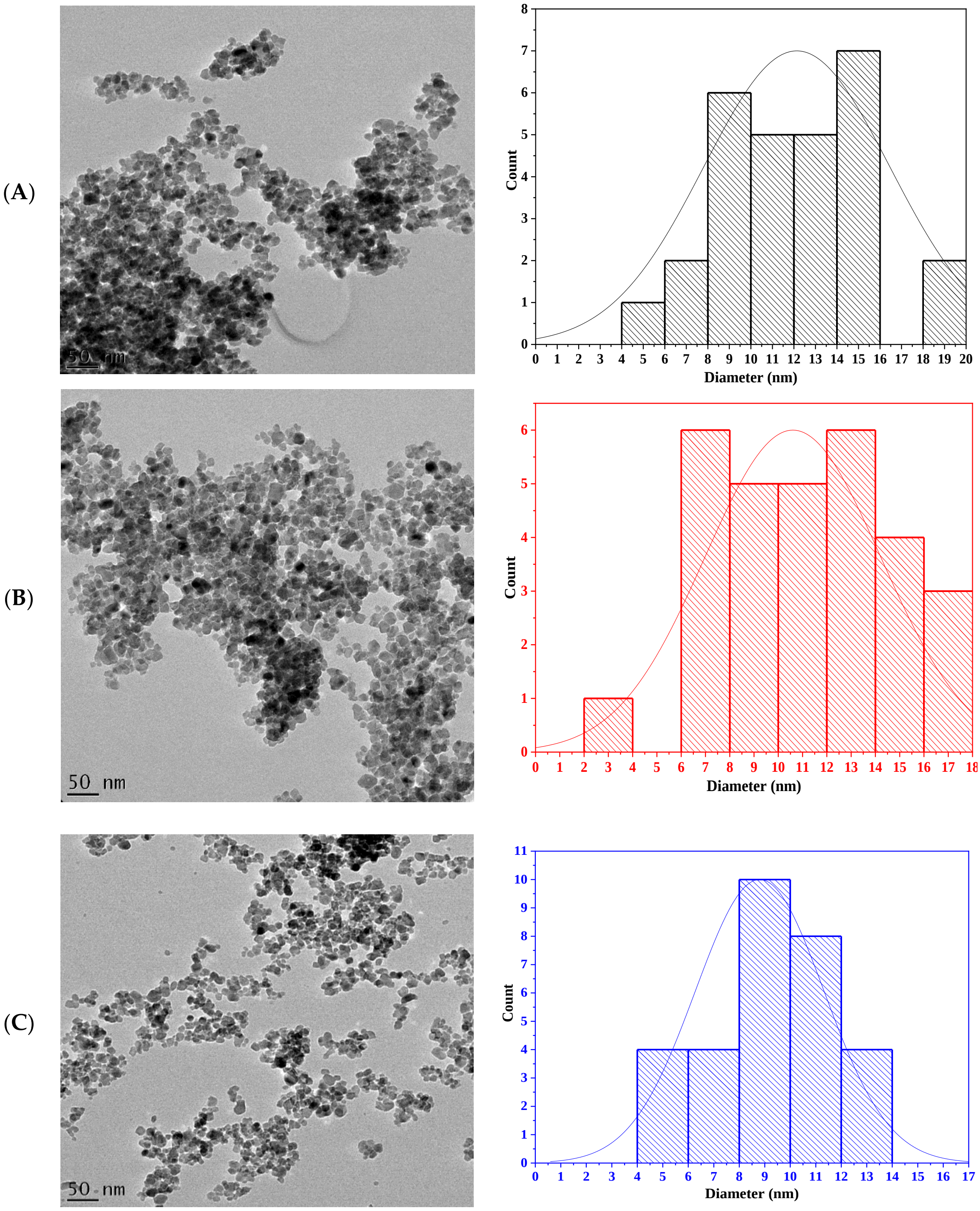

Figure 3. HRTEM image and size distribution of biosynthesized TiO_2 nanoparticles at (**A**) pH 8 (**B**) pH 10 (**C**) pH 12.

3.2. Photodegradation and Defluorination of PFOS

Figure 4 shows the photodegradation and defluorination of PFOS at various pH values. The photodegradation and defluorination at their maximum occurred at pH 2 were 95.62% and 56.13%, respectively. It was observed that as the pH increases, the degradation and defluorination rates are reduced. The variation in pH plays a key role in the distribution of radicals in the photocatalytic processes. The increase in the trend in PFOS with a decrease in pH solution could be attributed to the increase in the number of positive active sites on the nanoparticles at decreased pH values, leading to the photoinduced desulphonation of the parent molecule to produce by-products with lower toxicity. Thus, under basic conditions, PFOS reacts with the hydroxyl group, which is not sufficient for the degradation and defluorination of PFOS. This finding is similar to the study of Zhang et al. [6], which confirmed that the degradation of PFOA is higher at low pH values.

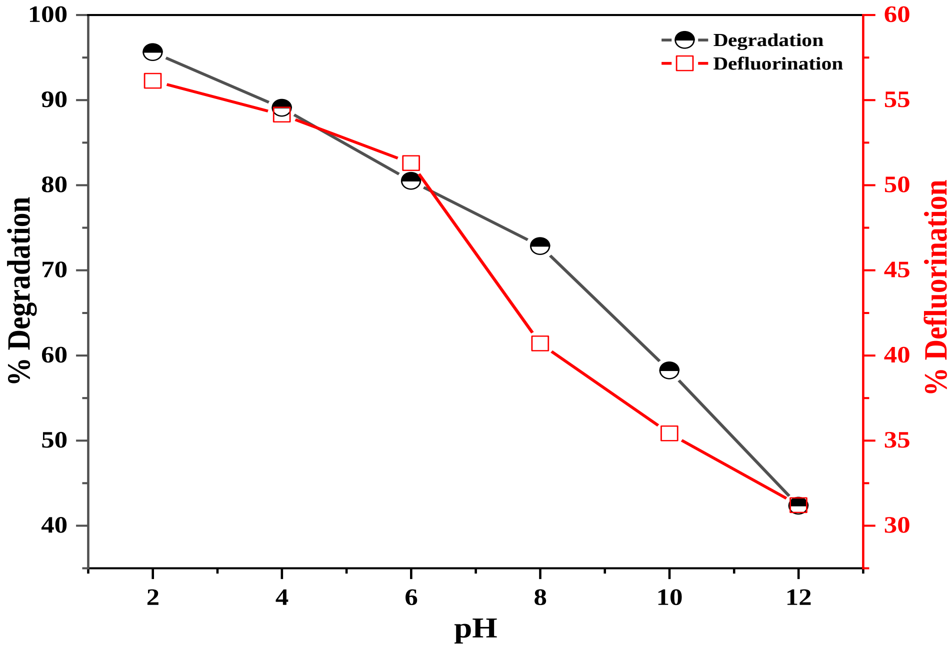

Figure 4. The effect of pH on the degradation and defluorination of PFOS.

4. Conclusions

In summary, biosynthesized TiO_2 nanoparticles were used to demonstrate the photodegradation and defluorination of PFOS. The influence of basic pH media on the biosynthesis of the anatase phase of TiO_2 was studied. The HRSEM and HRTEM results confirmed the spherical shapes of the synthesized nanoparticles. The biosynthesized TiO_2 exhibited the highest degradation and defluorination at low pH of PFOS under UV irradiation. Thus, the findings unveil the potential of biosynthesized TiO_2 nanoparticles as a photocatalytic material for the defluorination and degradation of PFOS in water.

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

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