

DEGRADATION OF ANTIBIOTIC SULFAMETHOXAZOLE IN AQUEOUS MEDIA BY UVA/TiO₂ PURE-BROOKITE PHOTOCATALYSIS

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Abstract. The appearance of antibiotic sulfamethoxazole (SMX) in natural environments poses a potential risk to human health and ecology. Among many developed treatment techniques to remove and degrade SMX from an aqueous environment, photodegradation using the phase-pure TiO₂ nanoparticles (NPs) in brookite structure as an active photocatalyst could be considered as a novel and effective strategy. The photocatalytic degradation of SMX in aqueous media followed an apparent first-order kinetics under the simulated UV-A irradiation. The higher the photocatalysts load, the higher photocatalytic efficiency. The SMX photodegradation over brookite nanoparticles depended on the pH of the SMX solution that was related to changes in chemical isomers of SMX molecules in the range of pH values between 2.0 and 10.0. The degradation efficiency was highest at pH 10.0 (up to 88 % after 180 min under UV-A irradiation) when SMX was in anionic form. With real matrices, the presence of metal ions (in mineral water) and fact-finding organic matter (in surface water) had a small effect on photodegradation efficiency due to either the complexation between SMX with metal ions or the inhibition of free radicals. The obtained results confirmed that the nano-sized TiO₂ brookite photocatalyst has a high potential for water and wastewater remediation.

Keywords: TiO₂, brookite, nanoparticles, sulfamethoxazole, photodegradation, water treatment.

Classification numbers: 2.1.3, 2.4.2, 2.5.1, 2.6.1, 3.4.2

1. INTRODUCTION

The persistence of pharmaceutically active compounds (PhACs) in effluents and surface waters is of substantial environmental concern in the last years [1]. These compounds are resistant to conventional treatment processes (biodegradation, physical adsorption, etc.), as shown by their global detection in wastewater treatment plant effluents, surface water and groundwater. Among them, sulfamethoxazole (SMX) is a worldwide used sulfonamide antibiotic drug, which is currently prescribed for treatment of bacterial infections such as urinary tract infections, bronchitis, and prostatitis [2]. The structure of SMX consists of a benzyl ring which requires high energy to break $-C=C-$ bonding. Complete SMX removal is thus quite hard to achieve and intermediate products could be formed after treatment. As a result, the mean concentration of SMX in a wastewater treatment plant in Leiria (Portugal) was found to be 489 ng.L^{-1} (influent) and 57 ng.L^{-1} (effluent) [3], and about $0.01 - 2.0 \text{ }\mu\text{g.L}^{-1}$ was detected in municipal sewage treatment plant effluents from the developed countries such as Spain, France, Greece, Italy, Sweden, and Germany [4]. As a popular antibiotic used in Vietnam, SMX has been found at high levels in surface water ecosystems, reaching to 21 ng.L^{-1} in Mekong Delta, Vietnam [5]. In the USA, 0.4 ng.L^{-1} of SMX has been detected in raw drinking water originating from Lake Erie [6]. SMX is able to inhibit gram-positive and gram-negative bacteria (such as *Listeria monocytogenes* and *E. coli*), and protozoa. Obviously, the widespread occurrence of SMX in the aquatic environments even at low-levels is of concern not only for the potential biocide effects on natural microbial populations involved in key ecosystem functions but also for the induction and spread of antibiotic resistance in both environmental and pathogenic bacteria.

Among various wastewater treatment processes, advanced oxidation processes (AOPs) have been shown to be a promising technology to highly degrade and mineralize PhACs present in wastewater into CO_2 , H_2O , or/and non-toxic degraded products [7]. AOPs are chemical processes designed to remove organic and inorganic materials from contaminated water sources. A number of AOPs have been investigated such as ozonation, Fenton and photo-Fenton oxidation, photolysis and UV/hydrogen peroxide (H_2O_2), and heterogeneous photocatalysis [8, 9]. In heterogeneous AOPs, the hydroxyl ($\cdot\text{OH}$) dominant radical is produced during the photoactivation process of photocatalysts in aqueous media, which is a strong oxidant, and can attack a wide range of organic compounds [10]. Photocatalytic decomposition with titanium dioxide (TiO_2) is considered to be an effective treatment option. Titanium dioxide (TiO_2) has been one of the most used photocatalytic materials (ZnO , CdS , BiVO_4 , etc.) due to its low cost and toxicity, and also due to its high reactivity and chemical stability [11]. Other advantages of heterogeneous photocatalysis compared with other AOPs are the possibilities to utilize sunlight as a natural irradiation source and perform the photocatalytic treatment process in the pollutant media.

The aim of this work was to investigate the photodegradation of sulfamethoxazole (SMX) in different water matrices of deionized (DI) water, surface water taken from West Lake, and mineral water used as a model for groundwater. To do so, photocatalytic degradation experiments with SMX were conducted in the presence of the active TiO_2 brookite nanoparticles under the simulated UV-A light irradiation and the low ratio between TiO_2 and SMX conditions. The phase-pure brookite was successfully synthesized and exhibited high photocatalytic activity in the photodegradation of different kinds of recalcitrant pollutants like pharmaceuticals, dyes, and X-ray contrast agents [11 - 13]. In the present work, the role of pH, the water matrices, and the photocatalyst loading were considered as the important factors to affect the SMX photodegradation behaviour. The SMX water samples before and after photocatalytic treatment were analyzed using ultrahigh performance liquid chromatography (UPLC) combined with positive ionization tandem mass spectrometry (MS/MS) in a multiple monitoring reaction mode.

It is noted that the sensitivity of the developed method has been allowed for the determination of target compounds at trace levels in environmental water samples [14].

2. MATERIALS AND METHODS

2.1. Materials

Sulfamethoxazole (C₁₀H₁₁N₃O₃S, 99 %, Sigma-Aldrich), formic acid (≥ 99 %, Merck), methanol (≥ 99.9 %, Merck), acetonitrile (≥ 99.9 %, Merck), sodium hydroxide (≥ 97 %, Merck), sulfuric acid (98 %, Merck), and as-prepared TiO₂ brookite powder (10 nm) [13].

2.2. Methods

Characterization: The structural property was analyzed by X-ray diffraction (XRD; ARL Equinox 5000) with Cu-K α radiation ($k = 1.54056 \text{ \AA}$) operating at 35 kV and 25 mA, and by Raman scattering spectra using an XploRAPlus Raman spectrophotometer with a 785 nm laser as an excitation source.

Photocatalytic experiments: TiO₂ powder as prepared (10 mg) was dispersed in an SMX solution (250 mL, 10 ppm) and magnetically stirred for 30 min in the dark in order to establish an adsorption - desorption equilibrium before illumination. After that, pH value of the reaction solution was determined. 3 M HCl and 3 M NaOH solutions were used to adjust the pH of the SMX solution before the beginning of UV illumination. The UVA fluorescent tubes (90 W, Philips) were used as a light source, which simulated the UVA part of sunlight, with a center wavelength of 365 nm. The distance from the applied lamps to the surface of the SMX solution was 15 cm. All photocatalytic experiments were conducted with continuous stirring at room temperature (RT). After a certain period of time, 1 mL of reaction solution was taken from the suspension by a syringe, separated from the TiO₂ photocatalyst by a 0.2 μm PTFE filter, and stored at -20 °C for later qualitative and quantitative analysis. Three types of water matrices were used to prepare SMX pollutants: Deionized water (DIW), surface water (SW), mineral water (MW).

UPLC-MS/MS analysis: Ultra-performance liquid chromatography combined with a tandem mass spectrometer (Waters, Xevo-TQD, USA) was used. Target analytes were separated on a C18 column (BEH, 50 \times 2.1 mm, 1.7 μm). The detection was carried out on a mass spectrometer via positive ionization mode. The column chamber's temperature was set at 30 °C. The mobile phase was water with 0.5 %v/v formic acid (phase A) and acetonitrile with 0.5 % (v/v) formic acid (phase B) at a constant flow rate of 0.3 mL.min⁻¹. The gradient of the mobile phase was linearly scheduled as follows: 100 % A for 01 min and a linear increase to 70 % B from 1–3 min, and then, it was kept for 1 min and decreased to the initial mobile phase condition for re-equilibrium column. The retention time of SMX was 3.51 min. This UPLC system was connected to mass spectrometry with an electrospray interface under the following conditions: capillary, 3 kV; cone voltage, 34 V; desolvation gas temperature, 350 °C; desolvation gas flow, 650 L.h⁻¹; and cone gas flow, 10 L.h⁻¹.

3. RESULTS AND DISCUSSION

3.1. Characterization of as-prepared TiO₂ brookite nanoparticles

Figure 1a displays the X-ray diffraction pattern of the as-prepared TiO₂ brookite NPs. It is an analytical technique for determining TiO₂-NPs crystallinity and phase formation. The XRD analysis was carried out using a copper radiation source ($K\alpha = 1.54056 \text{ \AA}$) in an X-ray diffractometer (XRD EQUINOX 5000, Thermo Scientific) in 2θ range from 15° to 85° . All main diffraction peaks of brookite phase were observed at 25.4° , 25.7° , 30.8° , and 36.3° which were assigned to the (210), (111), (121), and (102) lattice planes, respectively. These peaks are broad indicating a small crystallite size. By using the Debye–Scherrer equation, the crystallite size of the synthesized nanoparticles was calculated. The XRD results show that the average crystallite size is about 12 nm.

Further analysis on crystalline structures was affirmed by a Raman Spectrometer (XploRA PLUS, Horiba) with the 785 nm laser excitation to match the obtained XRD data. The presence of high-purity brookite was confirmed by Raman spectrum detected at 156, 241, and 318 cm^{-1} shown in Fig. 1b.

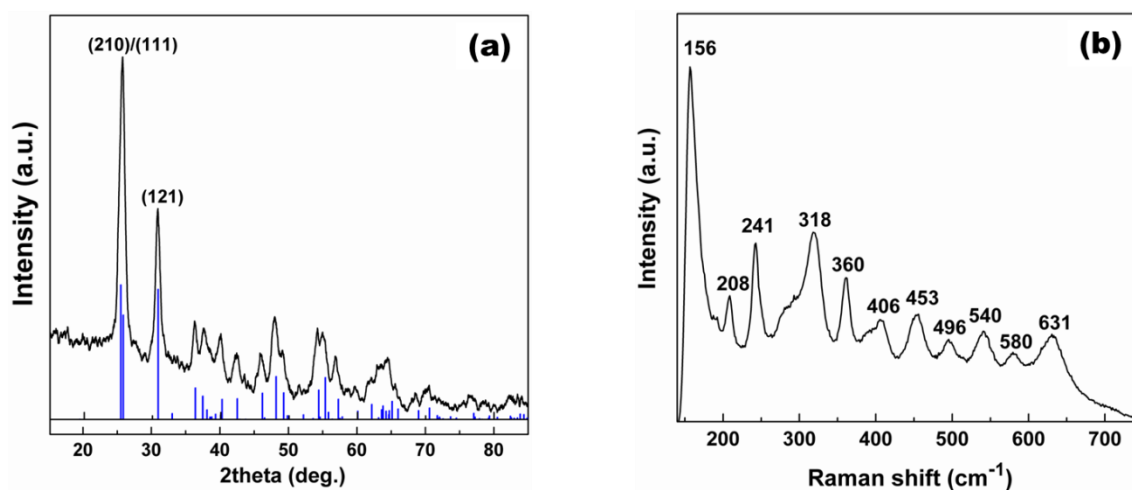


Figure 1. XRD pattern and Raman spectra of TiO₂ brookite nanoparticles.

3.2. Influence of pH on SMX photodegradation

pH is often one of the noticeable factors affecting the surface electrical charge of photocatalysts to control their ability to generate free electrons or holes under irradiation. Besides, organic compounds are actually affected by the value of pH in solution, which can change the standard oxidation/reduction potential of these compounds on their own. In fact, both the surface electrical charge of TiO₂ and the SMX forms that exist in solution were pH dependent. For example, Trovó *et al.* found that the SMX ($C_0 = 10 \text{ ppm}$) degradation was faster in distilled water ($\text{pH} = 4.8$) than in seawater ($\text{pH} = 8.1$) [4]. Niu *et al.* determined that the photodegradation of SMX ($C_0 = 5 \text{ ppm}$) in pure water was faster at lower pH values (between 3 and 10) [15]. In the present work, different pH values (2.0, 4.6, 10.0) were tested to figure out the relationship between the pH of SMX solution and the photodegradation of SMX over TiO₂ brookite NPs. In detail, when SMX was dissolved naturally in the DIW matrix, the pH value of pure SMX in water reached 4.6. At that point, SMX remained in a zwitterionic isomer. By controlling the pH of the working solution, we can change the zwitterionic isomer to either the cationic isomer with the presence of the $-\text{NH}_3^+$ functional group

at lower pH values or the anionic isomer with the =SO₂N⁻ functional group at higher pH values [16, 17].

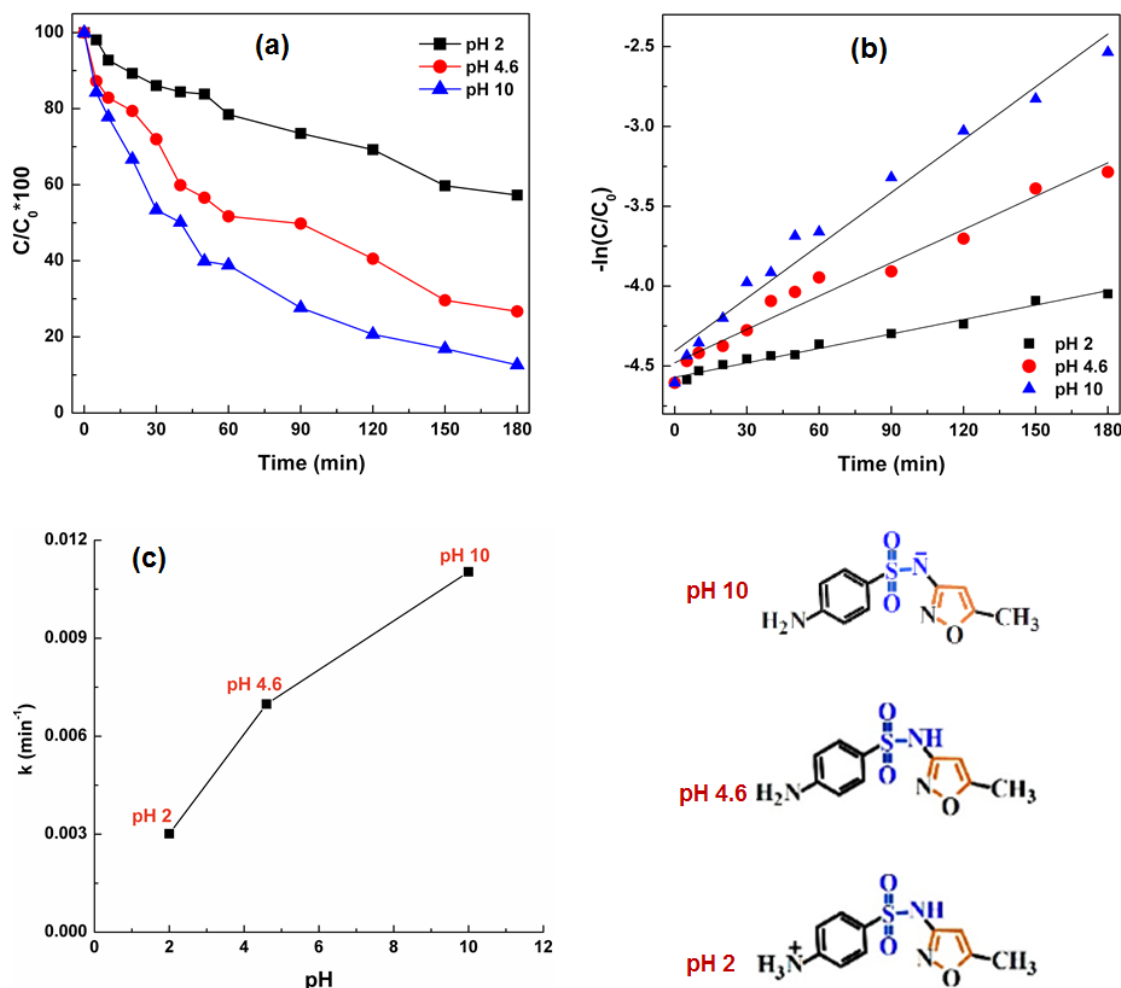


Figure 2. The effect of pH on the SMX photodegradation on TiO₂ brookite. Reaction conditions: SMX concentration: 10 ppm, reaction solution volume: 250 mL, TiO₂ loading: 10 mg.

To investigate the photocatalytic behaviour of TiO₂ brookite NPs for the degradation of each isomer of SMX molecules, we distributed the TiO₂ nanoparticles powder sample and dissolved SMX pollutant in a deionized water matrix well to obtain a proot solution with a pH value of 4.6, then divided the proot solution into 3 samples and adjusted the pH of two samples to 2.0 and 10.0 with the solutions of 3 M HCl and 3 M NaOH, respectively. The results of SMX photodegradation corresponding to these samples are shown in Fig. 2, which derived from UPLC MS/MS analysis. Figure 2a shows that in the first 20 min, there was an extremely minor difference in the photodegradation yield between samples at pH of 2.0 and pH of 4.6. Then after 180 min under UV-A irradiation, the photodegradation efficiency at pH 2.0 (49 %) is 1.4 times lower than at pH 4.6 (68 %) and 1.8 times lower that at pH 10.0 (88 %). It can be concluded that the higher the pH value, the better the photodegradability of SMX.

We have considered the relation between the natural logarithm of the division between the concentration of SMX at time (t) and the initial one ($\ln(C/C_0)$) and time of reaction t. The linear fit of the plot $\ln(C/C_0)$ versus irradiation time (t) was observed (Fig. 2b), which can be assigned to the first-order kinetics for the photodegradation as follows [12]:

$$\ln(C/C_0) = kt,$$

where k is the photodegradation rate constant, C_0 and C are the initial concentration of SMX solution and concentration of SMX at time (t), respectively. After calculation (Fig. 2c), the k values for photodegradation of the samples at pH of 2.0, 4.6, and 10.0 were 0.00301 ($R^2 = 0.98095$), 0.00698 ($R^2 = 0.97097$), and 0.01103 ($R^2 = 0.96392$) min^{-1} , respectively.

As the power laws for the first order kinetics, the initial rate (v_0) can theoretically be given as:

$$-v_0 = -dC/dt = kC_0,$$

where the rate coefficient of reaction k is constant and only depends on the reaction temperature and the own compounds, the surface area, the light irradiation and the catalysts for the reaction.

For the same reaction with the same photocatalyst, and at the same initial concentration and reaction temperature, the initial rates of all samples should be the same. In fact, the various values of k for each sample can be explained by the interaction between H^+ or OH^- and the active sites on the surface of TiO_2 NPs and between H^+ or OH^- and the type of isomers which can modify the activation energy of reaction, then a consequence to the various yields of photodegradation after 180 min. Another hypothesis that can be mentioned is that the concentration of H^+ can affect the surface electric charge that can make TiO_2 nanoparticles clustered or well disbanded a consequence to the change of the surface area and the less efficient irradiation. The obtained results are in good agreement with the work of Cheng *et al.*, who demonstrated that the SMX was degraded most rapidly in anionic forms [18]. The pH-dependent nature of both the SMX speciation and the surface charge of TiO_2 can be expressed by factors involved in controlling the pH values of the SMX solution.

Effect of water matrix

To determine the photocatalytic capability of the TiO_2 photocatalyst in real aqueous samples to photodegrade pollutants, three types of water matrices were thus used to prepare the SMX solution:

- Deionized water (DIW) was produced from a Simplicity®UVwater purify system (model: SIMS000WW, Millipore, France).
- Surface water (SW) was taken from West Lake (Ha Noi, Viet Nam) according to the guidance of government standard TCVN 6663-6:2018, kept in plastic bottles prerinsed with ultrapure water in the laboratory and rinsed with samples in the field, and filtered using glass fiber membrane (GF/F, Whatman, 0.7 μm) for removing suspended particles before testing.
- Mineral water (MW, Evian, France) with the main mineral composition of HCO_3^- (360 mg.L^{-1}); alkaline earth metal ions with high concentrations: Mg^{2+} (26 mg.L^{-1}), Ca^{2+} (80 mg.L^{-1}), Na^+ (6.5 mg.L^{-1}), K^+ (1 mg.L^{-1}); and NO_3^- (3.8 mg.L^{-1}), SO_4^{2-} (12.6 mg.L^{-1}) was stated on the products' label as a model for groundwater.

The experiments were set up under the same conditions of light irradiation, SMX concentration, and photocatalyst concentration. The concentrations of the SMX solutions were analyzed by the UPLC-MS/MS method at exact time points.

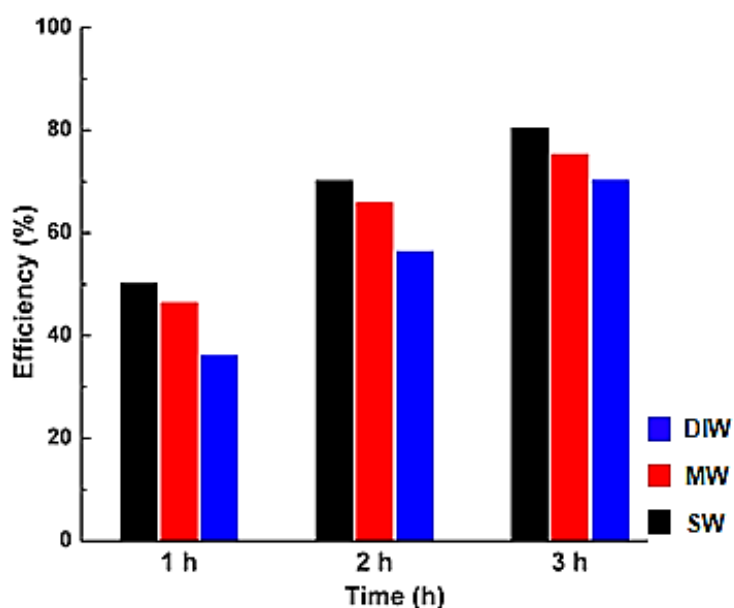


Figure 3. The effect of water matrix on the SMX photodegradation. Reaction conditions: SMX concentration: 10 ppm, reaction solution volume: 250 mL, TiO₂ loading: 10 mg.

The results are demonstrated in Fig. 3. TiO₂ brookite photocatalyst worked well in all SMX solutions with a high-degradation yield of 68, 75, and 80 %, respectively to water sources from deionized water, mineral water, and surface water after 3 h of treatment. The presence of metal ions (in the MW matrix) and natural organics (in the SW matrix) and the difference in pH values of SMX-TiO₂ solutions had a small effect on the photocatalytic ability of TiO₂ material for the SMX photodegradation. Mineral water was a matrix with various ions such as Ca²⁺, Mg²⁺, Na⁺, HCO₃⁻, SO₄²⁻ while Westlake's surface water was a highly intricate matrix with organic matter. In this case, the SMX-TiO₂ solutions had various pH values of 4.6, 5.8, and 8.7 corresponding to DIW, MW, and SW, respectively.

The results with SW and MW showed that the presence of metal ions and natural organic matter (NOM) actually affected the photocatalytic activity. Bicarbonate (HCO₃⁻) ions were reported to be an intermediate acceptor to trap the radical-electron from highly active •OH radicals [19]. In another report, Ioannidou's group suggested that bicarbonate ions reacted with hydroxyl radicals to form carbonate radicals ($E_0 = 1.78$ V) which had lower oxidizing strength than hydroxyl radicals ($E_0 = 2.3$ V) at the same pH [20]. Moreover, the presence of Ca²⁺ could induce the formation of CaCO₃ that precipitated on the surface of TiO₂ and was expected to reduce the photocatalytic activity [21]. In addition, the humic acid in NOM can have the photosensitizing or inhibitory effect. When it plays the role of photosensitizers, the rate of degradation could be increased since it may promote into transient states that easily react with dissolved oxygen to form more active radicals. However, the NOM played an opposite role in this case. The decrease of degradation rate could be explained by the inner filter effects, the scavenging/quenching of reactive species, and inhibitors [22]. In spite of the complicated system of these MW, and SW, the TiO₂ photocatalyst in our report still expressed high effectiveness to degrade SMX under fact-finding conditions.

Effect of photocatalyst loading

Figure 4 describes the photodegradation of SMX over different loads of TiO₂ brookite. With 10 mg of TiO₂ brookite loaded into the reaction, the degradation proceeded gently and reached 57 % after 2 h of photocatalytic treatment. At the same time, the experiments were performed with 20 and 50 mg of TiO₂ brookite. At the beginning, the concentration of SMX decreased dramatically and lost about 56 and 84 %, respectively, after the first 60 min. Then the velocity of the reaction decreased, and the yield was about 80 % with the 20 mg TiO₂ sample and nearly 100 % with the 50 mg TiO₂ sample after 120 min. This phenomenon can come from an increase in photocatalyst amount leading to an increase in the amount of active oxidizing chemical (radicals) species such as holes, electrons, hydroxyl radicals ($\cdot\text{OH}$), etc., thereby increasing the rate of photodegradation. However, at the end of the photocatalytic reaction, the concentration of pollutants was too small, therefore, the reaction rate decreased accordingly. The reaction will slowly reach equilibrium if the reaction time is prolonged.

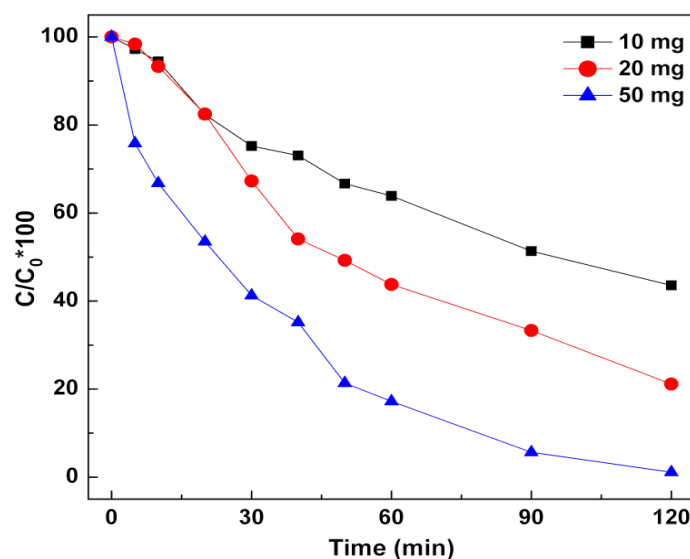


Figure 4. The effect of TiO₂ brookite loading on the SMX photodegradation. Reaction conditions: SMX concentration: 10 ppm, reaction solution volume: 250 mL.

The SMX degradation performance obtained in the study was compared with that obtained in previous reports. As shown in Table 1, sulfamethoxazole molecules were decomposed by various methods with different efficiencies. Methods using biological or oxidizing agents can achieve a high yield of SMX degradation, e.g. up to 98 % by Fenton reaction with the presence of H₂O₂ or 85 % with microbial fuel cells. However, the procedures often require advanced equipment such as large containers, pools for bio treatments, or the money-cost and dangerous oxidants. Other solutions with the use of noble metals such as gold and silver can also be considered to obtain effective photodegradation. Meanwhile, the disadvantage of precious metal-based photocatalysts is that they are always too expensive and less applicable for scale-up wastewater treatment applications.

In the present work, simulated UVA light used as an optical energy source and TiO₂ pure brookite acted as an active photocatalyst can be beneficial for SMX photodegradation under very low concentration conditions because of its strong photocatalytic performance, low-cost photocatalytic materials, and low photocatalyst-to-contaminant ratio. Brookite is also an

uncommon polymorph of TiO₂ material which has not been investigated in detail. That could be our selling point in the work.

Table 1. Comparison of sulfamethoxazole decomposition data of the current investigation with previous reports.

Method	Material	Degradation efficiency	Ref.
Biodegradation	Microbial fuel cells	85 % after 60 h	[23]
Biodegradation	Ni-MOF-74 in MFCs	61 %	[24]
Ozonation		44 % (TOC removal) in O ₃ /H ₂ O ₂ system	[25]
Fenton reaction	Commercial microscale zero-valent iron (mZVI)	98 % after 10 min, in the presence of H ₂ O ₂ for degradation of 25 μM SMX	[26]
Photocatalysis	AgBr-BaMoO ₄	62 % after 75 min under UV-vis light	[27]
Photocatalysis	Mono- (Au, Ag and Cu) and bi-metallic (Au-Ag and Au-Cu) deposited on TiO ₂ (P25)	100 % after 180 min under UVC light for degradation of 30 ppm SMX	[28]
Photocatalysis	TiO ₂ pure brookite	68, 75, and 80 % after 3 h of 10 ppm-SMX treatment, corresponding to water sources from deionized water, mineral water, and surface water, respectively	<i>This work</i>

4. CONCLUSIONS

A phase-pure TiO₂ brookite nanomaterial in powder form has been proved to be effective in the photodegradation of antibiotic compounds, exemplified by sulfamethoxazole. SMX molecules in the anionic form were most suitable for rapid degradation (at pH 10.0). With real matrices, the presence of metal ions in mineral water matrix and natural organic matter in surface water matrix did not deeply affect the photodegradation of sulfamethoxazole on TiO₂ brookite NPs, either by the possible complexation of SMX with cations or by the ability of anions to scavenge the hydroxyl radicals responsible for photodegradation. The photodegradation of SMX in aqueous systems followed an apparent first-order kinetics under simulated UV-A irradiation. The higher the photocatalyst load, the higher the photocatalytic efficiency. Further study is needed to optimize the TiO₂/UV-A light system for practical applications of the present heterogeneous photocatalytic process.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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