Degradation of enrofloxacin by photocatalysis using titanium dioxide nanomaterials

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Abstract. This work evaluates the ability to degrade Enrofloxacin (ENR) in synthetic high concentration wastewater by the photocatalytic method using pure TiO2 nanomaterials. The material properties, including morphology, crystalline structure, UV-Vis absorption, and surface acidity-basicity, were also characterized. The treatment efficiency of 50 mgENR/L reached over 80% after 2 h of UVA irradiation, at pH 6 and 1 gP25/L. The antibacterial level of ENR after treatment was checked by Bacillus subtilis activity. After treatment, the activity of ENR residue was no longer sufficient to cause inhibition of the bacteria while the degraded product was not toxic to it. The research results show that the photocatalysis material has a good ability to degrade ENR as well as other antibiotic residues in the water environment.

1. Introduction
Antibiotic, literally "opposing life" originating from the ancient Greek language, is widely used to fight bacteria for the treatment and prevention of infections in human medicine and animal husbandry. Antibiotics were revolutionized in the 20th century after Alexander Fleming discovered today's penicillin in 1928. However, its effectiveness and overuse resulted in the presence of more and more antibiotics in the environment [1]. Through accumulation, human and animal excretion along with economic development, social activities, health care, antibiotic residues and antibiotic resistance have emerged as a problem. The World Health Organization has issued recommendations that antibiotic resistance is widespread. It is an injurious threat that is happening, and will likely affect everyone anywhere in the world [2]. Because of the severity of antibiotic resistance, biological treatments no longer seem to be as preferred as they used to be for other contaminants, and the ability to metabolize antibiotics by this method is often unstable. Advanced oxidation processes (AOPs) have been reported to be highly effective in removing antibiotics from wastewater [3]. The photocatalytic process was
found and developed after scientists discovered the photocatalytic ability of TiO$_2$ in 1972 [4]. Illumination from a light source with higher photon energy than the bandgap promotes the formation of strongly oxidizing free radicals that break down the pollutants to eventually form CO$_2$ and H$_2$O. Titanium dioxide is an extremely popular photocatalytic nanomaterial. It has been used in many different industries, including the field of environmental treatment [5] with many publications [6-13]. Enrofloxacin (C$_{19}$H$_{22}$FN$_3$O$_3$, denoted as ENR) is an antibiotic of the fluoroquinolones group. In high doses, ENR causes many side effects and leaves sequelae in young organisms, with effects especially on immature articular cartilage, urinary tract, digestive tract, and central nervous system. Therefore, it is recommended for use in terms of frequency and dose as well as for future pharmacokinetic studies [14]. In Vietnam, antibiotics were used for uncontrolled livestock. In recent years, it has become a hot topic in terms of residue and usage. The concentration of antibiotics detected in the environment was recorded and found to increase in concentration [15-18]. The use of TiO$_2$ as a photocatalytic material in antibiotic treatment has also been widely reported. There are studies using TiO$_2$ to eliminate the most commonly used families of antibiotics such as β-lactams (e.g., amoxicillin, penicillin, ampicillin) [19, 20], sulfonamides (e.g., sulfamethoxazole, sulfamethazine, sulfadiazine, sulfamerazine, and sulfathiazole) [21-25], fluoroquinolones (e.g., enrofloxacin, ciprofloxacin, ofloxacin, and levofloxacin) [6, 26], tetracycline [27, 28], and chloramphenicol [29]. In general, these reports show the high efficiency of photocatalysis using TiO$_2$ nanomaterials for antibiotic treatment in the environment and most of the degraded products were not more toxic than the original precursors. Although the application of photocatalysis for antibiotics seems to be very promising, there has not been any study on photocatalytic degradation of ENR by pure TiO$_2$.

In this research, photocatalytic degradation of ENR using TiO$_2$ nanomaterial was conducted. The effects of operational parameters such as ENR concentration, catalytic dose, pH, and UVA irradiation were investigated to find out the suitable treatment condition. Besides, the antimicrobial property of ENR after the photocatalytic test was examined with a Bacillus subtilis strain.

2. Experiments and methods

2.1. Photocatalytic experiment

Enrofloxacin (C$_{19}$H$_{22}$FN$_3$O$_3$) was imported from Zhejiang Goubang Pharmaceutical Co., Ltd (Zhejiang, China). TiO$_2$ nanomaterial (Degussa P25) was manufactured by Merck (Germany). A simple experimental design was set up, consisting of a 2-L vertical cylindrical glass bottle and a long UVA lamp with a wavelength of 365 nm (Panasonic, Japan) mounted inside a glass tube to protect the
lamp from the damage of water and catalytic materials. The light was positioned vertically in the center of the glass bottle to ensure that when the light was on, UVA could illuminate the entire system. A rectangular box was covered with a coated aluminum foil to cover all the light emitted by the UVA lamp. Above the model, there was a small hole for sampling over time. The whole system was placed on a magnetic stirrer (Figure 1). Solution pH was adjusted by 0.1 M NaOH and HNO₃ solutions.

The concentration of ENR was determined by using a photoLab 6100 Vis spectrophotometer at 320 nm wavelength about every 30 min after centrifuging the taken samples at 60,000 rpm and through two layers of filter. The degradation efficiency (H%) of the model was calculated using Equation 1:

\[ H\% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \]  

Where \( C_0 \) and \( C_t \) are the initial and at time \( t \) concentration of ENR (mg/L).

2.2. Antibacterial activity

The diffusion method was used to determine the antibacterial ability of ENR to *Bacillus subtilis* bacteria after treatment. A bacterial density of about \( 10^8 \) CFU/mL was spread on the surface of a Petri containing a tryptic soy agar (TSA). Then, a hole was made at the center of the agar with 7 mm of diameter. The ENR solution was pumped into the agar hole position before and after photocatalytic degradation. The Petri was incubated at 37°C for 24-48h before measuring the diameter of the antibacterial ring and recording the results [30].

3. Results and discussion

3.1. Photocatalyst characterization

The photocatalytic material used in this study was pure P25 TiO₂ (Degussa, Merck, Germany). P25 is a very popularly commercialized nanomaterial, in a form of 0D nanoparticle with a combination of anatase and rutile in its crystalline phase. The 0D morphology of the TiO₂ usually gives out high photocatalytic activity because of its high area/volume ratio, high surface area, good light adsorption capacity, and very good dispersibility in water. The properties of the P25 TiO₂ material are summarized in Table 1.

| Features                  | Value  |
|---------------------------|--------|
| Zeta potential            | -13.2  |
| The conductivity of the suspension (μS/cm) | 0.0303 |
| Electrophoresis (μm.cm/V.s) | -1.033 |
| Cluster diameter (nm)     | 563.2  |
| pHzpc                     | 6.3    |
| Surface area (m²/g)       | 52.8   |
| Pore volume (cm³/g)       | 0.13   |
| Pore diameter (nm)        | 9.6    |
| Particle size (nm)        | 10 – 30 |

To determine the microscopic morphology and material structure, SEM (scanning electron microscopy) and TEM (transmission electron microscopy) were applied. Figure 2 shows that P25 are nano-sized particles distributed in clusters of about 560 nm. The individual particle size ranged from 10 - 30 nm, which was primarily at 20 nm.

The specific surface area based on the BET surface analysis method of this TiO₂ material was determined to be 52.8 m²/g while the parameter for pure TiO₂ material is 84.69 m²/g. The result
showed that this material tended to combine in clusters. The pore size distribution of the material is shown in Figure 3. This material had a wide pore distribution size from 2 - 127 nm, providing a large photon absorption capacity. The BET method was evaluated through the ability to adsorb and desorb N\textsubscript{2} gas. Figure 4 depicts the N\textsubscript{2} adsorption-desorption isotherms of the photocatalytic materials used. The adsorption and desorption curves are likely structured in the adsorption hysteresis of the cylinder. Considering the adsorption isotherms, this is the type of U-adsorption, where N\textsubscript{2} is mainly adsorbed onto nonporous and macroporous pores and the adsorption force is smaller than the gas molecular bonding force.

Figure 2. (a) SEM and (b) TEM images of P25 TiO\textsubscript{2}.

Figure 3. The pore size distribution of P25 TiO\textsubscript{2}.

Figure 4. The N\textsubscript{2} adsorption-desorption isotherms of P25 TiO\textsubscript{2}.
X-ray diffraction (XRD) was used to examine the crystal structure of the TiO\(_2\) material. The XRD pattern of the TiO\(_2\) material is shown in Figure 5. Obviously, at the TiO\(_2\) peaks, the crystal structure was in anatase and rutile form. In which case, anatase was the main structure due to having high peaks and accounting for the majority in XRD analysis range at 2\(\theta\) of 25.24 (101), 37.72 (004), 38.53 (112), 48.00 (020), 54.98 (121), 62.62 (204), 68.92 (301), 69.04 (112), 70.2 (220), and 75.02 (215). In addition, the peaks of rutile configuration also appeared at 2\(\theta\) = 27.4 (110), 35.82 (101), and 41.22 (111) [31]. The mixed phase of anatase and rutile is usually considered as an advantage of the material, which increases the charge separation and prevents the photo-excited electron-hole recombination.

![Figure 5. The XRD pattern of P25 TiO\(_2\).](image)

The bandgap energy value of a TiO\(_2\) material is a significant parameter in evaluating the photocatalytic efficiency of one material relative to another. Besides, the UV-Vis absorption of the material is also important when considering the actual application of the material. For TiO\(_2\), the bandgap energies (and adsorption edges) were determined at 3.2 eV (\(\approx\) 387.5 nm) and 3.0 eV (\(\approx\) 413.3 nm) for anatase and rutile crystal structures, respectively (Figure 6). These high bandgaps implied that TiO\(_2\) mostly works under UV irradiation conditions.

![Figure 6. UV-visible results and bandgap energies of P25 TiO\(_2\).](image)
The surface acidity and the basicity partly determine the efficiency of a material's pollution treatment as well as the actual operating conditions. The temperature programmed desorption (TPD) analysis method was applied to check the acidity and basicity of the material surface. The adsorption spectra of NH$_3$ and CO$_2$ according to the temperature program are plotted in Figure 7. Both NH$_3$-TPD and CO$_2$-TPD showed two peaks, proving that the material had both Bronsted/Lewis acid/basic sites on their surface, which could enhance the oxidation-reduction reaction.

Figure 7. NH$_3$- and CO$_2$-TPD results of P25 TiO$_2$.

3.2. Photocatalytic degradation of ENR

The treatment ability of P25 during the reaction time for ENR is shown in Figure 8. With an initial concentration of 50 mg/L, original pH of 6.53, and 0.5 gP25/L, the removal efficiency rapidly reached 51.4% after 30 minutes of UVA irradiation. The efficiency was then slowly increased to 62.1% after 2 h of UVA irradiation. In order to ensure there was enough time for the reaction to occur, 120 min was chosen as reaction time for further investigation of the effects of pH, dosage P25, and ENR initial concentration.

Figure 8. The photodegradation of ENR during 120 minutes of irradiation (50 mgENR /L, 0.5 gP25/L, pH 6.53).
The experiments at pH range from 5 to 7.5 were performed to evaluate the effect of pH on P25 ENR degradation. The efficiency of ENR removal at different pH is illustrated in Figure 9. The possibility of ENR degradation was higher at neutral and weak alkaline levels than at weak acid conditions. After 120 minutes of irradiation by UVA lamp, ENR degradation efficiency was up to 80% at pH 6. The efficiency dropped faster in acidic environments but slower in alkaline environments. The effect of the solution pH on treatment efficiency is a complex process. It involves the ionization state of the catalytic material surface, the formation of free radicals, and other reactions in the system. The analytical result of pH_{pzc} of the P25 TiO_2 was 6.3 while the pK_{a1} and pK_{a2} values of ENR were 6.03 and 8.70, respectively [5]. Accordingly, at pH < 6, the photocatalytic surface of P25 was positively charged. It is similar to ENR, which is usually present as cations below pK_{a1} and anion above pK_{a2}. Here, it is not clear about the effect of pH since both the catalyst and the ENR substrate exist in the form of cations and anions under acidic or alkaline conditions. The highest ENR removal efficiency at pH 6 could be explained by the adsorption onto the surface of the TiO_2 nanoparticles or the negatively charged post-mineralization products of the ENR, resulting in an attractive electrostatic interaction between them.

**Figure 9.** The effect of pH on ENR degradation (120 min, 50 mgENR /L, 0.5 gP25/L).

**Figure 10.** Effect of P25 loading on ENR degradation (120 min, 50 mgENR/L, pH 6).
The catalytic dosage is an important factor when considering the practical application of a photocatalytic process. The effect of P25 dosage was studied from 0.25 to 2 g/L and the results are demonstrated in Figure 10. The removal efficiency of ENR increased with the increasing dose of P25 from 0.25 to 1.00 gP25/L and then began to decrease with a further increase of the dosage to 2 g/L. When the P25 concentration reached a value, it could increase light scattering and hinder light exposure to pollutants [32]. Meanwhile, the ability of combination and deposition of TiO\textsubscript{2} particles would also be increased at high concentrations [33, 34], which decreases the degradation efficiency. In the case of practical application in wastewater, the concentration of catalyst should be increased because of the existence of anions (e.g., chloride, sulfate, phosphate, and bicarbonate) that could interfere with the formation of oxidative free radicals or the turbidity that reduce the light density in the wastewater.

The relationship between the input pollutant concentrations and the pollutant degradation efficiency is described by the pseudo-first-order kinetics (1). At the same time, the heterogeneous photocatalytic process is often described by the Langmuir-Hinshelwood (L-H) equation (2). These are two equations widely used to describe a photocatalytic degradation process.

\[
\ln \left( \frac{C_t}{C_0} \right) = -K_{obs} \times t \quad (1)
\]

\[
\frac{1}{K_{obs}} = \frac{1}{K_C} \times K_{L-H} \times t \quad (2)
\]

Where \(K_{obs}\) is the degradation rate constant ENR (1/min) in linear first-order and \(C_0\) is the initial concentration of ENR (mg/L). \(K_C\) refers to the surface reaction rate constant (mg/(L.min)) and \(K_{L-H}\) represents the adsorption equilibrium constant according to the L-H model (L/mg).

![Figure 11](image-url)

**Figure 11.** Pseudo-first order with initial ENR concentration changes 10 – 50 mg/L (1 gP25/L, pH 6, inset is the L-H kinetic model).

The results obtained from the kinetic models are provided in Figure 11. The correlation coefficient (\(R^2\)) for the regression line was 0.9539, showing that the kinetics of the ENR degradation reaction follows the L–H model. The ENR initial concentration increase leads to increased photon absorption. The amount of photons used by TiO\textsubscript{2} is reduced, resulting in a lack of photons on the TiO\textsubscript{2} active surface. At the same time, the high concentration of ENR occupies a larger number of TiO\textsubscript{2} active
sites, which prevents the formation of free oxidizing radicals and results in a decrease in degradation efficiency [6]. The degradation rates were different for each different ENR concentration. However, the correlation coefficient $R^2$ of the first-order linear equations were all high for all investigated concentration ranges, proving the reliability of this equation.

3.3. Antibacterial activity
Toxicity testing of contaminants after degradation is the basis for determining the impact on the environment. As for antibiotic residues, it is especially important to check their antimicrobial level after treatment. The concentration of ENR and its products/by-products after photocatalytic degradation was used to test the growth and development of *Bacillus subtilis*. This is a common strain that exists in many different environments and is very sensitive to ENR. After 48 hours of incubation in a plate agar, the antibacterial of ENR shown by inhibition halo can be seen very clearly in Figure 12. Accordingly, after only 60 minutes of irradiation, the antibacterial activity of ENR was reduced and completely disappeared after 90 minutes. Using TiO$_2$ for the photocatalytic degradation of ENR, the products and by-products did not cause any biological toxicity.

![Figure 12. Bacillus subtilis inhibition halo at different times of UVA irradiation in the presence of P25 TiO$_2$.](image)

4. Conclusion
The ability to degrade ENR by P25 TiO$_2$ was evaluated and the effect of operating factors was also investigated. The degradation efficiency of 50 mgENR/L was over 80% when using 1 gP25/L after 2 hours of UVA irradiation at pH 6. In addition, the antimicrobial activity of ENR on *Bacillus subtilis* disappeared completely after 60 minutes of photocatalytic reaction. This result shows a very promising application of TiO$_2$ photocatalysts for the degradation of antibiotic residues, which is an emerging pollutant that has many potentials to cause ecological imbalances, environmental pollution, and affect human health in the future.

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References

[1] NHS 2014 Antibiotics.

[2] WHO 2014 Antimicrobial resistance: global report on surveillance: World Health Organization

[3] Homem V and Santos L 2011 Degradation and removal methods of antibiotics from aqueous matrices—a review J. Environ. Manage. 92 2304-47

[4] Fujishima A, Rao T N and Tryk D A 2000 Titanium dioxide photocatalysis J. Photochem. Photobiol. C 1 1-21

[5] Nakata K and Fujishima A 2012 TiO\textsubscript{2} photocatalysis: Design and applications J. Photochem. Photobiol. C 13 169-89

[6] Li W, Guo C, Su B and Xu J 2012 Photodegradation of four fluoroquinolone compounds by titanium dioxide under simulated solar light irradiation J. Chem. Technol. Biotechnol. 87 643-50

[7] Jiang Y, Zhang M, Xin Y, Chai C and Chen Q 2019 Construction of immobilized CuS/TiO\textsubscript{2} nanobelts heterojunction photocatalyst for photocatalytic degradation of enrofloxacin: synthesis, characterization, influencing factors and mechanism insight J. Chem. Technol. Biotechnol. 94 2219-28

[8] Zhang R, Yu Y, Wang H and Du J 2020 Mesoporous TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composites with O-Ti-N bridge for improved visible-light photodegradation of enrofloxacin Sci. Total Environ. 138280

[9] Yu Y, Yan L, Cheng J and Jing C 2017 Mechanistic insights into TiO\textsubscript{2} thickness in Fe\textsubscript{3}O\textsubscript{4}@TiO\textsubscript{2}-GO composites for enrofloxacin photodegradation Chem. Eng. J. 325 647-54

[10] Xekoukoulotakis N P, Drosou C, Brebou C, Chatzisymeon E, Hapeshi E, Fatta-Kassinos D and Mantzavinos D 2011 Kinetics of UV-A/TiO\textsubscript{2} photocatalytic degradation and mineralization of the antibiotic sulfamethoxazole in aqueous matrices Catal. Today 161 163-8

[11] Su Y, Chen P, Wang F, Zhang Q, Chen T, Wang Y, Yao K, Lv W and Liu G 2017 Decoration of TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} Z-scheme by carbon dots as a novel photocatalyst with improved visible-light photocatalytic performance for the degradation of enrofloxacin RSC Advances 7 34096-103

[12] Topkaya E, Konyar M, Yatmaz H C and Öztürk K 2014 Pure ZnO and composite ZnO/TiO\textsubscript{2} catalyst plates: A comparative study for the degradation of azo dye, pesticide and antibiotic in aqueous solutions Journal of Colloid Interface Science 430 6-11

[13] Huang J, Li D, Li R, Chen P, Zhang Q, Liu H, Lv W, Liu G and Feng Y 2020 One-step synthesis of phosphorus/oxygen co-doped g-C\textsubscript{3}N\textsubscript{4}/anatase TiO\textsubscript{2} Z-scheme photocatalyst for significantly enhanced visible-light photocatalysis degradation of enrofloxacin J. Hazard. Mater. 386 121634

[14] Mitchell M A 2006 Enrofloxacin Journal of Exotic Pet Medicine 15 66-9

[15] Binh V N, Dang N, Anh N T K and Thai P K 2018 Antibiotics in the aquatic environment of Vietnam: sources, concentrations, risk and control strategy Chemosphere 197 438-50

[16] Chau N D G, Sebesvari Z, Renaud F G, Rosendahl I, Hoang Minh Q and Amelung W 2015 Occurrence and dissipation of the antibiotics sulfamethoxazole, sulfadiazine, trimethoprim, and enrofloxacin in the Mekong Delta, Vietnam PLoS One 10 e0131855

[17] Giang C N D, Sebesvari Z, Renaud F, Rosendahl I, Minh Q H and Amelung W 2015 Occurrence and dissipation of the antibiotics sulfamethoxazole, sulfadiazine, trimethoprim, and enrofloxacin in the Mekong Delta, Vietnam PloS One 10 e0131855

[18] Duong H A, Pham N H, Nguyen H T, Hoang T T, Pham H V, Pham V C, Berg M, Giger W and Alder A C 2008 Occurrence, fate and antibiotic resistance of fluoroquinolone antibacterials in hospital wastewaters in Hanoi, Vietnam Chemosphere 72 968-73

[19] Elmolla E S and Chaudhuri M 2010 Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/TiO\textsubscript{2} and UV/H\textsubscript{2}O\textsubscript{2}/TiO\textsubscript{2} photocatalysis Desalination 252 46-52
[20] Klauson D, Babkina J, Stepanova K, Krichevskaya M and Preis S 2010 Aqueous photocatalytic oxidation of amoxicillin *Catal. Today* **151** 39-45

[21] Abellán M, Bayarri B, Giménez J and Costa J 2007 Photocatalytic degradation of sulfamethoxazole in aqueous suspension of TiO$_2$ *Appl. Catal., B* **74** 233-41

[22] Hu L, Flanders P M, Miller P L and Strathmann T J 2007 Oxidation of sulfamethoxazole and related antimicrobial agents by TiO$_2$ photocatalysis *Water Res.* **41** 2612-26

[23] Calza P, Medana C, Pazzi M, Baiocchi C and Pelizzetti E 2004 Photocatalytic transformations of sulphonamides on titanium dioxide *Appl. Catal., B* **53** 63-9

[24] Kaniou S, Pitarakis K, Barlagianni I and Poulios I 2005 Photocatalytic oxidation of sulfamethazine *Chemosphere* **60** 372-80

[25] Baran W, Sochacka J and Wardas W 2006 Toxicity and biodegradability of sulfonamides and products of their photocatalytic degradation in aqueous solutions *Chemosphere* **65** 1295-9

[26] Michael I, Hapeshi E, Michael C and Fatta-Kassinos D 2010 Solar Fenton and solar TiO$_2$ catalytic treatment of ofloxacin in secondary treated effluents: evaluation of operational and kinetic parameters *Water Res.* **44** 5450-62

[27] Palominos R A, Mondaca M A, Giraldo A, Peñuela G, Pérez-Moya M and Mansilla H D 2009 Photocatalytic oxidation of the antibiotic tetracycline on TiO$_2$ and ZnO suspensions *Catal. Today* **144** 100-5

[28] Addamo M, Augugliaro V, Di Paola A, García-López E, Loddo V, Marci G and Palmisano L 2005 Removal of drugs in aqueous systems by photoassisted degradation *J. Appl. Electrochem.* **35** 765-74

[29] Chatzitakis A, Berberidou C, Paspaltsis I, Kyriakou G, Sklaviadis T and Poulios I 2008 Photocatalytic degradation and drug activity reduction of chloramphenicol *Water Res.* **42** 386-94

[30] CLSI 2015 *M45: Methods for antimicrobial dilution and disk susceptibility testing of infrequently isolated or fastidious bacteria* (Wayne, PA: Clinical and Laboratory Standards Institute)

[31] Chelbi S, Djouadi D, Chelouche A, Hammiche L, Touam T and Doghmane A 2020 Effects of Ti-precursor concentration and annealing temperature on structural and morphological properties of TiO$_2$ nano-aerogels synthesized in supercritical ethanol *SN Applied Sciences* **2** 1-10

[32] Kansal S, Singh M and Sud D 2007 Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts *J. Hazard. Mater.* **141** 581-90

[33] San N, Kılıç M, Tuiebakhova Z and Çınar Z 2007 Enhancement and modeling of the photocatalytic degradation of benzoic acid *Journal of Advanced Oxidation Technologies* **10** 43-50

[34] So C, Cheng M Y, Yu J and Wong P 2002 Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation *Chemosphere* **46** 905-12