



Synthesis of S doped TiO₂ (S-TiO₂) to enhance photocatalytic degradation of Ciprofloxacin in aqueous solutions under visible light

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ABSTRACT

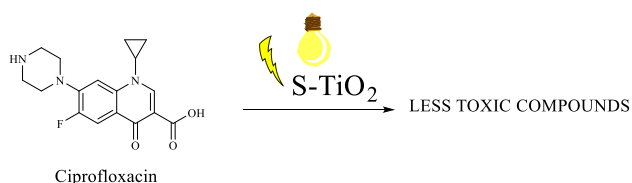
In this study, the sol-gel method was successfully used to synthesize S-TiO₂ for efficient photocatalytic degradation of Ciprofloxacin solution under visible irradiation. These synthesized materials were characterized by various analytical methods such as XRD, SEM-EDX, FT-IR, and UV diffuse reflectance spectroscopy (DRS). XRD, SEM-EDX, and FT-IR confirmed the successful preparation of these materials. The UV-DRS demonstrated that the material has a lower bandgap in comparison with prime TiO₂. The photodegradation results reported that the 0.33S-TiO₂ had shown high efficiency in the degradation of Ciprofloxacin in comparison with TiO₂. The decomposition of 10 mg/L Ciprofloxacin concentration reached approximately 90% for 150 minutes of visible light irradiation at room temperature at pH = 4.

Introduction

Nowadays, Ciprofloxacin is the most frequently detected fluoroquinolone antibiotic in hospital wastewater, wastewater treatment plants, and raw drinking water [1-4]. Its harmful effects are pretty severe not only to humanity but also to other organisms. Humans use Ciprofloxacin water, resulting in vomiting, tremors, nausea, headache, diarrhea, and nervousness [5-7]. Other reported effects include stomatitis, leukopenia, skin disorder, and damage to the immune system [8]. Apart from the detrimental impact on water quality, the presence of Ciprofloxacin in the environment alters the capability of high surface areas soil components such as clay minerals and metal oxides.^[9]Therefore, developing methods to remove wastewater contaminants has gained considerable interest in commercial and academic worldwide.

Photocatalysis is a promising advanced water treatment process [10].

Titanium dioxide (TiO₂) is the most popular photocatalyst with high photocatalytic activity, non-toxic, comparatively cheap cost, and chemical stability within a wide range of pH [11-13]. However, various research indicated that TiO₂ is limited practical application under visible light conditions due to the bandgap of anatase phase is 3.2 eV which only absorbs UV light [14-16]. To improve its problems, the modifications of TiO₂ via doping with metals, non-metals, or through the formation of heterojunctions lead to enhance the photocatalytic activity was investigated [17-20]. Among those, sulfur (S) doped TiO₂ (S-TiO₂) photocatalysts have been widely used to treat polluted water [21]. From the view of this point, this paper aims at the catalytic activity of S-TiO₂ in the degradation of this antibiotic (Scheme 1).



Scheme 1: Proposed photodegradation reaction of S-TiO₂

Experimental

Chemicals and methods

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification include Titanium isopropoxide (TiOT) Ti(OC₃H₇)₄ 98%, HNO₃ 63-65%, Ethanol (C₂H₅OH 99,9%), Thiourea CS(NH₂)₂, Deionized water and Ciprofloxacin.

The XRD pattern was collected from XRD Miniflex 600 apparatus (Rigaku, Japan). Fourier- transform infrared spectroscopy was measured by FT-IR 4600 of Jasco, Japan. The SEM images were taken by TM4000Plus, Hitachi, Japan. The EDX analysis was calculated from EDX Oxford measurement.

Synthesis of TiO₂ and S-TiO₂

TiO₂ materials were synthesized by a simple method following a previous report using Titanium isopropoxide as the source of Ti [22]. Firstly, solution A included 1.5 mL H₂O, 40 mL of Ethanol was kept at room temperature under stirring. At the same time, solution B, including 40 mL of Ethanol, 10 mL of Titanium isopropoxide, and amount of HNO₃ for adjusting to pH = 2, was prepared. Subsequently, solution B was added dropwise into solution A and kept stirring for 24 hours. Then the resultant mixture was aged at 180°C for 3 hours. Finally, the solid was filtered, washed with Deionized water, and dried in an oven at 70°C overnight. S-TiO₂ was synthesized via a similar process in the presence of thiourea as Sulfur dopants precursors. The synthesized materials was obtained and denoted as xS-TiO₂ (x is the mole ratio of S/Ti = 0.25; 0.33; 0.50, respectively).

Degradation of Ciprofloxacin

In a typical experiment, 50 mg catalysts were suspended in 100 mL of the Ciprofloxacin solution with the concentration of 10 mg/L in the absence of light for 30 min to ensure adsorption-desorption equilibrium. Then the suspension was irradiated by a 36 W compact

lamp under constant stirring, while the temperature inside the reactor was maintained at room temperature by the following water out the site of the reactor. A lamp is hanging at a distance of 10 cm from the surface of the solution. During the 150 minutes irradiation at room temperature, 5 mL of the mixture was continuously taken from the mixture reaction at a 30 minutes interval for the Ciprofloxacin degradation analysis by UV-VIS spectrophotometer (UV 4150, Hitachi, Japan).

Results and discussion

Characterization of materials

Figure 1 shows the XRD patterns of TiO₂ and S-TiO₂. It is clearly noticed that all diffractive peaks of TiO₂ and 0.33S-TiO₂ are congruently indexed with anatase phase TiO₂. Peaks located at 2θ = 25.2, 37.7, 47.9, 54.0, 54.9, 62.8, 68.9, 70.1, and 75.1° are corresponded to the crystal planes of (101), (004), (200), (105), (211), (204), (116), (220), and (215) [23]. Moreover, no other impurities can be detected, implying the high purity of the prepared materials. It is hard to see the lattice distortion of TiO₂ after S doping since S (1.84 Å) has a larger ionic radius than O (1.40 Å). The prepared materials show grey-white color, confirming the existence of S atoms in TiO₂ [24].

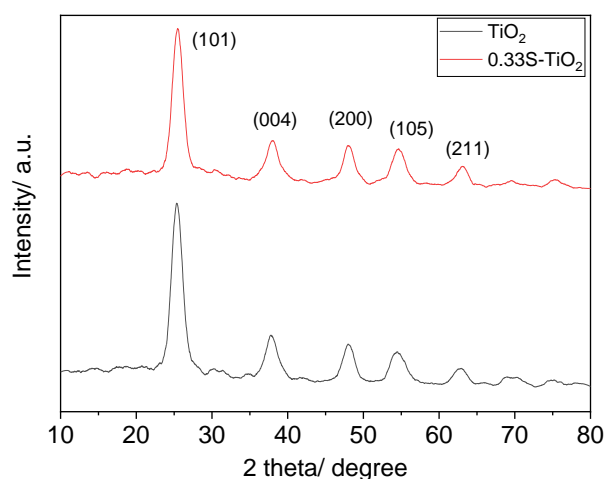


Figure 1: XRD patterns of TiO₂ and 0.33S-TiO₂

FT- IR is performed on samples to identify materials composition and functional group present in the material. The FT-IR spectra were measured for all the materials in the spectral range from 400 to 4000 cm⁻¹ at room temperature and shown in Figure 2.

It was hardly seen that the peaks at 483 cm⁻¹ in these obtained FT-IR spectra of this synthesized TiO₂ and S-TiO₂ corresponded to O-Ti bond.

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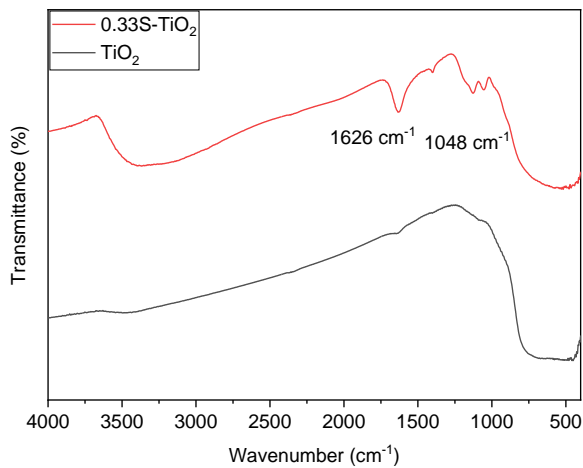


Figure 2: FT-IR of synthesized TiO₂ and 0.33S-TiO₂

These peaks at 1626 and 1048 cm⁻¹ in the FT-IR range of the S-TiO₂ reached an oscillation of this S-O bonds, respectively [25]. It confirmed that S was successfully doped into TiO₂ material. Figure 3 presents the SEM images of TiO₂ and S-TiO₂. The SEM results show that the S-TiO₂ particles are relatively uniform in size and more porous than TiO₂. Figure 3 also showed that all materials were successfully synthesized.

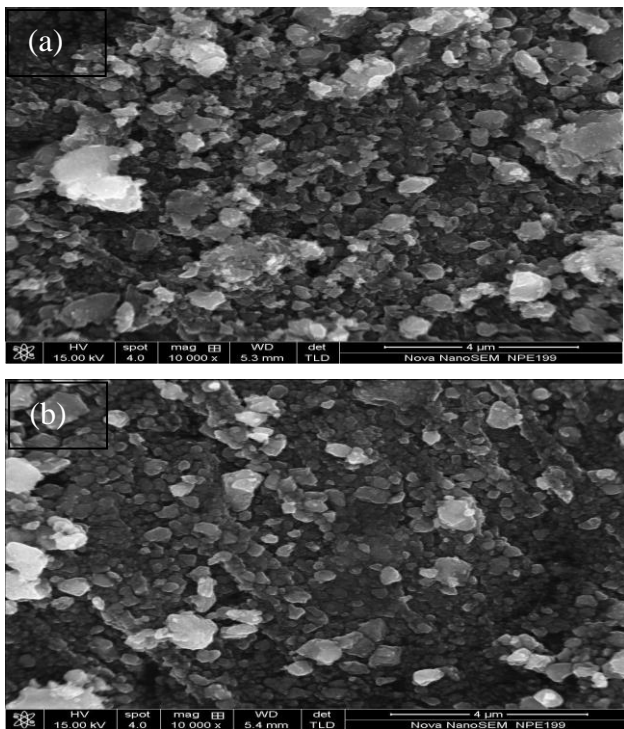


Figure 3: SEM images of TiO₂ (a) and 0.33S-TiO₂ (b)

To confirm the successfully S doped TiO₂, EDX of target materials was also analyzed and shown in figure 4. From these results, the S was good dispersion in the S-TiO₂. It was suggested that the sulfur was successfully doped TiO₂.

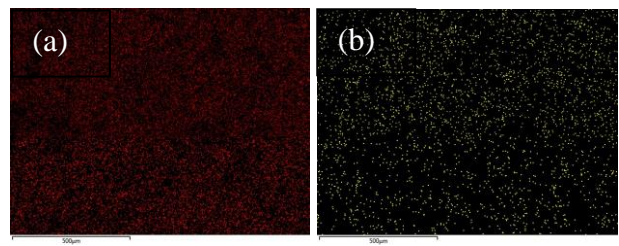


Figure 4: EDX mapping of 0.33S-TiO₂: Ti Kα1 (a) and S Kα1 (b)

In addition, electronic and optical properties are of fundamental importance to determine the photoactivity of a catalyst. UV-DRS was used for characterizing the absorption properties of synthesized materials. The estimated bandgap energies of materials TiO₂ and S-TiO₂ were calculated at 3.16 and 2.85 eV (figure 5b). The decrease in E_{bg} of the S-TiO₂ could be explained due to the existence of S dopants in the TiO₂ structure. These dopants would modify the potential band of the TiO₂ leading to a decrease in E_{bg} [26]. So it may be promoted S-TiO₂ is more active than TiO₂ under visible light irradiation

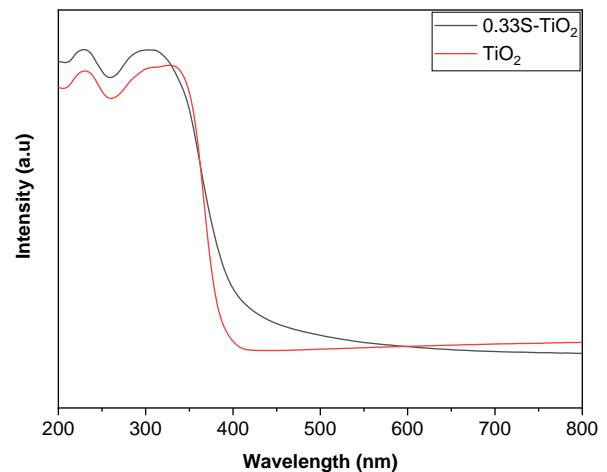


Figure 5a: UV – Vis spectra of TiO₂ and 0.33S-TiO₂

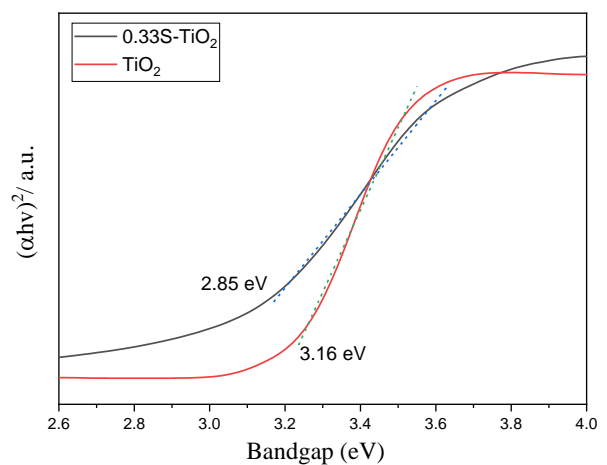


Figure 5b: Tauc plot of TiO₂ and 0.33S-TiO₂

Photodegradation of Ciprofloxacin

The photocatalytic activity of target materials was investigated for the photodegradation of Ciprofloxacin in water. The effect of the ratio S/Ti on materials was shown in Figure 6. The blank test was carried out (the data is not shown here) without any catalyst. The self decomposition of Ciprofloxacin was only less than 5 %, while the conversion is about 10% in the absence of light event the procedure prolongs 24 h. It means that visible light and catalysts are necessary for the photodegradation of Ciprofloxacin. From figure 6, the results indicated that all materials xS-TiO₂ could see a higher degradation of Ciprofloxacin than TiO₂. The photodegradation of Ciprofloxacin is increased from 74 % to 91 % under 150 minutes of visible light irradiation, coincident with the rise of mol ratio S/Ti from 0.25 to 0.33. In addition, it was seen that the mol ratio S/Ti increased up to 0.50, the degradation decreased (80 %). It might be explained that S covers the surface of TiO₂ and interfere exposure of TiO₂ crystals with light. These results suggest that 0.33S-TiO₂ was the best catalyst and used to test other conditions. These results were in accordance with the UV-DRS results.

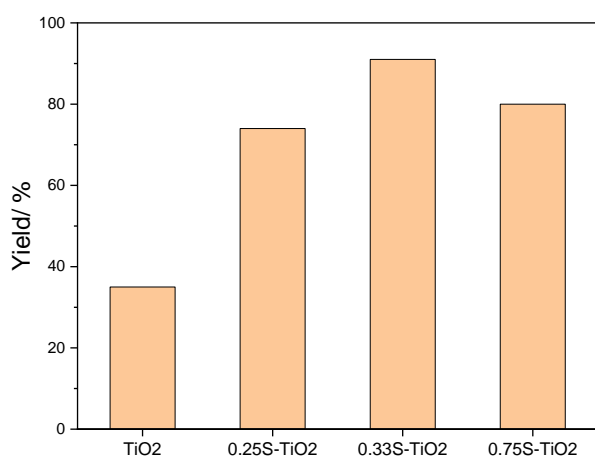


Figure 6: Effect of mol ratio S/Ti on the material to degradation of Ciprofloxacin

Moreover, to orientate for practical application, the effects of pH value are studied and shown in Figure 7.

As shown in Figure 7, the pH value introduced in the reaction affects the degradation of Ciprofloxacin. The result reveals that the rising pH value from 3 - 4 significantly increases the yield from 41.5 to 91 % under 150 minutes of visible light irradiation. Besides, the pH value was in the range of 4 - 9, and the yield changed not so much. It suggested that the material 0.33S-TiO₂ has high applicability in the wastewater environment, which often has a neutral or base media.

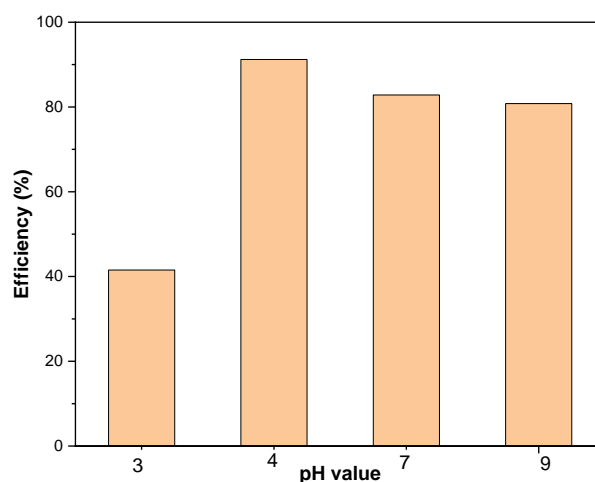


Figure 7: Effects of pH value on the degradation of Ciprofloxacin in water

To further investigate the reaction kinetics of the Ciprofloxacin photodegradation by 0.33S-TiO₂, the experimental data were fitted by applying a pseudo-first-order model as expressed by $\ln(C_0/C) = -kt$ where k is the apparent first-order rate constant (h^{-1}). C_0 and C are the initial concentration and at time t of ciprofloxacin solution. Figure 8 shows a linear relationship between $\ln(C_0/C)$ and the irradiation time for Ciprofloxacin degraded by 0.33S-TiO₂, and it was obviously seen that the photocatalytic degradation curve fitted well with pseudo-first-order kinetics. Furthermore, according to the model, the apparent rate constants k were calculated and illustrated in Figure 8. The rate constants k values were 0.921 h^{-1} for ciprofloxacin photodegradation, which was much higher than that obtained for other photocatalysts reported recently.

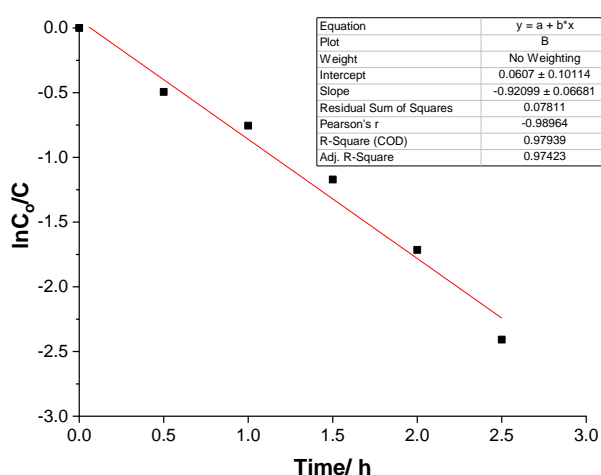


Figure 8: The first-order kinetics of Ciprofloxacin degradation on 0.33S-TiO₂

On the other hand, to confirm the effect of the concentration of Ciprofloxacin, weight of the catalyst,

various experiments were carried out, and data for the degradation is shown in figures 9 and 10.

With 50 mg catalyst $0.33S-TiO_2$, the result showed that the best rate of the process when the ciprofloxacin concentration in water is between 5-15 mg/L (yield > 70%) under 150 minutes visible light irradiation at pH=4. From figure 10, the best efficiency with mass catalyst is 50 mg at the concentration of antibiotic 10 mg/L (the yield is 91%). However, when the amount of material increased up to 70 mg, the processing efficiency of the material decreased significantly (80%). It can be explained by increasing the amount of catalyst, increasing the turbidity of the solution, causing photoresistance and scattering of light, thus reducing the antibiotic degradation efficiency.

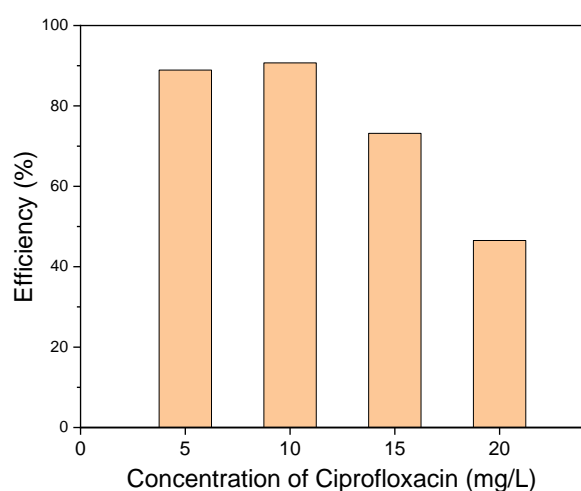


Figure 9: Effects of the concentration of Ciprofloxacin

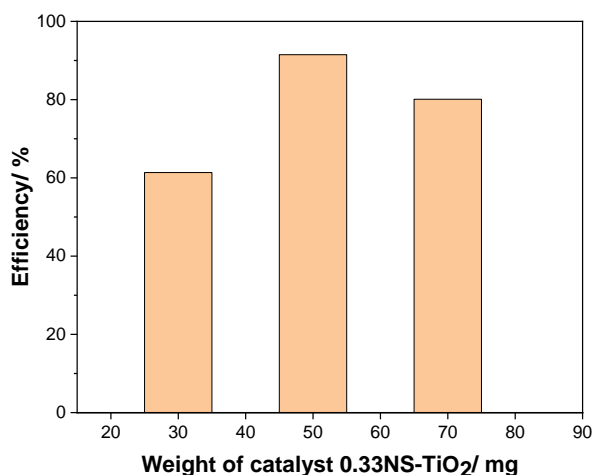


Figure 10: Effect of the weight of catalyst on the degradation of Ciprofloxacin in water

Conclusion

This study reported the $S-TiO_2$ exhibited novel photocatalytic ability for degradation of Ciprofloxacin in water. The catalyst was synthesized via the sol-gel

method and characterized by various model measurements such as XRD, SEM, FT-IR, UV-DRS. The XRD, SEM-EDX, and FT-IR have confirmed the successful preparation of materials. The UV-DRS demonstrated that the synthesized materials have a lower bandgap in comparison with prime TiO_2 . Under the optimized condition, the highest photocatalytic efficiency of the synthesized $0.33S-TiO_2$ for degradation was approximately 90% under 150 minutes of visible light irradiation at pH = 4 and room temperature.

Acknowledgments

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References

1. J.B. Parsa, T. M. Panah, F. N. Chianeh, Removal of Ciprofloxacin from Aqueous Solution by a Continuous Flow Electro-Coagulation Process., *Korean Journal of Chemical Engineering* 33(3) (2016) 893–901. <https://doi.org/10.1007/s11814-015-0196-6>
2. Q. Wu, Z. Li, H. Hong, K. Yin, L. Tie, Adsorption and Intercalation of Ciprofloxacin on Montmorillonite, *Applied Clay Science* 50(2) (2010) 204–211. <https://doi.org/10.1016/j.clay.2010.08.001>
3. C. Liu, V. Nanaboina, G. V. Korshin, W. Jiang. 2012. Spectroscopic Study of Degradation Products of Ciprofloxacin, Norfloxacin, and Lomefloxacin Formed in Ozonated Wastewater., *Water Research* 46(16) (2012) 5235-5246. <https://doi.org/10.1016/j.watres.2012.07.005>
4. S. Rakshit, D. Sarkar, E. J. Elzinga, P. Punamiya, R. Datta, Mechanisms of Ciprofloxacin Removal by Nano-Sized Magnetite., *Journal of Hazardous Materials* 246 (2013) 221–226. <https://doi.org/10.1016/j.jhazmat.2012.12.032>
5. Y. Fei, Y. Li, S. Han, J. Ma., Adsorptive Removal of Ciprofloxacin by Sodium Alginate/Graphene Oxide Composite Beads from Aqueous Solution., *Journal of Colloid and Interface Science* 484 (2016) 196–204. <https://doi.org/10.1016/j.jcis.2016.08.068>
6. S. Wu, X. Zhao, Y. Li, C. Zhao, Q. Du, J. Sun, Y. Wang, L. Xia, Adsorption of Ciprofloxacin onto Biocomposite Fibers of Graphene Oxide/Calcium Alginate., *Chemical Engineering Journal* 230 (2013) 389–395.

<https://doi.org/10.51316/jca.2021.077>

- <https://10.1016/j.cej.2013.06.072>
7. SK. Bajpai, M. Bajpai, N. Rai., Sorptive Removal of Ciprofloxacin Hydrochloride from Simulated Wastewater Using Sawdust: Kinetic Study and Effect of pH., *Water SA* 38(5) (2012) 673–682. <https://10.4314/WSA.V38I5.4>
 8. P W Choo, N M Gantz, Reversible leukopenia related to ciprofloxacin therapy., *Southern Medical Journal* 83 (5) (1990) 597–598. <https://10.1097/00007611-199005000-00032>
 9. P. Trivedi, D. Vasudevan, Spectroscopic Investigation of Ciprofloxacin Speciation at the Goethite Water Interface., *Environmental Science & Technology* 41(9) (2007) 3153–3158. <https://doi.org/10.1021/es061921y>
 10. Lu Lin, Wenbin Jiang, Treatment of Produced Water with Photocatalysis: Recent Advances, Affecting Factors and Future Research Prospects, *Catalysts* 10(8) (2020) 924. <https://doi.org/10.3390/catal10080924>
 11. Z. Shayegan, C.S. Lee, F. Haghghat, TiO₂ photocatalyst for removal of volatile organic compounds in the gas phase — a review. *Chem Eng J* 334 (2018) 2408–2439. <https://doi.org/10.1016/j.cej.2017.09.153>
 12. Y. Shu, J. Ji, Y. Xu, J. Deng, H. Huang, Promotional role of Mn doping on catalytic oxidation of VOCs over mesoporous TiO₂ under vacuum ultraviolet (VUV) irradiation., *Appl Catal B* 220 (2018) 78–87. <https://doi.org/10.1016/j.apcatb.2017.08.019>
 13. Thanh Tung MH, Dieu Cam NT, Novel direct Z-scheme AgI/N–TiO₂ photocatalyst for removal of polluted tetracycline under visible irradiation. *Ceram Int* 46 (2020) 6012–6021. <https://10.1016/j.ceramint.2019.11.058>
 14. M. Nasirian, Y. Lin, P. Bustillo-Lecompte, Enhancement of photocatalytic activity of titanium dioxide using non-metal doping methods under visible light: a review., *International Journal of Environmental Science and Technology*, 15(9) (2017) 2009–2032. <https://10.1007/s13762-017-1618-2>
 15. John Moma, Jeffrey Baloyi, Modified Titanium Dioxide for Photocatalytic Applications, *Photocatalysts - Applications and Attributes* <https://10.5772/intechopen.79374>
 16. Dette C., Pérez-Osorio, TiO₂ Anatase with a Bandgap in the Visible Region. *Nano Letters* 14(11) (2014) 6533–6538. <https://10.1021/nl503131s>
 17. X. Wang, Y. Tang, M.Y. Lee, T. T. Lim, Solvothermal synthesis of Fe-C co-doped TiO₂ nanoparticles for visible-light photocatalytic removal of emerging organic contaminants in water, *Applied Catalysis A: General*, 409-410 (2011) 257-266. <https://doi.org/10.1016/j.apcata.2011.10.011>
 18. X. Yang, C. Cao, L. Erickson, K. Klabunde, Photocatalytic degradation of Rhodamine B on C-, S-, N-, and Fe-doped TiO₂ under visible-light irradiation, *Applied Catalysis B: Environmental* 91 (2009) 657-666. <https://doi.org/10.1155/2020/4310513>
 19. Qingliang Chen, Yulian Zhang, Dongdong Zhang, Yingqin Yang, Ag, and N co-doped TiO₂ nanostructured photocatalyst for printing and dyeing wastewater, *Journal of Water Process Engineering* (2017) 14-20. <https://10.1016/j.jwpe.2016.11.007>
 20. Masood Hamadaniana, Sajad Karimzadeh, Vahid Jabbari, Synthesis of cysteine, cobalt, and copper-doped TiO₂ nano photocatalysts with excellent visible-light-induced photocatalytic activity, *Materials Science in Semiconductor Processing* (2016) 168-176. <https://10.1016/j.mssp.2015.06.085>
 21. Vishnu Vijayan Pillai, Sunil P. Lonkar, Facile synthesis of sulfur doped TiO₂ nanoparticles with enhanced photocatalytic activity, *Conference: International Journal of Materials and Metallurgical* (2017).
 22. M. M. Karkare, Choice of precursor not affecting the size of anatase TiO₂ nanoparticles but affecting morphology under broader view. *International Nano Letters* 4(3) (2014). <https://10.1007/s40089-014-0111-x>
 23. J. He, Y.e- Du, Formation of Anatase/Rutile TiO₂ Nanocomposites with Enhanced Photocatalytic Activity. *Molecules* 24 (2019) 2996. <https://doi.org/10.3390/molecules24162996>
 24. Q. Xiang, J. Yu, M. Jaroniec, Nitrogen and sulfur co-doped TiO₂ nanosheets with exposed {001} facets: synthesis, characterization and visible-light photocatalytic activity. *Phys. Chem. Chem. Phys.* 13(11) (2011) 4853–4861. <https://10.1039/c0cp01459a>
 25. Y.-H. Lin, H.-T. Hsueh, The visible light-driven photodegradation of dimethyl sulfide on S-doped TiO₂: Characterization, kinetics, and reaction pathways. *Applied Catalysis B: Environmental* 199 (2016) 1–10. <https://10.1016/j.apcatb.2016.06.024>
 26. Le Thi Hoang Yen, D. Van Thuan, Synthesis of N and S Co-doped TiO₂ Nanotubes for Advanced Photocatalytic Degradation of Volatile Organic Compounds (VOCs) in Gas Phase. *Topics in Catalysis*. (2020). <https://10.1007/s11244-020-01347-3>