

REMOVAL OF NORFLOXACIN BY TiO₂-SBA-15 PHOTOCATALYST

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Abstract. Ordered SBA-15 mesoporous silica support was synthesized by a sol-gel method using triblock copolymer Pluronic P123 and immobilized with different amounts of photocatalyst TiO₂. The synthesized composites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and N₂ adsorption-desorption isotherms. The synthesized materials possessed specific surface areas S_{BET} of 768 m²/g, 544 m²/g, 421 m²/g and 333 m²/g at the TiO₂:SiO₂ ratio of 0, 0.25, 1.0 and 5.0, respectively. The adsorption capacities and photocatalytic activities under UV light irradiation of these materials were evaluated for Norfloxacin degradation. Experimental results indicate that the highest activity was observed on the sample with TiO₂:SiO₂ ratio of 1.

Keywords: Norfloxacin, SBA-15, titanium dioxide, photocatalysis, mesoporous materials.

Classification numbers: 2.4.2, 2.6.1, 3.4.2.

1. INTRODUCTION

Norfloxacin (NFX) is an antibiotic that belongs to the class of fluoroquinolone antibiotics. It is used to treat urinary tract infections, gynaecological infections, inflammation of the prostate gland, gonorrhoea and bladder infection. Besides, NFX was detected not only in wastewater from wastewater treatment plants but also in surface water and other water environments with concentrations of up to 3.54 µg/L (in Hong Kong) [1]. The study of Duong Hong Anh *et al.* [2] detected antibiotic ciprofloxacin and NFX in wastewater from 6 hospitals in Hanoi with the concentration of 900 - 17,000 ng/L. NFX is used in many shrimp farms. Nearly 70 % of NFX remains in the sludge of biological treatment plants. Thus, pathogens are increasingly resistant to drugs, causing a significant threat to aquatic and terrestrial organisms as well as humans. NFX in the water environment can lead to adverse environmental impacts [3], including the development of antibiotic-resistant bacteria in fisheries [4], directly poisoning microorganisms and risks possible for human health through drinking water or food chain [4]. Over the past decade, a lot of research has been done to remove NFX. Photocatalytic decomposition by ultraviolet

irradiation, zero-valent iron nanoparticles with H₂O₂, electrochemical Fenton, thermally activated sulfur and gamma irradiation have been developed to remove NFX. However, these methods still have disadvantages such as high energy consumption, low efficiency treatment and environmental friendliness. While, the use of adsorbents was found to be an effective method, since NFX can be adsorbed by activated sludge [5], activated carbon [6], carbon nanotubes [6] and silica/alumina [7]. However, the removal of NFX is only physical, NFX is retained on the adsorbent and presents a risk of release to the aquatic environment if the adsorbent is improperly used. The development of active catalytic materials for NFX removal remains a critical problem and challenge.

Although there are essential properties such as simple synthesis, non-toxicity, high activity, the specific surface area of TiO₂ photocatalyst is low. Therefore, this limits the number of centres that adsorb pollutant molecules on the TiO₂ surface. In order to increase TiO₂ surface area, many studies of fabrication of mesoporous TiO₂ or fixed TiO₂ on mesoporous silica materials such as SBA-15, MCM-41, etc. have been carried out. The results showed that the specific surface area of the mesoporous TiO₂ material was up to 430 m²/g, 4 - 5 times larger than the conventional TiO₂ nanomaterials [8]. Also, as a catalyst substrate, mesoporous silica oxide materials such as SBA-15 receive much attention due to its high surface area, adjustable pore size, and thick pore walls and ordered porous framework. Mesoporous material SBA-15 possesses a uniform pore size of 2 - 30 nm with a narrow pore size distribution indicating the high order structure. SBA-15 has a large specific surface area of about 600 - 1000 m²/g.

The fixation of TiO₂ on these substrate increases the dispersion of TiO₂ on the substrate, improve the adsorption capacity of pollutants, besides the presence of Ti-O-Si bond is favourable for activation of organic pollutants [9]. Thus, TiO₂ catalytic fixation on mesoporous silica oxide material will create an adsorption catalyst system with the advantages of photocatalyst materials and mesoporous materials, enhance the efficiency of the treatment of durable organic compounds.

2. METHODS

2.1. Preparation of TiO₂/SBA-15

The following procedures synthesized TiO₂/SBA-15: P123 was added to 2M HCl solution and stirred until mixed evenly. Under constant stirring, a certain amount of TiO₂ powder was added and stirred for a further 4 hours. TEOS was added to the above suspension and stirred for 24 hours at 40 °C. After that, the obtained mixture was transferred into a Teflon-covered stainless steel autoclave.

The autoclave was placed in a furnace without stirring for the thermal treatment (temperature: 80 °C; time: 24 h). After the reaction, the precipitates were collected by centrifugation and washed with deionized water. The washed precipitates were dried in an oven at 80 °C for 10 h and calcinated at 500 °C for 5 h. The TiO₂/SiO₂ atomic ratios changed from 0; 0.25; 1.0 to 5.0 corresponding to the samples denoted by SBA-15, 0.25TiO₂/SBA-15, 1.0TiO₂/SBA-15, 5.0TiO₂/SBA-15.

2.2. Characterization of materials

The characterization methods include small-angle X-ray diffraction (SAXRD) and wide-angle X-ray diffraction (WAXRD, Siemen D5000 diffractometer, CuK α radiation, $\lambda = 1.5406 \text{ \AA}$).

The specific surface area of powder photocatalyst was measured using the Brunauer-Emmett-Teller method (BET) with a MicroActive TriStar II Plus 2.03 for N₂ BET at 77.3 K with a 10 s equilibration interval. The texture of the catalysts was observed by transmission electron microscopy (TEM, JEM-2100).

2.3. Removal of Norfloxacin

The activities of TiO₂/SBA-15 samples were evaluated for the photocatalytic oxidation of NFX. The photoreaction was conducted in a 250 ml glass beaker. UV irradiation was provided by a 4 × 8W Ultraviolet lamp ($\lambda = 365$ nm). The amount of catalysts was chosen as 0.5 g/l. The initial NFX concentration was 10 mg/l, the volume of NFX solution was 200 ml, and the temperature of the reaction solution was maintained at 30 ± 0.5 °C. Some aqueous samples were withdrawn at regular intervals, and the residual concentration of NFX was measured at 273 nm with a spectrophotometer.

The stability of photocatalyst was assessed through repeated use of 1.0TiO₂/SBA-15. Experiments were carried out with 10 mg/l NFX concentration, 0.5 g/l photocatalyst, and 150 min irradiation for cycling run. After the first photocatalytic reaction, the remaining solution was replaced with new NFX solution of 10 mg/L. The used 1.0TiO₂/SBA-15 was dried at 105°C in 24 h before repeating the above procedure.

The degradation efficiency (%) of NFX was calculated as follows:

$$D\% = (C_0 - C_t) \times 100 / C_0,$$

where C_0 and C_t are the initial NFX and the remaining concentration of NFX at a certain time, respectively.

3. RESULTS AND DISCUSSION

3.1. Characteristics of materials

The physicochemical structure of synthesized samples was characterized by SXRD, WXR, TEM, and BET. As shown in Figure 1, the SXRD patterns exhibit a very intense peak at $2\theta = 0.9^\circ$, together with two other weak peaks between 1.7° and 1.9° , which correspond to the (100), (110), and (200) reflections of the hexagonal mesoporous structure. The results also show that after loading TiO₂, the intensity of the low angle XRD peaks corresponding to the hexagonal symmetry decrease and shift slightly to higher angle with increasing TiO₂ loading and the distortion of the mesoporous framework is increased by the intercalated TiO₂.

The WXR patterns of TiO₂/SBA-15 samples synthesized with different TiO₂:SiO₂ molar ratios are shown in Figure 2. The distinctive peaks at $2\theta = 25.3^\circ$, 37.8° ; 47.7° ; 54° , and 62.4° correspond to the anatase [10]. Peak intensity of the anatase phase increases with increasing titania content.

The morphology of synthesized TiO₂/SBA-15 composite photocatalysts is observed further by TEM images. Figure 3 represents the TEM images of SBA-15 and TiO₂/SBA-15 samples. The images of the samples show highly ordered hexagonal arrays of the mesoporous with a uniform pore size corresponding to the results from SXRD. The TEM images of TiO₂/SBA-15 samples reveal that the spherical TiO₂ nanoparticles are highly dispersed in the interior of the SBA-15 channels and lead to a disordered mesoporous texture. The average TiO₂ nanoparticle sizes are determined from 20 to 50 nm.

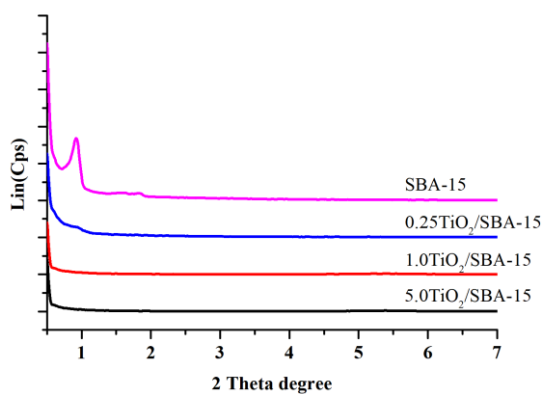


Figure 1. SAXRD patterns of samples.

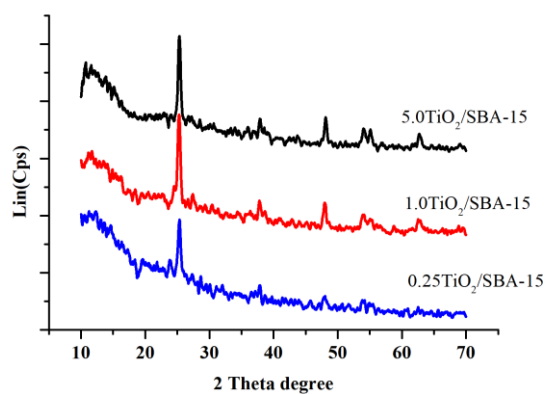


Figure 2. WAXRD patterns of samples.

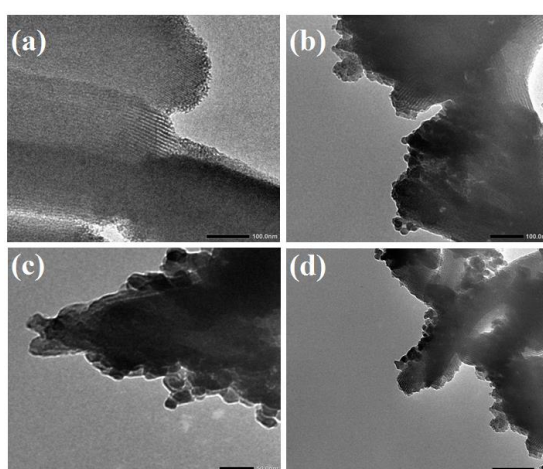


Figure 3. TEM images of $\text{TiO}_2/\text{SBA-15}$ samples

(a) SBA-15; (b) $0.25\text{TiO}_2/\text{SBA-15}$; (c) $1.0\text{TiO}_2/\text{SBA-15}$; (d) $5.0\text{TiO}_2/\text{SBA-15}$.

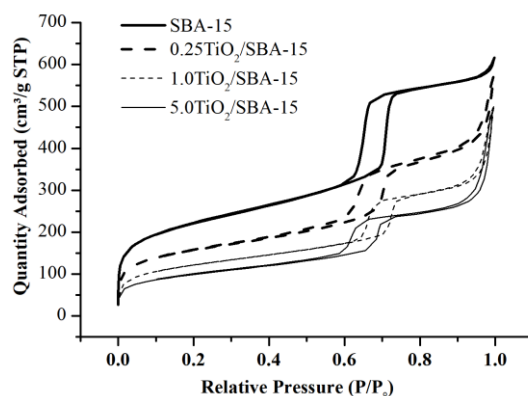


Figure 4. Nitrogen adsorption and desorption isotherms of the samples.

Figure 4 shows that the TiO_2 immobilization changed the hysteresis loops of the samples due to the penetration of TiO_2 into the mesoporous system of SBA-15 support. The data in Table 1 indicate that the TiO_2 content increases, the surface area and the pore volume of the nanomaterials decreases. Specifically, the BET surface area of SBA-15 of $768 \text{ m}^2/\text{g}$ is 2.3 times

higher than that of 5.0TiO₂/SBA-15, total pore volume decreases from 0.94 to 0.74, and the pore diameter increases 1.7 times. This is due to the presence of TiO₂, causing pore blocking effect. Besides, the pore diameter increases due to increased TiO₂ agglomeration on the surface lead to create large secondary porosity channels. The TiO₂ content increases, the agglomeration increases, appearing more secondary porosity channels system with large pore size, resulting in an average value of pore size of the material increases.

Table 1. Morphology and pore structure of samples.

| Sample | S _{BET} (m ² g ⁻¹) | V _{tot} (cm ³ g ⁻¹) | D (nm) |
|------------------------------|----------------------------------------------------|-----------------------------------------------------|--------|
| SBA-15 | 768 | 0.94 | 4.90 |
| 0.25TiO ₂ /SBA-15 | 544 | 0.87 | 6.41 |
| 1.0TiO ₂ /SBA-15 | 421 | 0.76 | 7.26 |
| 5.0TiO ₂ /SBA-15 | 333 | 0.74 | 8.56 |

3.3. Photocatalytic activity

The adsorption of NFX on TiO₂, SBA-15, 0.25TiO₂/SBA-15, 1.0TiO₂/SBA-15 and 5.0TiO₂/SBA-15 samples were carried out in dark condition for 30 minutes to reach the adsorption equilibrium, and the results are shown in Fig. 5. After adsorption for 30 minutes, NFX removal efficiency of 37 % is the highest on SBA-15 material. In the absence of irradiation, the TiO₂/SBA-15 materials present a higher adsorption capability of the NFX than pure titania. The superior activity of the hybrid materials is due to their much higher specific area and pore volume. This result indicates that the photocatalytic activity of hybrid TiO₂/SBA-15 samples depends insignificantly on their adsorption ability. The photocatalytic activity of TiO₂ is the main factor affecting the catalyst performance. When increasing TiO₂ content, NFX absorption efficiency decreases. After 30 minutes adsorption by TiO₂, the removal of NFX is lowest with 19.6 %.

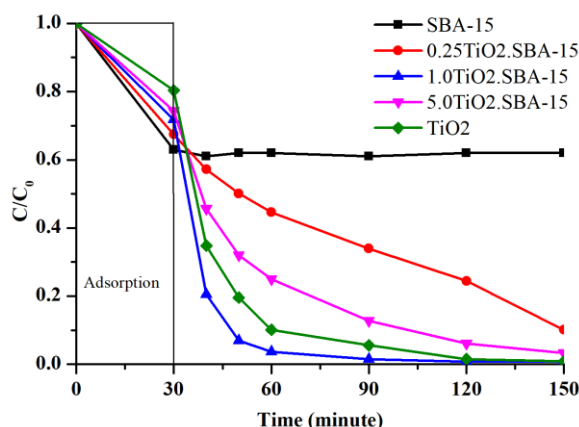


Figure 5. NFX concentration change of the photocatalytic degradation by use of SBA-15, 0.25TiO₂/SBA-15, 1.0TiO₂/SBA-15, 5.0 TiO₂/SBA-15 under UV irradiation.

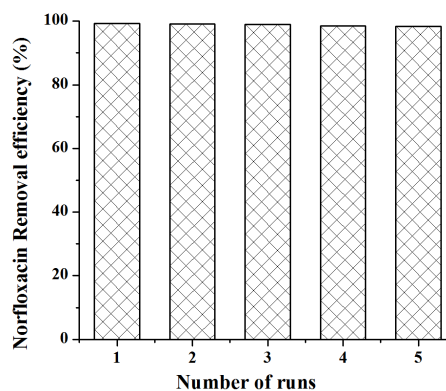


Figure 6. Removal of NFX during photocatalytic degradation by repeated use of TiO₂/SBA-15 under UV irradiation ([NFX]₀ = 10 mg/l, catalyst dosage = 0.5 g/l, pH = 7, irradiation time = 150 min).

Figure 5 shows NFX degradation under UV irradiation by SBA-15, 0.25TiO₂/SBA-15, 1.0TiO₂/SBA-15 and 5.0TiO₂/SBA-15 catalysts. It can be seen that the photocatalytic activity obeys the following order: 1.0TiO₂/SBA-15 > TiO₂ > 5.0TiO₂/SBA-15 > 0.25TiO₂/SBA-15 > SBA-15. NFX removal efficiencies during adsorption and photocatalytic degradation for 150 min UV irradiation by SBA-15, 0.25TiO₂/SBA-15, 1.0TiO₂/SBA-15, 5.0TiO₂/SBA-15 and TiO₂ catalysts are 38.1 %; 89.9 %, 99.3 %; 96.6 % and 99.2 %, respectively. At 150 minutes, the photocatalytic efficiency of 1.0TiO₂/SBA-15 and TiO₂ was approximately the same. However, during the entire process, the NFX removal efficiency of 1.0TiO₂/SBA-15 is always higher than pure TiO₂. Thus, immobilizing TiO₂ on SBA-15 improves the photocatalytic activity of these photocatalysts. According to Yang *et al.*, the photocatalytic activity of TiO₂ was improved because fixing TiO₂ on SBA-15 mesoporous material increases the thermal stability of TiO₂ anatase phase on SBA-15 and prevents the development of large crystals [11]. Besides, the porous structure of the SBA-15 substrate promotes adsorption of reactants into the porous system of SBA-15 material, enhances the phase contact between the reactants and the catalyst phase. Also, TiO₂ is inside the porous system and thus increases the efficiency of the reaction.

However, when increasing TiO₂ content to TiO₂: SBA-15 = 5: 1 ratio, photocatalytic activity did not increase compared to TiO₂. The reason may be that increasing TiO₂ content may increase the possibility of the blocking carrier material, decreasing the adsorption effect of the porous system as well as the catalytic effect of TiO₂ nanoparticles inside the porous system. Besides, the increase in TiO₂ content also increases the agglomeration of TiO₂ nanoparticles, reducing the dispersion of these semiconductor particles on the SBA-15 substrate and the photocatalytic efficiency. Otherwise, reducing TiO₂ content to TiO₂: SBA-15 = 0.25: 1 ratio leads to decrease photocatalytic activity due to insufficient catalyst/reactant ratio. From this order, it is possible to see the role of SBA-15 in dispersing TiO₂ catalysts as well as promoting diffusion and adsorption of reactants.

The stability of 1.0TiO₂/SBA-15 catalyst under UV irradiation was investigated by repeating the photocatalytic reaction of NFX, as shown in Figure 6. Under UV irradiation condition, the removal of NFX is insignificantly reduced after 5 times reuse, from 99.3 % to 98.4 %. It is clear that the photocatalytic activity of 1.0TiO₂/SBA-15 catalyst is high and stable due to the complete mineralization of the pollutants over TiO₂. Thus the adhesion of the by-products on the catalytic surface is negligible, resulting in quick regeneration of the catalyst.

4. CONCLUSION

The mesoporous TiO₂/SBA-15 nanomaterials were synthesized successfully by sol-gel method with varying titanium loadings, and the photocatalytic activities of synthesized TiO₂/SBA-15 materials are tested by the degradation of NFX. The structure of synthesized materials includes spherical anatase TiO₂ nanoparticles distributed over-ordered hexagonal mesoporous SBA-15 support with a pore diameter of 6.41-8.56 nm. The specific surface areas BET are 768, 544, 421 and 333 m²/g at the TiO₂:SBA-15 molar ratios of 0, 0.25, 1 and 5, respectively. In all cases, the decomposition of NFX increase with increasing the TiO₂ content. The results of the activity test indicate that 1.0TiO₂/SBA-15 hybrid material has better photocatalytic activity performance than pure TiO₂.

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