Photocatalytic degradation of ethyl paraben wastewater by mixed crystal molecularly imprinted TiO_2

Liangxiao ZHANG¹, Lei ZHU¹, Xun WANG^{1,*}, Xiumei TAO¹, Xian LIU¹

¹Wuhan University of Science and Technology, School of Urban Construction, Wuhan 430065, China

Abstract. Using ethyl paraben as the template molecule and n-tetrabutyl titanate as the titanium source, the molecularly imprinted titanium dioxide (MIP- TiO_2) photocatalyst was prepared by the sol-gel method. The effects of different pH values, imprinting molecular weights and other factors on the degradation of ethyl paraben were studied, and the materials were analyzed by TEM, XRD, FT-IR and other characterization methods. The results show that the catalyst has a mixed crystal structure in which anatase and rutile ore coexist, and the rutile ore content of MIP- TiO_2 is calculated to be 78.5%. Catalytic degradation of ethyl paraben by reacting for 40 min under ultraviolet light, the removal rate of ethyl paraben by pure TiO_2 is 80.74%, and the removal rate of ethyl paraben by MIP- TiO_2 can reach 96.27%. MIP - TiO_2 is 15.53% higher than TiO_2 . MIP- TiO_2 has imprinting holes, which can target the target pollutants and effectively improve the selectivity of the photocatalyst MIP- TiO_2 . The selectivity factor of MIP- TiO_2 is 1.69 times that of TiO_2 .

1 Introduction

Ethyl paraben (chemical formula is $\text{C}_9\text{H}_{10}\text{O}_3$) has the characteristics of antibacterial, low cost, and stable chemical properties. It is often used in industries such as medicine, food and cosmetics (PPCPs). However, the estrogenic activity of ethyl paraben has endocrine disrupting effects and the possibility of carcinogenesis([1]).

Ethyl paraben is a refractory organic matter, and the conventional water treatment process of sewage treatment plants cannot effectively treat ethyl paraben, which easily leads to long-term pollution of the water environment. TiO_2 is a non-toxic and harmless substance, and it also has good photocatalytic activity([2]). However, TiO_2 is not selective for the degradation of organic matter, and cannot degrade organic matter with high toxicity and low concentration, which restricts the application of TiO_2 . Combining molecular imprinting technology with nano- TiO_2 materials can improve the selectivity and processing ability of TiO_2 in treating organic matter([3]).

In this study, ethyl paraben was used as a template molecule to prepare MIP- TiO_2 photocatalyst, and its photocatalytic activity and selectivity to ethyl paraben removal will be studied.

2 Experimental part

2.1 Catalyst preparation

Figure 1 shows the preparation method of TiO_2 and MIP- TiO_2 photocatalyst. The preparation method of TiO_2 is as follows: A solution is obtained by stirring 20 mL of absolute ethanol and 0.5 mL of deionized water; 20 ml of

n-tetrabutyl titanate and 10 ml of glacial acetic acid are dissolved in 40 ml of absolute ethanol, stirred to form B solution. Then, A solution was slowly added into B solution, and white sol was obtained by stirring for 2 hours after dripping. After aging for A certain time, gel was formed. Dry the obtained gel at 60 °C for 8-12 h, then grind it into a powder state. Finally, heating it in a muffle furnace at a rate of 3 °C/min at 200 °C for 1 h and at 700 °C for 2 h, TiO_2 powder can be obtained.

The preparation method of MIP- TiO_2 as follows: add template molecules (ethyl paraben) of different quality to solution B during the preparation, and the other operations remain unchanged to obtain MIP- TiO_2 powder. In this experiment, the molar ratio of functional monomer (TiO_2) and template molecule (ethyl paraben) was adjusted to: 4.5:1, 5:1, 5.5:1, 6:1, and MIP- TiO_2 powders of different ratios were prepared.

Fig. 1 Preparation method of catalyst (A, B represent different solution)

* Corresponding author: 867685846@qq.com

2.2 Preparation of pollutant stock solution

Weigh 10 mg of ethyl paraben and dissolve it in 1 L of deionized water to obtain a solution of 10 mg/L of ethyl paraben, which can be used to determine the performance of the photocatalytic experiment. Weigh 10 mg of salicylic acid and dissolve it in 1 L of deionized water to obtain a 10 mg/L salicylic acid solution. The structure of salicylic acid is similar to that of ethyl paraben and is used as a comparative pollutant to judge its selectivity.

2.3 Characterization of the catalyst

In this study, HRTEM, XRD, FT-IR, BET were used to characterize the performance of the photocatalyst. The characterization instruments used were Xertpro X-ray diffractometer, FT-IR650 Fourier infrared spectrometer, JGM-3100F STEM/EDS transmission electron microscope, ASAP2060 specific surface area and porosity analyzer.

2.4 Photocatalytic performance experiment

Fig. 2 Schematic diagram of photocatalytic reactor 1- Magnetic stirring; 2- Quartz glass tube; 3 - Cold trap; 4 -Mercury lamp; 5- Water inlet; 6 - Outlet

Weigh 150 mg of the prepared catalyst separately, and add 50 ml of the prepared ethyl paraben solution and the prepared salicylic acid solution into a quartz glass test tube. The light source of the reaction process is a 500 W mercury lamp, and the distance between the light source and the quartz glass tube is about 10 cm, and the reactor is shown in Figure 2. Samples were taken at regular intervals, centrifuged at 9000 r/min for 6 min, and the supernatant was taken. A spectrophotometer was used to measure the absorbance of the supernatant. The degradation rate can be obtained by absorbance, and the specific formula is shown in formula (1).

$$\eta = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

Where η is removal rate of pollutants (%), A_0 is initial absorbance of pollutant solution (abs), A is timed sampling absorbance (abs).

3 Results and discussion

3.1 Characterization of photocatalyst

3.1.1 HRTEM characterization

Fig. 3 HRTEM image of TiO₂

Fig. 4 HRTEM image of MIP-TiO₂

It can be seen from Figures 3 and Figures 4 that both TiO₂ and MIP-TiO₂ have a certain agglomeration phenomenon, but the TiO₂ agglomeration phenomenon is more serious and there is a problem of uneven particle size. Serious agglomeration will reduce the specific surface area of the catalyst, which is not conducive to the removal of pollutants by the catalyst. Compared with TiO₂, MIP - TiO₂ dispersion is better, the agglomeration phenomenon is better improved, the particle size is more uniform, the specific surface area is large, which helps to improve the catalytic activity of the catalyst. This may be because the imprinted molecules can be better dispersed in the system when added to the solvent. This can increase the degree of dispersion of TiO₂, thereby reducing the agglomeration of TiO₂.

It can be seen in the 10 nm electron micrograph that TiO₂ and MIP-TiO₂ all have obvious lattice fringes, indicating that the sample has good crystallinity. It can be seen from Figure 3 that TiO₂ has lattice fringes with lattice spacing of $d=0.332$ nm and $d=0.354$ nm, which correspond to the rutile {110} atomic planes and the anatase {101} atomic planes of TiO₂. Can be obtained from Figure 4, MIP-TiO₂ has lattice fringes with lattice spacing of $d=0.327$ nm and $d=0.351$ nm, corresponding to the rutile {110} atomic planes and the anatase {101} atomic planes of TiO₂. Both samples exist The crystal faces of the anatase and rutile ore phases of TiO₂ indicate that the two samples are both anatase and rutile ore mixed crystal structures.

3.1.2 XRD characterization

Fig. 5 XRD patterns of TiO₂ and MIP-TiO₂

Figure 5 is the XRD patterns of TiO₂ and MIP-TiO₂. It can be seen from the figure that both samples have strong diffraction peaks at 25.281°, 37.800°, 48.049°, 27.446°, 36.085°, 54.322° and so on. Among them, 25.281°, 37.800°, and 48.049° correspond to the {101}, {004}, and {200} atomic planes of the anatase phase. The diffraction peaks at 27.446°, 36.085° and 54.322° correspond to the {100}, {101} and {211} atomic planes of the rutile ore phase. It shows that the samples are all mixed crystal structure of anatase phase and rutile phase, which is consistent with the TEM analysis. The content of rutile can be calculated by the following formula([4]):

$$F_R = 1/[1 + 0.79(I_A / I_R)] \quad (2)$$

Where I_A is the diffraction intensity of the anatase phase {101} crystal plane, I_R is the diffraction intensity of the {110} crystal plane of the rutile ore phase, F_R is the content of rutile.

Using formula (2), the content of rutile ore of TiO₂ and MIP-TiO₂ can be calculated to be 62.6% and 78.5% respectively, indicating that the addition of imprinting molecules contributes to the formation of rutile ore. TiO₂ with anatase phase and rutile phase mixed crystal structure has high catalytic activity ([5]).

3.1.3 FT-IR characterization

Figure 6 shows the infrared spectroscopic characterization results of TiO₂, MIP-TiO₂ and MIP-TiO₂ precursor (not calcined). The MIP-TiO₂ precursor showed multiple absorption peaks. The absorption peak at 3320 cm⁻¹ is strong and broad, which is caused by the stretching vibration of the alcoholic hydroxyl group O-H([6]). The absorption peak at 1690 cm⁻¹ is caused by the strong stretching vibration of C=O in -COO-([7]). The absorption peaks at 1570 cm⁻¹ and 1460 cm⁻¹ are the -C=C stretching vibration peaks on the benzene ring skeleton([8]). At 1280 cm⁻¹ are the C-O vibrations connected by C=O in aromatic esters. The absorption peaks at 1170 cm⁻¹, 1110 cm⁻¹, and 1030 cm⁻¹ are in-plane bending vibrations of aromatic C-H. The Ti-O stretching vibration peak at 666 cm⁻¹([9]). The appearance of these absorption peaks indicates that the imprinted molecule successfully combined with the TiO₂ precursor before calcination.

Fig. 6 Infrared spectrogram of TiO₂ and MIP-TiO₂

Both TiO₂ and MIP-TiO₂ only showed absorption peaks at 3440 cm⁻¹, 1640 cm⁻¹ and 536 cm⁻¹. The absorption peak at 3440cm⁻¹ is due to O-H stretching vibration. At 3440cm⁻¹ is the stretching vibration peak of the alcoholic hydroxyl group O-H. At 1640cm⁻¹ is the absorption peak caused by the angle of crystalline H₂O. The Ti-O-Ti stretching vibration peak at 536 cm⁻¹. It can be seen that there is no absorption peak of C=O and benzene ring in MIP-TiO₂, that is, there is no characteristic peak of template molecule ethyl paraben, indicating that the imprinted molecules have been completely eluted, and imprinted holes are formed on the surface of the catalyst.

3.1.4 BET characterization

Figure 7 shows the BET characterization results of TiO₂ and MIP-TiO₂. It can be seen from Figure 7 that both TiO₂ and MIP-TiO₂ samples have H3 hysteresis loops under relative pressures of 0.6 to 1.0, which belong to the IV isotherm in IUPAC, indicating that both samples have a mesoporous structure ([10],[11]).

Fig. 7 BET characterization result graph

Tab. 1 BET test data

sample	Specific surface area/(m ² /g)	pore volume (mm ³ /g)	Average pore size/nm
TiO ₂	1.7897	4.584	5.9382
MIP-TiO ₂	3.4810	14.237	8.5784

It can be seen from Figure 7 that the pore diameters of TiO₂ and MIP-TiO₂ are mainly distributed in 5~10 nm, which belongs to the range of mesopores. It can be seen from Table 1 that the average pore diameters of TiO₂ and MIP-TiO₂ are 5.9382 nm and 8.5784 nm respectively,

which are consistent with the above analysis. In addition, the specific surface area of TiO_2 and MIP- TiO_2 are $1.7897 \text{ m}^2/\text{g}$ and $3.4810 \text{ m}^2/\text{g}$ respectively. The specific surface area of MIP- TiO_2 is 1.94 times that of TiO_2 , indicating that the formation of molecular imprinting will increase the specific surface area of the particles, which helps to increase the contact surface between the catalyst and the pollutants and improve the activity of the catalyst.

3.2 Study on the photocatalytic performance of MIP- TiO_2

3.2.1 The molar ratio of functional monomer (TiO_2) and template molecule (ethyl paraben) on the photocatalytic effect

It can be seen from Figure 8 that when the ratio of functional monomer to template molecule is 5:1, the degradation rate of MIP- TiO_2 is the highest, and the degradation rate of ethylparaben can reach 96.27%. That is, the best molecular imprinting ratio is 5:1. When the molecular imprinting ratio is greater than 5:1, the template molecular weight is insufficient, and the imprinted holes formed by the prepared MIP- TiO_2 are relatively small, so the catalyst activity is low. When the molecular imprinting ratio is less than 5:1, the template molecular weight is too much, which affects the bonding between the template molecule and the functional monomer, which will inhibit the formation of imprinted holes, thereby reducing the catalytic activity.

Fig. 8 Effects of different molecular imprinting ratios on photocatalytic activity.

3.2.2 The influence of pH on the photocatalytic effect

Figure 9 shows the treatment effect of MIP- TiO_2 photocatalyst on ethyl paraben under different pH conditions. It can be seen from the figure that the degradation rate of ethyl paraben is the highest when $\text{pH}=5.7$ (stock solution). With the decrease of pH, the degradation rate of ethyl paraben drops sharply, indicating that the degradation of ethyl paraben is inhibited under acidic conditions. Under alkaline conditions, the degradation rate of ethyl paraben gradually decreases, but it is gentler than under acidic conditions.

Fig. 9 Effects of different pH on photocatalytic activity

3.2.3 Analysis of photocatalytic degradation effect

As shown in Figure 10, a small amount of ethyl paraben was degraded in the blank experimental group, and the degradation rate at 40 min was 1.15%, indicating that ethyl paraben would undergo self-sensitization and photolysis under light conditions. After 40 minutes of reaction in the dark, the degradation rates of TiO_2 and MIP- TiO_2 to ethyl paraben were 1.28% and 2.68% respectively. The prepared catalyst did not show high adsorption to ethyl paraben. That is, it has little effect on the photocatalytic effect. Under the condition of ultraviolet light irradiation for 40 min, the degradation rates of TiO_2 and MIP- TiO_2 to ethyl paraben are 80.74% and 96.27% respectively. MIP- TiO_2 is 15.53% higher than that of TiO_2 .

Fig. 10 The removal rate of nipagin ethyl ester with different catalyst

Therefore, it can be seen that the TiO_2 modified by molecular imprinting, namely MIP- TiO_2 , can enhance the photocatalytic performance. This is because MIP- TiO_2 will generate imprinted holes during the formation process, which makes the photocatalyst have higher photocatalytic activity against the target pollutant.

3.2.4 MIP- TiO_2 selectivity factor

It can be seen from Figure 11 that the degradation rates of TiO_2 and MIP- TiO_2 to salicylic acid after 40 minutes are 61.63% and 61.34% respectively. The degradation rates of TiO_2 and MIP- TiO_2 to ethyl paraben are 80.74% and 96.27%, respectively. It shows that the introduction of imprinted molecules can effectively improve the degradation effect of the photocatalyst on the target pollutants. The degradation process is analyzed through the first-order reaction kinetics, and the selectivity factor can be calculated from the following formula:

$$R = \frac{K_a}{K_b}, \quad \alpha = \frac{R_a}{R_b} \quad (3)$$

Where K_a , K_b is the rate constant of MIP-TiO₂ and TiO₂, R is the selectivity coefficient, R_a , R_b is selectivity coefficient of ethyl paraben and salicylic acid, α is selectivity factor. The calculation results are shown in Table 4.

Fig. 11 Degradation rate of Salicylic acid and niprojin ethyl ester by TiO₂ and MIP-TiO₂.

Tab. 2 First order reaction kinetics analysis parameters

Pollutants	catalyst	k	R	α
Ethyl Paraben	MIP-TiO ₂	6.90	1.71	1.69
	TiO ₂	4.04		
Salicylic acid	MIP-TiO ₂	2.33	1.01	
	TiO ₂	2.30		

It can be seen from Table 2 that the value of R_a is $1.71 > 1$, indicating that MIP-TiO₂ is easier to remove ethyl paraben compared to TiO₂. The value of R_b is 1.01, and the result is not significantly greater than 1, indicating that MIP-TiO₂ does not degrade salicylic acid more easily than TiO₂. The calculated selectivity factor of MIP-TiO₂ is 1.69 times that of TiO₂. This is because MIP-TiO₂ has imprinting holes, which can target the target pollutants, thereby effectively improving the photocatalytic activity and selectivity of the photocatalyst MIP-TiO₂.

4 Conclusion

Using ethyl paraben as the imprinting molecule and preparation of MIP-TiO₂ by gel sol method. The prepared TiO₂ and MIP-TiO₂ are all mixed crystal structures in which anatase and rutile ore coexist. TiO₂ with anatase phase and rutile phase mixed crystal structure has higher catalytic activity. After calculation, the rutile content of MIP-TiO₂ is higher than that of TiO₂, and the rutile content of TiO₂ and MIP-TiO₂ are 62.6% and 78.5% respectively.

By comparing the photocatalytic activity of different molecular imprinting ratios (functional monomer: template molecule), the best molecular imprinting ratio can be obtained as 5:1. By comparing the photocatalytic activity at different pH, the best pH value can be obtained as 5.7. Under 40 minutes of ultraviolet light, the removal rate of ethyl paraben by TiO₂ is 80.74% and the removal rate of ethyl paraben by MIP-TiO₂ can reach 96.27%.

MIP-TiO₂ is 15.53% higher than TiO₂, indicating that the addition of molecular imprinting made MIP-TiO₂ exhibit higher photocatalytic activity than TiO₂.

MIP-TiO₂ has imprinting holes, which can be targeted to target pollutants and can better degrade target pollutants. It effectively improves the selectivity of the photocatalyst MIP-TiO₂ and The selectivity factor of MIP-TiO₂ is 1.69 times that of TiO₂.

Acknowledgments

This article is one of the phased achievements of the National Natural Science Foundation of China Project "Research on the Synergistic Degradation Mechanism of Titanium-Fe-based Composite Nanomaterials Based on Selective Photocatalysis" (51672196).

References

1. KOMARAI AH D, RADHA E, SIVAKUMAR J, et al. Opt. Materials, 108: 110401 (2020)
2. KOMARAI AH D, RADHA E, SIVAKUMAR J, et al. Opt. Mate, 108: 110401 (2020)
3. BI L, CHEN Z, LI L, et al. J. HAZARD. MATER, 407: 124759 (2021)
4. J J He, H L Du, X Du, et al. J. Synth. Cryst, 2014,43(6): 1529-1534.
5. OHNO T, SARUKAWA K, TOKIEDA K, et al. J. Cata, 203(1): 82-86 (2001)
6. MAITI M, SARKAR M, MAITI S, et al. J. Clean. Prod, 255: 120183 (2020)
7. TRIVEDI N S, KHARKAR R A, MANDAVGANE S A. Resource-Efficient Technologies, 2: S39-S46 (2016)
8. STORCK S, BRETINGER H, MAIER W F. APPL. CATAL. A-GEN, 174(1-2): 137-146 (1998)
9. BA-ABBAD M, KADHUM A, MOHAMAD A B, et al. Int. J. Electrochem. Sci, 7: 4871-4888 (2012)
10. HONG K J, KIM S O. Energy. Sto. Mater, 2: 27-34 (2016)
11. CHENG Y, CHEN Z, WU H, et al. Adv. Funct. Mate, 26(9): 1338-1346 (2016)