# Photocatalytic degradation of ethyl paraben wastewater by mixed crystal molecularly imprinted TiO<sub>2</sub>

Liangxiao ZHANG<sup>1</sup>, Lei ZHU<sup>1</sup>, Xun WANG<sup>1,\*</sup>, Xiumei TAO<sup>1</sup>, Xian LIU<sup>1</sup>

<sup>1</sup>Wuhan 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<sub>2</sub>) 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<sub>2</sub> 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<sub>2</sub> is 80.74%, and the removal rate of ethyl paraben by MIP-TiO<sub>2</sub> can reach 96.27%. MIP -TiO<sub>2</sub> is 15.53% higher than TiO<sub>2</sub>. MIP-TiO<sub>2</sub> has imprinting holes, which can target the target pollutants and effectively improve the selectivity of the photocatalyst MIP-TiO<sub>2</sub>. The selectivity factor of MIP-TiO<sub>2</sub> is 1.69 times that of TiO<sub>2</sub>.

## 1 Introduction

Ethyl paraben (chemical formula is  $C_9H_{10}O_3$ ) 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> powder can be obtained.

The preparation method of MIP-TiO<sub>2</sub> 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<sub>2</sub> powder. In this experiment, the molar ratio of functional monomer (TiO<sub>2</sub>) and template molecule (ethyl paraben) was adjusted to: 4.5:1, 5:1, 5:1, 6:1, and MIP-TiO<sub>2</sub> powders of different ratios were prepared.



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

<sup>\*</sup> Corresponding author: 867685846@qq.com

<sup>©</sup> The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (http://creativecommons.org/licenses/by/4.0/).

### 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 Xrertpro 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).

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

Where  $\eta$  is removal rate of pollutants (%), A<sub>0</sub> 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-TiO<sub>2</sub>

It can be seen from Figures 3 and Figures 4 that both  $TiO_2$  and MIP- $TiO_2$  have a certain agglomeration phenomenon, but the  $TiO_2$  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 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.



Fig. 5 XRD patterns of TiO<sub>2</sub> and MIP-TiO<sub>2</sub>

Figure 5 is the XRD patterns of TiO<sub>2</sub> and MIP-TiO<sub>2</sub>. 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]):

$$F_R = 1/[1 + 0.79(I_A / I_R)]$$
(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  $TiO_2$  and MIP-TiO<sub>2</sub> 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.  $TiO_2$  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 TiO<sub>2</sub>, MIP-TiO<sub>2</sub> and MIP-TiO<sub>2</sub> precursor (not calcined). The MIP-TiO<sub>2</sub> precursor showed multiple absorption peaks. The absorption peak at 3320 cm<sup>-1</sup> 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<sup>-1</sup> is caused by the strong stretching vibration of C=O in -COO-([7]). The absorption peaks at 1570 cm<sup>-1</sup> and 1460 cm<sup>-1</sup> are the -C=C stretching vibration peaks on the benzene ring skeleton([8]). At 1280 cm<sup>-1</sup> are the C-O vibrations connected by C=O in aromatic esters. The absorption peaks at 1170 cm<sup>-1</sup>, 1110 cm<sup>-1</sup>, and 1030 cm<sup>-1</sup> are in-plane bending vibrations of aromatic C-H. The Ti-O stretching vibration peak at 666 cm<sup>-1</sup>([9]). The appearance of these absorption peaks indicates that the imprinted molecule successfully combined with the TiO<sub>2</sub> precursor before calcination.



# $\begin{array}{c} 4000\ 3500\ 3000\ 2500\ 2000\ 1500\ 1000\ 500\\ \lambda/cm^{-1} \end{array}$

Fig. 6 Infrared spectrogram of TiO<sub>2</sub> and MIP-TiO<sub>2</sub>

Both TiO<sub>2</sub> and MIP-TiO<sub>2</sub> only showed absorption peaks at 3440 cm<sup>-1</sup>, 1640 cm<sup>-1</sup> and 536 cm<sup>-1</sup>. The absorption peak at 3440cm<sup>-1</sup> is due to O-H stretching vibration. At 3440cm<sup>-1</sup> is the stretching vibration peak of the alcoholic hydroxyl group O-H. At 1640cm<sup>-1</sup> is the absorption peak caused by the angle of crystalline H<sub>2</sub>O. The Ti-O-Ti stretching vibration peak at 536 cm<sup>-1</sup>. It can be seen that there is no absorption peak of C=O and benzene ring in MIP-TiO<sub>2</sub>, 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  $TiO_2$ and MIP-TiO<sub>2</sub>. It can be seen from Figure 7 that both  $TiO_2$ and MIP-TiO<sub>2</sub> 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 <sup>2</sup> /g)	pore volume $(mm^3/g)$	Average pore size/nm
TiO <sub>2</sub>	1.7897	4.584	5.9382
MIP- TiO <sub>2</sub>	3.4810	14.237	8.5784

It can be seen from Figure 7 that the pore diameters of  $TiO_2$  and MIP- $TiO_2$  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  $TiO_2$  and MIP- $TiO_2$  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 m<sup>2</sup>/g and 3.4810 m<sup>2</sup>/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 $\ensuremath{\mathsf{MIP}}\xspace{-}\ensuremath{\mathsf{TiO}}\xspace_2$

# 3.2.1 The molar ratio of functional monomer (TiO<sub>2</sub>) 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<sub>2</sub> 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<sub>2</sub> are relatively small, so the catalyst activity is low. When the 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<sub>2</sub> 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 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<sub>2</sub> and MIP-TiO<sub>2</sub> 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<sub>2</sub> and MIP-TiO<sub>2</sub> to ethyl paraben are 80.74% and 96.27% respectively. MIP-TiO<sub>2</sub> is 15.53% higher than that of TiO<sub>2</sub>.



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<sub>2</sub>, can enhance the photocatalytic performance. This is because MIP-TiO<sub>2</sub> 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<sub>2</sub> 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:

Where Ka, Kb is the rate constant of MIP-TiO<sub>2</sub> and TiO<sub>2</sub>, R is the selectivity coefficient, Ra, Rb is selectivity coefficient of ethyl paraben and salicylic acid,  $\alpha$  is selectivity factor. The calculation results are shown in Table 4.



Fig. 11 Degradation rate of Salicylic acid and niprojin ethyl ester by TiO<sub>2</sub> and MIP-TiO<sub>2</sub>.

Tab. 2 First order reaction kinetics analysis parameters

Pollutants	catalyst	k	R	α
Ethyl Paraben	MIP- TiO <sub>2</sub> TiO <sub>2</sub>	6.90 4.04	1.71	1.69
Salicylic acid	MIP- TiO2 TiO2	2.33 2.30	1.01	

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

# 4 Conclusion

Using ethyl paraben as the imprinting molecule and preparation of MIP-TiO<sub>2</sub> by gel sol method. The prepared TiO<sub>2</sub> and MIP-TiO<sub>2</sub> are all mixed crystal structures in which anatase and rutile ore coexist. TiO<sub>2</sub> with anatase phase and rutile phase mixed crystal structure has higher catalytic activity. After calculation, the rutile content of MIP-TiO<sub>2</sub> is higher than that of TiO<sub>2</sub>, and the rutile content of TiO<sub>2</sub> and MIP-TiO<sub>2</sub> 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  $TiO_2$  is 80.74% and the removal rate of ethyl paraben by MIP-TiO<sub>2</sub> can reach 96.27%.

MIP-TiO<sub>2</sub> is 15.53% higher than TiO<sub>2</sub>, indicating that the addition of molecular imprinting made MIP-TiO<sub>2</sub> exhibit higher photocatalytic activity than TiO<sub>2</sub>.

MIP-TiO<sub>2</sub> 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-TiO<sub>2</sub> and The selectivity factor of MIP-TiO<sub>2</sub> is 1.69 times that of TiO<sub>2</sub>.

# 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

- KOMARAIAH D, RADHA E, SIVAKUMAR J, et al. Opt. Materials, 108: 110401 (2020)
- KOMARAIAH D, RADHA E, SIVAKUMAR J, et al. Opt. Mate, 108: 110401 (2020)
- 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.
- OHNO T, SARUKAWA K, TOKIEDA K, et al. J. Cata, 203(1): 82-86 (2001)
- MAITI M, SARKAR M, MAITI S, et al. J. Clean. Prod, 255: 120183 (2020)
- 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)
- 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)
- CHENG Y, CHEN Z, WU H, et al. Adv. Funct. Mate, 26(9): 1338-1346 (2016)