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Persulfate-enhanced degradation of propranolol over BiOCl$_{0.5}$I$_{0.5}$ under visible light irradiation

Yuehua Deng, a,b Jiating Luo, a Hongyu Cao, a Danni Chen, a Yani Li, a Qianqian Che, a Yan He, a Xiang Gao, a Xiaobin Hu, a Wei Zhao, a and Fei Wang a

The photodegradation of propranolol (PRO) by BiOCl$_{0.5}$I$_{0.5}$/persulfate under visible light was comprehensively investigated. The results demonstrated a significant increase in the removal efficiency of PRO under visible light irradiation, achieved by the combination of BiOCl$_{0.5}$I$_{0.5}$ solid solution and persulfate (PS). The photocatalytic activity of the system was found to be enhanced with an increase in pH value. Additionally, the addition of a certain amount of PS improved the degradation of PRO. The presence of typical water constituents, Cl$^-$ and NO$_3^-$, had a negligible impact on PRO removal. In contrast, the increasing concentration of humic acid (HA) exhibited apparent inhibition of PRO degradation. Furthermore, Radical scavenging experiments revealed that the removal of PRO was primarily facilitated by active free species, including h$^+$ and $\bullet$O$_2^-$. The presence of characteristic peaks of •OH (peak ratio 1:2:2:1), $\bullet$O$_2$ and $\bullet$SO$_4$ in the EPR spectrum indicates that these three radicals are also involved in the degradation process. Moreover, the BiOCl$_{0.5}$I$_{0.5}$/PS system demonstrated excellent photocatalytic activity, as well as favorable reusability and stability. This study offers new insights into the photocatalytic degradation of PRO, presenting a promising approach in this field.

1 Introduction

Water pollution caused by pharmaceutical and personal care product residuals (PPCPs) is getting serious in an alarming way. However, owing to the incomplete metabolism and insufficient removal efficiency of traditional wastewater treatment technologies, beta-blockers, which are widely used to treat cardiovascular disease due to their significant therapeutic effects, are often detected in various water resources. Propranolol (PRO), one of the largest sales beta-blockers, has the highest acute and chronic toxicity within the beta-blockers class. Despite low concentrations of PRO, it can still affect the reproductive system of animals and the photosynthesis of aquatic plants seriously, which may eventually jeopardize human health and life safety. Therefore, developing effective approaches to PRO removal is critical to mitigating the risks associated with environmental contamination.

Semiconductor photocatalysis technology has been identified as an attractive technology for improving the environment. In the last several decades, many varieties of photocatalytic materials have been created. Among them, bismuth oxychloride (BiOCl), an attractive p-type semiconductor, has received significant interest in the realm of photocatalysis. Its specific layered structure [Cl]-O-Bi-O-Cl] provides the self-built internal electric field between [Bi$_2$O$_3$] and Cl layers, which assists in preventing the recombination of photoinduced electron-hole pairs and fabricating solid solutions. Nevertheless, BiOCl has the disadvantage of a large band gap, which only shows good photocatalytic performance when exposed to UV light irradiation. Thus, many efforts have been made to realize the better photocatalytic performance of BiOCl under visible light, including establishing heterojunctions, doping elements and fabricating solid solutions. Among them, solid solution photocatalysts have received a significant amount of attention recently. The structure of them allows for continuous alteration of the energy band structure and accomplishes the suitable balance between light absorption and redox capacity. So far, many reports have intended the fabrication of bismuth oxyhalide solid solutions to improve photocatalytic activity. Yang et al. developed a 3D...
flowerlike BiOCl$_{1-x}$ nanostructure with a hydrothermal process, and the compounds showed excellent adsorption ability and photocatalytic activity for the photodegradation of methyl orange under visible light. Liu et al.\(^\text{35}\) achieved the continuous modulation of a group of BiO(Cr)$_{1-x}Cl_x$ solid solutions across a comparatively large energy range of 2.88 to 1.82 eV by manipulating the composition ratio of three elements, and these materials exhibited good photocatalytic efficiency for degrading 2-propanol under visible light. Deng et al.\(^\text{30}\) prepared BiOCl$_{0.8}$Br$_{0.2}$, BiOCl$_{0.3}$I$_{0.3}$, and BiOBr$_{0.7}$Br$_{0.3}$ by simple solvothermal strategy, which removed Cr(VI) almost completely within 60 min. Chou et al.\(^\text{36}\) found that the BiO$_{1-x}$/GO material synthesized by the hydrothermal method showed high photocatalytic activity for the degradation of crystal violet (CV). Until now, solid bismuth oxyhalide solutions are a potential class of visible light photocatalysts, but they have insufficient photodegradation capacity for practical application.

Currently, PS is widely utilized to degrade various organic pollutants, including tetracycline\(^\text{37}\), phenol, and sulfamethoxazole, in advanced oxidation technology\(^\text{38}-\text{39}\). Notably, in the photocatalytic process, the addition of PS into the reaction system as an electron acceptor has been demonstrated to effectively reduce the recombination of electrons and holes within the photocatalyst, thereby enhancing the degradation capability for organic pollutants\(^\text{40}-\text{43}\). Under the lights, photocatalysts may activate PS to create $\bullet$SO$_2^-$ or to transfer electrons from pollutants\(^\text{44}\), which could further enhance the degradation efficiency of the target pollutants through the synergistic effect of the photocatalysts and PS. For example, Shi et al.\(^\text{45}\) used a magnetic BiOCl@Fe$_3$O$_4$ catalyst to activate PS for atenolol degradation. The results showed that h$^+$ and $\bullet$OH were the principal reaction active species due to PS trapping electrons. Liu et al.\(^\text{46}\) fabricated 3D flower sphere-like BiOI/Fe$_3$O$_4$ microspheres to activate PS for Rhodamine B degradation by visible light and $\bullet$SO$_2^-$ generated from PS responsible for pollutant degradation. Zhang et al. successully formed a heterojunction by combining BiOCl$_{0.3}$I$_{0.7}$ with NH$_2$-MIL-88B (Fe), which promoted the efficient separation and transfer of photo-induced e$^-$/h$^+$ pairs. This heterojunction design not only improves the utilization rate of visible light but also effectively enhances the photocatalytic reaction, improves the activity of persulfate and significantly improves the degradation efficiency of tetracycline hydrochloride\(^\text{47}\). These findings manifested that Bi-based materials can effectively interact with PS to improve the removal efficiency of pollutants under light irradiation\(^\text{48}\). As far as we know, limited research has been studied on the interactions between PS and bismuth oxyhalide solid solution for the treatment of PRO under visible light.

In this study, a sequence of BiOCl$_{1-x}$ (x=1, 0.9, 0.7, 0.5, 0.3, 0) was prepared and the BiOCl$_{1-x}$/PS/vis-light system was investigated systematically for the elimination of PRO. Degradation processes were carried out to better understand the effects of key variables, including PS dosage, solution pH, PRO initial concentration, common anions, and humic acid (HA). By employing techniques such as free radical identification and electron paramagnetic resonance (EPR) experiments, the plausible main degradation mechanism of propranolol (PRO) degradation was elucidated.

## 2 Experimental

### 2.1 Materials

PRO (99%) was obtained from Alfa Aesar (Tianjin, China). Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$•5H$_2$O) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Tianjin Komiou Chemical Reagent Co., Ltd supplied the polyvinylpyrrolidone (PVP) (Tianjin, China). Sodium chloride (NaCl), potassium iodide (KI), ethylene glycol 49, tert-butanol (TBA), furfuryl alcohol (FFA), methanol (MeOH) and sodium oxalate 50 were acquired from Guangdong Guanghua Sci-Tech Co., Ltd (Guangdong, China). P-Benzoylquinone (PBQ) was obtained from Shanghai Aladdin Co., Ltd (Shanghai, China). All chemical reagents were used as received, with no further purification.

### 2.2 Preparation of BiOCl$_{1-x}$

0.972 g Bi(NO$_3$)$_3$•5H$_2$O and 0.4 g PVP were added to a combination of 19 mL deionized water and 19 mL EG with continuous stirring for 60 min. A total of 2 mL NaCl and KI mixture with different molar ratios was added to the solution. After 30 minutes of continuous stirring, the mixture solution was transferred to a Teflon-lined stainless-steel autoclave. It was heat preservation at 160 °C for 6 h. Later, the final products cooled down naturally to room temperature and dried at 60 °C after washing with water and ethanol.

### 2.3 Experimental procedures

The PRO degradation processes were conducted in a photochemical reactor (Beijing Zhongjiao Jinyuan Technology Co., Ltd.). The irradiation wavelength was maintained at > 400 nm by UV cut-off filters to simulate visible light with a 500W Xe lamp. In the
general PRO photocatalytic test, the mixture contained 0.01g of the samples, and 40 mL PRO solution (10 mg/L) was stirred continuously for 30 min in the dark for the elimination of adsorption equilibrium. A certain concentration of PS was introduced into the system after the dark reaction. At given irradiation time intervals, the PRO concentration was determined by a spectrophotometer (UV2600, Shimadzu). It can be seen from Fig. 1 (e, f) that the sample was analyzed by transmission electron microscopy. The fringe spacing d = 0.263 nm corresponds to the (110) crystal plane of the tetragonal BiOCl crystal\(^{19}\).

The XRD pattern of BiOCl prepared by the method of the present work is presented in Fig. 2 (a). The microstructure of the prepared BiOCl sample was analyzed by transmission electron microscopy. The fringe spacing d = 0.263 nm corresponds to the (110) crystal plane of the tetragonal BiOCl crystal\(^{19}\).

Fig. 1 SEM images of the prepared catalysts: BiOCl (a, b) and BiOCl\(_{0.5}\) (c, d); TEM images (e) and HRTEM images (f) of BiOCl\(_{0.5}\).

The BET results show that the specific surface area of BiOCl\(_{0.5}\) is 1.422 m\(^2\) g\(^{-1}\). The microstructure of the prepared BiOCl\(_{0.5}\) sample was analyzed by transmission electron microscopy. It can be seen from Fig. 1 (e) that the sample has a nano-scale flake morphology with round edges. Fig. 1 (f) further characterizes the high crystallinity and lattice fringes of the prepared BiOCl\(_{0.5}\) nanosheets by HRTEM. The fringe spacing d = 0.263 nm corresponds to the (110) crystal plane of the tetragonal BiOCl\(_{0.5}\) crystal\(^{19}\).
BiOCl crystal. The diffraction peaks at 12° and 46.6°, especially 32.5° (Fig. 2(b)) shift to lower angles at 9.6°, 45.4° and 29.6°, which may be attributed that the iodine atoms with a larger radius replaced the chlorine atoms with a smaller radius increasing the lattice spacing. The synthesized materials were not a mechanical blend of BiOCl and BiOI phases but a solid solution by lattice substitution of Cl and I atoms with each other. No other impurities existed in the samples, demonstrating the excellent high purity and single phase.

Fig. 2 The XRD patterns of BiOCl$_{1-x}$, solid solution in the range of 5°-90°

The FT-IR spectra of BiOI, BiOCl and BiOCl$_{0.5}$.5$_{0.5}$ are shown in Fig. S1. The peaks around 3419 cm$^{-1}$ and 1645 cm$^{-1}$ were attributed to the bond stretching vibrations of O-H, which were caused by the water molecules adsorbed on the catalyst surface. The absorption peaks at 1420 cm$^{-1}$ and 1282 cm$^{-1}$ are attributed to the C-H bond of the residual PV. The characteristic peak at 527 cm$^{-1}$ is attributed to the Bi-O bond, and the absorption peak of Bi-O occurs at 485 cm$^{-1}$ in the BiOI spectrum. In the BiOCl spectrum, 1107 cm$^{-1}$ and 836 cm$^{-1}$ are the absorption peaks of O-Cl and Bi-Cl, respectively. The distinctive peak of Bi-Cl was enhanced in the spectrum of BiOCl$_{0.5}$.5$_{0.5}$, while the absorption peak of O-Cl practically vanished, showing that BiOCl$_{0.5}$.5$_{0.5}$ was not a simple mixing of BiOCl and BiOI.

The optical properties of BiOCl, BiOCl$_{0.5}$.5$_{0.5}$ and BiOI were studied using UV-vis. As shown in Fig. 3 (a), the absorption edge of pure BiOCl and pure BiOI were presented at approximately 370 nm and 660 nm, respectively. The absorption edge of BiOCl$_{0.5}$.5$_{0.5}$ is between pure BiOCl and pure BiOI, which was about 520 nm. BiOCl$_{0.5}$.5$_{0.5}$ and pure BiOI had strong absorption for visible light. Compared with BiOCl, the absorption edge of BiOCl$_{0.5}$.5$_{0.5}$ occurred a remarkable red-shifting with the introduction of I to BiOCl, whereas it was still smaller than that of BiOI. The phenomenon revealed that the establishment of a solid solution could adjust the absorption edge to a certain degree. The corresponding optical band gap energy$^{49}$ may be estimated using Tauc’s law:

$$\alpha h \nu = A(h \nu - E_g)^{1/n}$$ (1)

where and A are the optical absorption coefficient, photonic energy, and proportionality constant, respectively. n decided by photocatalyst transition type, is equal to 2 (both BiOCl and BiOI are indirect transitions between bands). As shown in Fig. 3 (b), the Eg of BiOI, BiOCl$_{0.5}$.5$_{0.5}$, and BiOI were estimated to be 1.74, 2.07 and 2.97 eV, respectively. So, stronger visible light collecting ability and narrower band gap for BiOCl$_{0.5}$.5$_{0.5}$ were both beneficial to improving photocatalytic performance.

Fig. 3 UV-vis diffuse reflectance spectra (a) and plots of $(\alpha h \nu)^{2}$ versus $h \nu$ (b) of BiOCl, BiOCl$_{0.5}$.5$_{0.5}$ and BiOI

The chemical composition and surface chemical states of
BiOCl$_{0.5}$ solutions were investigated using XPS, and the resulting spectra are displayed in Fig. 4. The sample’s survey XPS spectra revealed Bi, O, Cl and I peak (Fig. 4 (a)). The peak of Cl 1s may be due to the adventitious carbon of the XPS instrument used to rectify the charge. The Cl 2p spectrum was decomposed into two peaks with binding energies of 197.5 and 199.0 eV (Fig. 4 (b)), which were dedicated to the binding energies of Cl 2p$_{3/2}$ and Cl 2p$_{1/2}$, respectively. Bi 4f spectra (Fig. 4 (c)) revealed two well-resolved peaks at 158.7 eV and 164.0 eV, which were almost consistent with the properties of Bi$^{3+}$ in BiOCl. This indicates that the solid solution synthesis did not change the valence state of the Bi element. In Fig. 4 (d), the peaks of O 1s appeared at 529.55 and 531 eV were ascribed to the lattice oxygen Bi-O bond in [Bi$_2$O$_3$]$^{2+}$ slabs and the surface oxygen O-H bond of water on the BiOCl$_{0.5}$ surface, respectively. The binding energies of 618.5 and 630.05 eV should be attributed to the I 3d$_{5/2}$ and I 3d$_{3/2}$ peaks in Fig. 4 (e), indicating that the elemental iodine is -1 valence. The experience results proved BiOCl$_{0.5}$ was a new substance formed by lattice substitution of chlorine and iodine, not a simple mixture of BiOCl and BiOI.

The solid solution’s band gap may be adjusted by changing the molar ratio of Cl and I. The degradation performance of PRO by the solid solutions of different ratios of Cl and I was shown in Fig. S4. It can be observed that the BiOCl/PS system showed a weak degradation rate of PRO after 2 h irradiation only reached 16.7%. Encouragingly, BiOCl$_{0.5}$/PS obtained the greatest photocatalytic efficiency, and PRO was entirely decomposed after 2 h. The order of degradation rate was as follows: BiOCl$_{0.5}$/PS > BiOCl$_{0.25}$ > BiOCl/PS > BiOCl = BiOI = PS. The photocatalytic degradation process followed the Langmuir-Hinshelwood pseudo-first-order kinetic model ($-\ln(C/C_0) = kt$). Fig. S3 was depicted -ln(C/C$_0$) as a function of the irradiation time and the corresponding apparent reaction rate constant (k value, the slope of the linear fitting curve). k of PRO degradation was 0.0232 min$^{-1}$, much greater than that of other catalysts (0.0094 min$^{-1}$ for BiOCl$_{0.25}$/PS, BiOCl/PS for 0.00159 min$^{-1}$).

### 3.2 PRO degradation kinetics of different processes

The adsorption of PRO by the catalysts and the direct hydrolysis of PRO were excluded. The visible-light photocatalytic reduction performance of BiOCl$_{0.5}$ and the relative materials for PRO are exhibited in Fig. 5 (a). The photocatalytic decomposition ability of PS and BiOCI for PRO under visible light irradiation was negligible. BiOCl$_{0.5}$/PS showed a higher removal efficiency than pure BiOCI, which indicated that the introduction of the iodine element optimized the photocatalytic activity of BiOCl. Adding PS to the reaction system, BiOCl/PS showed weak photocatalytic efficiency, and the photodegradation rate of PRO after 2 h irradiation only reached 16.7%. Encouragingly, BiOCl$_{0.5}$/PS obtained the greatest photocatalytic efficiency, and PRO was entirely decomposed after 2 h. The order of photodegradation efficiency was as follows: BiOCl$_{0.5}$/PS > BiOCl$_{0.25}$ > BiOCl/PS > BiOCl = BiOI = PS. The photocatalytic degradation process followed the Langmuir-Hinshelwood pseudo-first-order kinetic model ($-\ln(C/C_0) = kt$). Fig. S3 was depicted -ln(C/C$_0$) as a function of the irradiation time and the corresponding apparent reaction rate constant (k value, the slope of the linear fitting curve). k of PRO degradation was 0.0232 min$^{-1}$, much greater than that of other catalysts (0.0094 min$^{-1}$ for BiOCl$_{0.25}$/PS, BiOCl/PS for 0.00159 min$^{-1}$).

### 3.3 Effect of different ratios of Cl and I

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of Cl to I was 5:5 and more than 95% of PRO was removed. According to the trend, the addition of iodine narrowed the band gap width of BiOCl and increased the range of visible light absorption, resulting in more photogenerated carriers to interact with PS and target pollutants. However, when the proportion of I element led to the forbidden band of the solid solution being too narrow. Although it could be efficiently stimulated by visible light, the photogenerated electron-hole pairs generated are also extremely easy to recombine, resulting in low carrier utilization. The result was consistent with the finding that PRO was hardly degraded by the BiOCl/PS system.

3.4 Effect of PS concentration

The number of PS has an important impact on the photocatalytic system. As seen in Fig. 5 (b), the photodegradation efficiency of PRO improved when the PS dosage was raised from 0 to 1 mM, indicating that the removal rate of PRO depended on the number of PS when the dosage of solid solution in the system was fixed. However, the degradation efficiency of PRO slightly dropped when 2 mM PS was added. The opposite result may be due to some reasons. The dosage of the photocatalyst will become a significant limiting factor, with the dosage of PS being much higher. There were not enough BiOCl$_{0.5}$ to generate e$^-$ to react with PS in the system. Hazime et al. mentioned that excessive PS might cover the surface of the photocatalyst to inhibit the generation of $\bullet$SO$_4^-$ and $\bullet$OH. Furthermore, some studies pointed out that the quenching of $\bullet$SO$_4^-$ and $\bullet$OH (reactions (2) and (3)) may be another reason for the reduction of PRO degradation rate under high concentrations of PS.

$$\text{S}_2\text{O}_4^{2-} + \bullet\text{SO}_4^- \rightarrow \text{S}_2\text{O}_8^{2-} + \text{SO}_4^{2-} \quad (2)$$
$$\text{S}_2\text{O}_8^{2-} + \bullet\text{OH} \rightarrow \text{S}_2\text{O}_4^{2-} + \text{OH} \quad (3)$$

3.5 Effect of pH

Solution pH is a critical factor in pollutant decomposition because it determines the speciation of pollutants and the generation of principal free radical types. The pH value strongly correlated with the degrading efficiency of PRO (Fig. 5 (c)). Fig. S5 showed that $k$ was increased from 0.0081 to 0.02489 min$^{-1}$ when pH raised from 3 to 9, and then decreased to 0.00957 min$^{-1}$ with alkaline further enhancing. A low pH inhibited PRO degradation and a high pH favored its removal. Although $\bullet$SO$_4^-$ can be generated from PS activated by the photogenerated electrons produced by BiOCl$_{0.5}$ under visible light, part of PS was consumed through a non-radical pathway to generate invalid anions or weaker free radicals rather than generating $\bullet$SO$_4^-$ at acidic conditions, which was responsible for the lower PRO removal rate. Compared with acidity and neutrality, PS was activated by not only a solid solution, but also OH$^-$ in alkaline conditions, and thus a larger number of radicals were generated. The result can also be proven by the pH value decreasing following the reaction (Fig. S6). Further, the degradation efficiency was closely linked to the speciation of PRO. PRO is an ionic compound with $pK_a = 9.53$. It existed as a cation form when pH was lower than $pK_a$. As pH increased, the ratio of protonated PRO was decreased and the cation form was gradually changed to the neutral molecule. It was studied that the deprotonation of the amino group can weaken the electron-withdrawing effect of this part and strengthen the oxidation of radicals, so the degradation rate was enhanced. Furthermore, PS may self-decompose when pH $> 10$, resulting in a decline in degradation efficiency.

3.6 Effect of PRO concentration

The impact of initial PRO concentration was examined, and the curves are depicted in Fig. S7. It was clear that the PRO photodegradation rate was gradually inhibited as the concentration of PRO increased. The corresponding efficiency reduced from 100% to 39.9% with the initial PRO concentration varying from 5 mg/L to 25 mg/L. When the initial PRO concentration in the system was relatively low, the BiOCl$_{0.5}$/PS photocatalytic system provided sufficient active free radicals to interact with PRO molecular, and each molecule tended to be oxidized easily, so that the system could achieve a higher removal rate. However, when the concentration of PRO increased, the active free radicals generated by the photocatalytic system were gradually insufficient to decompose all the pollutant molecules, leading to a decline in PRO degradation efficiency. This was mostly caused by the reality that the quantity of photogenerated electron-hole pairs remained almost constant under the same BiOCl$_{0.5}$/PS and PS dosages. Furthermore, when the concentration of PRO was raised, the intermediate products in the system also increased. More and more PRO molecules and their conversion products competing for reactive free radicals could also reduce the photocatalytic activity of the system.
3.7 Effect of HA concentration

HA is a natural organic matter widely distributed in the environment, and its existence will affect the degradation of pollutants. Therefore, the degradation of PRO was also evaluated at different HA concentrations. As exhibited in Fig. 5 (d), the degradation of PRO by BiOCl₀.₅₆/PS was gradually inhibited as the concentration of HA added to the system increased. When the HA concentration varied from 0 to 50 mg/L, the corresponding k value decreased from 0.02168 min⁻¹ to 0.00456 min⁻¹ (Fig. S8). Generally, HA has a certain ability to absorb visible light. In the conversion of pollutants in water, HA played as a photosensitizer and inhibitor competing with other optically active substances to absorb visible light. Especially when the HA concentration was higher, more photons were filtered out of the system to minimize the formation of photo-generated electron-hole pairs, reducing active free radicals for PRO degradation. In addition, some electron-rich parts of HA can easily interact with PS and compete with PRO for reactive free radicals, which may inhibit the degradation of PRO.

3.8 Effect of anion concentration

The photodegradation of PRO was investigated in the presence of the common anions Cl⁻ and NO₃⁻. As depicted in Fig. 5 (e) and Fig. 5 (f), it was found that the degradation process was weakly promoted by Cl⁻ and low concentration levels of NO₃⁻, but this promotion effect was diminished when the NO₃⁻ concentration increased. As reported, after adding Cl⁻ to the system, Cl⁻ might react with •SO₄⁻ and •OH to form chlorine radicals (Cl• and •Cl₂) which easily interacted with electron-rich organics to form chlorides. Hence, the promotion effect of Cl⁻ on PRO degradation could be determined through the interaction between chlorine-free radicals and the naphthalene ring of PRO. On the other hand, the main active species of the degradation system was h⁺ in this study, therefore the promotion effect of Cl⁻ on PRO was very weak. The impact of a low concentration of NO₃⁻ on the degradation was attributed to the reaction of NO₃⁻ and H₂O in the photolysis system to produce NO₂• and •OH. The increase of active species promoted the degradation of PRO. However, when the concentration of NO₃⁻ in the system reached high, the shading effect of NO₃⁻ appeared, which weakened the utilization of photons in the catalytic system, thereby reducing the formation of active species.

3.9 Evaluation of the stability and recyclability of BiOCl₀.₅₆

To study the recyclability and stability of BiOCl₀.₅₆ photocatalysts, the five cyclic degradation experiments of PRO were conducted. According to Fig. S9 (a), the photocatalytic activity of BiOCl₀.₅₆ was slightly reduced which may be ascribed to the accumulation of intermediates and products generated by the reaction on the photocatalyst surface, covering the photocatalyst active site. Fig. S9 (b) shows XRD pictures of fresh and utilized photocatalysts, the peak intensity of BiOCl₀.₅₆ photocatalyst decreased after several cycles. Still, the position of the diffraction peak remained unchanged, demonstrating that the BiOCl₀.₅₆ heterojunction had high chemical stability. Overall, the BiOCl₀.₅₆ catalyst had a high multiplexing rate and good stability.
Fig. 5 PRO degradation kinetics under different processes (a); The effect of different PS dosage (b), different pH (c), different concentrations of HA (d), different concentrations of Cl⁻ (e), different concentrations of NO₃⁻ (f) on PRO degradation.

3.10 Identification of reactive species

Experiments involving active species trapping experiments were conducted to determine the main free radicals produced and clarify the mechanism of the photocatalytic reduction process. MeOH, TBA, SO₄⁻, PBQ, and FFA were used as the *OH scavenger, *SO₄⁻ scavenger, h⁺ scavenger, *O₂⁻ scavenger and ¹O₂ scavenger, respectively. From Fig. 6, it was clear that the PRO removal rate was greatly depressed with SO and PBQ, which suggested that holes (h⁺) and the super radicals (*O₂⁻) dominated the photocatalytic process.
degradation process. MeOH, FFA and TBA had a weak inhibitory effect on the degradation of propranolol, indicating that •SO$_4^-$, O$_2^-$ and •OH occupy a secondary position in photodegradation.

In order to prove whether •OH and •SO$_4^-$ are involved and the role of O$_2$ in the air in the reaction. EPR experiments were carried out using DMPO as a trapping agent for •OH and •SO$_4^-$, and TEMP as a trapping agent for O$_2$. As seen in Fig. S10 (a), the system after the addition of BiOCl$_{0.5}$ showed a stronger signal peak of •OH with an intensity ratio of 1:2:2:1, and a characteristic signal peak of •SO$_4^-$ also appeared. In the spectrogram of Fig. S10 (b), only PS in the system can be seen to have a weak characteristic peak of O$_2$, but an obvious O$_2$ signal peak of 1:1:1 appeared after the reaction system was added to BiOCl$_{0.5}$ and PS, and a lot of O$_2$ was generated in the system, show that BiOCl$_{0.5}$ stimulates PS to produce more O$_2$. After adding PRO, the process of degrading pollutants consumes a certain amount of O$_2$, resulting in a decrease in the peak value. Therefore, •OH, •SO$_4^-$, and O$_2$ play a role in the PRO degradation process either.

**Fig. 6** Photocatalytic degradation of PRO by BiOCl$_{0.5}$/PS system with different scavengers [PS = 0.4 mM, BiOCl$_{0.5}$ = 0.01 g, PRO = 10 mg/L]

**3.11 PRO degradation pathway**

Based on the above experimental results, a possible degradation pathway of PRO was proposed (Fig. 7). The narrow bandgap structure of BiOCl$_{0.5}$ can efficiently capture visible light, so it has good photocatalytic activity. The band gap of the solid solution was 2.07 eV (Fig. 3 (b)) and the VB potential of that was measured as 1.03 eV (Fig. S11), thus, CB potential was calculated as -1.04 eV. It seemed that the CB potential was more negative than E(O$_2$/*/O$_2$) = -0.33 eV. As a result, •O$_2^-$ could be generated by the reaction of e$^-$ and O$_2$. Furthermore, •OH could be generated from the interaction of •O$_2^-$ and H$_2$O. An unobvious effect of MeOH and TBA on PRO photodegradation was exhibited because h$^+$ cannot directly oxidize H$_2$O to •OH due to lower VB potential than E(•OH/OH$^-$) = 1.99 eV. Instead, h$^+$ can directly oxidize PRO to intermediates. As an electron capture agent, PS interacted with e$^-$ to reduce the recombination rate of h$^+$ and e$^-$ so that more pollutants could be removed by photogenerated carriers. Meanwhile, a small number of PS reacted with e$^-$ to form •SO$_4^-$ and part of them could react further to generate •OH under neutral conditions, which explained the weak influence of MeOH and TBA.

**Fig. 7** The possible degradation mechanism of PRO in BiOCl$_{0.5}$/PS system under visible light

4 Conclusions

In summary, a solid solution BiOCl$_{0.5}$ photocatalyst was successfully synthesized and a dual system BiOCl$_{0.5}$/PS was applied to remove PRO efficiently under visible light. BiOCl$_{0.5}$ exhibited higher photocatalytic activity for PRO photodegradation than pure BiOCl under visible light, which revealed that the addition of iodine improved the efficiency with which electron-hole pairs are separated. Increasing the pH from 3 to 10 increased the PRO removal efficiency, which could be due to the more active species in the alkaline solution. The inhibitory effect of HA on the reaction rate was observed. h$^+$ and •O$_2^-$ were the primary active species for PRO removal provided by the radical quenching experiment. EPR experiments demonstrated that not only free radicals but also non-free radicals are involved in the reaction. Moreover, the BiOCl$_{0.5}$/PS photocatalytic system had good stability and recyclability. All results demonstrated that the
BiOCl_{0.310.3}/PS system is a viable oxidation technology for the degradation of refractory organic contaminants, which significantly broadens the application of photocatalysts in the purification of water.

**Author contributions**

Yuehua Deng: Conceptualization, Resources, Supervision, Funding acquisition; Jiating Luo: Investigation, Formal analysis, Visualization, Writing-original draft; Hongyu Cao: Visualization, Writing-original; Danni Chen: Visualization, Writing-original; Yani Li: Investigation, Formal analysis, Visualization, Writing-original draft; Qianqian Che: Investigation, Formal analysis, Visualization, Writing-original draft; Yan He: Validation, Funding acquisition; Xiang Gao: Validation, Funding acquisition; Xiaobin Hu: Writing-review & editing Weizhao: Writing-review & editing; Fei Wang: Funding acquisition. All authors have agreed to their contributions.

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**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**

49. L. O. Conte, G. Legnettino, D. Lorenzo, S. Cotillas, M. Prisciandaro and A. Santos, Applied Catalysis B: Environmental, 2023, 324, 122288.
59. Y. Deng and Y. Li, Nanomaterials, 2020, 10, 205.