

Photodegradation of Antibiotic Drugs by BiVO₄ Nanocomposites

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BiVO₄ and its composites were prepared and compared with tetracycline hydrochloride, chlortetracycline hydrochloride and hygromycin hydrochloride to simulate the target degradation species for photocatalytic degradation experiments. All the prepared samples were found to have strong degradation effects on the three antibiotics, and the composite photocatalysts (GO/BiVO₄) GB, (PPy/BiVO₄) PB and (PPy/GO/BiVO₄) PGB showed faster photocatalytic reaction rates and higher photocatalytic activity than the pure BiVO₄. In addition, the degradation of each sample to each antibiotic solution was in accordance with the primary reaction kinetic equation. The UV detection of PGB degradation of antibiotics was also carried out, and the results showed that the catalyst has a strong oxidation ability to degrade antibiotics to small molecules.

Keywords: composite material, photocatalysis, degradation, antibiotics.

1. INTRODUCTION

Heilongjiang is located in the northeastern part of China with four distinct seasons and beautiful scenery. However, the ecological environment has gradually deteriorated in recent years, and investigations have revealed a gradually increasing demand for antibiotics in several fields such as health care, livestock breeding and aquaculture [1, 2]. Unfortunately, due to their antibacterial properties, treatment of antibiotics by sewage treatment plants is limited, resulting in the direct discharge of antibiotics into the environment from pharmaceutical wastewater, hospital wastewater, agricultural runoff, and aquaculture. It's a threat to public health. Therefore, as an emerging organic micropollutant, antibiotics have attracted great attention from researchers in the environmental field [3]. Since 2000, tetracycline (TCs), sulfonamides, quinolones, β -lactam and macrolides have been the five most studied antibiotics in the field of water treatment [4].

Tetracycline antibiotics (TCs) is a broad-spectrum antibiotic with a wide range of antibacterial activity produced by actinomycetes and is widely used to treat diseases related to the respiratory system, renal function and lung infection in humans and animals [5]. They can also be used as an additive in animal feed to accelerate their growth [6], it is often used as an additive in livestock feed [7, 8].

Tetracycline hydrochloride (TC) is widely used to treat human and animal infections due to its extensive activity against bacterial species and is one of the main antibiotics used in veterinary medicine, human therapy and agriculture. Tetracycline hydrochloride has low volatility and hydrophilicity, resulting in its significant and long-lasting presence in the water. Most tetracycline drugs cannot be removed by conventional means, and long-term exposure of humans or animals to the environment may induce drug

resistance genes [9].

Aureomycin hydrochloride (CTC·HCl) is a kind of broad-spectrum antibacterial drug, which has antibacterial and bactericidal effects, and is a kind of tetracycline antibiotics. Environmental CTC·HCl not only interferes with the respiration, nitrification, and phosphatase activity of soil microorganisms, but also causes resistance of pathogenic organisms, leading to increasing environmental problems. Soluble in water, often used in livestock and poultry breeding and aquaculture. Due to the water-soluble, persistent and refractory nature of antibiotics, a large amount of treated wastewater containing antibiotics and their transformation products is discharged into the water environment, resulting in the widespread existence of antibiotics in the water, soil and gas phases, and continuous accumulation in animals, plants and water bodies, posing a threat to health and environment [10–15].

Oxytetracycline hydrochloride (OTC) is a yellow, crystalline powder, easily soluble in water. OTC has an obvious inhibitory effect on Gram-positive and gram-negative bacteria, actinomycetes, rickettsia and spirochete. The general way of administration is internal administration, which is easy to absorb, but the absorption is not complete. Sometimes it is also used for injection, which has a long-term effect.

Various methods have been developed for the removal of antibiotics in water, such as adsorption [16, 17], biodegradation, electrochemical oxidation [18, 19] and photocatalysis [20, 21]. However, adsorption can only physically separate antibiotics from wastewater, and can not effectively degrade pollutants completely. The antibacterial effect of antibiotics on bacterial activity, and the removal rate of biodegradation is low; due to the high price of electrode materials, electrochemical oxidation has not been widely used. Among these technologies, photocatalysis has

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attracted wide attention due to its characteristics of non-toxicity, high efficiency, low cost and environmental friendliness. The disadvantages of the current photocatalytic system are low utilization rate of visible light, fast charge recombination, and low photo-generated electrons and hole migration ability, which limit the industrial application of the photocatalytic system. Therefore, the development of efficient and recyclable photocatalysts is the key to degradation. BiVO₄ is a new photocatalyst with narrow forbidden bandgap and high visible light photocatalytic activity and good stability, which belongs to a new generation of environmentally friendly materials [22]. BiVO₄ can effectively utilize visible light from sunlight and has good visible light response properties, and the preparation process is simple, non-toxic and stable [23–25]. Poly-pyrrole (PPy), as one of the common polymer conducting polymers, is a conjugated conductive polymer, obtained by oxidative polymerization of C and N five-membered heterocyclic pyrrole monomers, and is one of the heterocyclic conducting polymers that have been widely studied and used in recent years [26, 27]. Polypyrrole has a wide range of applications in electro-luminescence, solar cells, and conductive materials [28–31]. Graphene oxide (GO) is an excellent carrier for multiphase nanoparticle catalysts with good electrical, mechanical and thermal properties [32, 33]. It has a very promising future in the fields of energy, environment and biology. It also has important applications in the treatment of wastewater [34–36].

In this paper, BiVO₄, GO/BiVO₄(GB), PPy/BiVO₄(PB), PPy/GO/BiVO₄(PGB) composite photocatalysts were used for the degradation of tetracycline hydrochloride, chrysomycin hydrochloride and oxytetracycline hydrochloride in wastewater from Heilongjiang province. A UV-Vis spectrophotometer was used to detect the absorbance of the target degrader under different photocatalytic reaction times, and the catalytic activity of the photo-catalysts was investigated under visible light conditions. The photocatalytic performance was evaluated. It lays a foundation for future research.

2. EXPERIMENTAL DETAILS

2.1. Preparation of sample

2.1.1. Preparation of BiVO₄

Solution 1 is prepared by dissolving 0.487 g of Bi(NO₃)₃·5H₂O in 20 mL 2 mol/L HNO₃. Solution 2 is prepared by dissolving 0.118 g NH₄VO₃ in 20 mL 2 mol/L NaOH. Solution 2 was slowly added dropwise to solution 1, stirred for 30 min, and the pH was adjusted to 7 with 2 mol/L NaOH. A uniformly mixed clear yellow suspension was found to be obtained. 100 ml of the above solution was placed in a Teflon sealed autoclave, filled with deionized water to 2/3 of the volume, sealed and baked in an oven at 180 °C for 6 h. After natural cooling to room temperature, the sample was centrifuged 3 times and cleaned 7 times with deionized water. It was dried in a vacuum drying oven at 60 °C for 12 h to obtain a yellow solid BiVO₄.

2.1.2. Preparation of GO/BiVO₄

0.036 g of GO was added to 20 mL deionized water and

sonicated for 1 h. 2 mol/L NaOH solution was added to the above BiVO₄ solution, with the pH value adjusted to 7.3. After adding GO solution to it, the ultrasound continued for 1 hour. 100 ml of the above solution was placed in a Teflon sealed autoclave, filled with deionized water to 2/3 of the volume, sealed and baked in an oven at 180 °C for 6 h. It was slowly cooled to room temperature, centrifuged 3 times, and washed with deionized water 7 times. It was dried in a vacuum drying oven at 60 °C for 12 h to obtain a green powder called GO/BiVO₄(GB).

2.1.3. Preparation of PPy/BiVO₄

5 % of polypyrrole was dissolved in 20 mL water. 10 mL of bismuth vanadate prepared above was mixed with it, and sonicated for 25 min. Then 10 mL of (NH₄)₂S₂O₈ (as an oxidant) was added. It is left to sit for 1 hour and then filtered 7 times with deionized water and 7 times with anhydrous ethanol. The solid PPy/BiVO₄ (PB) was dried in a vacuum oven at 60 °C for 12h to obtain a yellow-green solid.

2.1.4. Preparation of PPy/GO/BiVO₄

Add 1.003 g GO/BiVO₄ and 0.055 g PPy to 20 mL deionized water and sonicate for 30 min. Add 5 mL of (NH₄)₂S₂O₈ solution (as an oxidant) to it and stir for 12 h. Allow to stand for 1 h and filter. Washed 7 times with deionized water and 7 times with anhydrous ethanol to obtain a yellow-green solid. It is PPy/GO/BiVO₄ (PGB).

2.2. Preparation of stock solution

Preparation of tetracycline hydrochloride reserve solution: 10 mg/L tetracycline hydrochloride solution was provided for ultrasonic assisted dissolution, and then filled with distilled water in a 500 mL volumetric bottle and placed in a refrigerator at 4 °C for later use.

The preparation of aureomycin hydrochloride and tetracycline hydrochloride was done similarly to tetracycline hydrochloride as mentioned above.

2.3. Photodegradation performance test

The photocatalytic experiment was performed as follows: 0.05 g of the sample was taken and placed in 100 ml of a solution with a concentration of 10 mg/L to simulate the target degradation. Magnetic stirring was turned on and the dark reaction was performed for 20 min, followed by photocatalytic experiments. 5 ml of the solution was taken every 20 min, and the supernatant was taken after centrifugal separation of the solution, and the absorbance was measured by UV spectrophotometer at a certain wavelength range with the zero concentration solution as a reference. Under the condition of 25 °C, the mass concentration of antibiotics in a certain range was proportional to the absorbance value A. The degradation rate of antibiotics at different moments was calculated according to the Lambert-Bier law.

2.4. Performance evaluation of catalyst

The kinetics of photocatalytic degradation of TC, CTC.HCl, and OTC were investigated by fitting a first-order kinetic method with the expression:

$$\ln(C_0/C_t) = kt, \quad (1)$$

where C_0 and C_t are the concentrations of TC, CTC, HCl, and OTC at times 0; t and k is the first-order velocity constant.

3. RESULTS AND DISCUSSION

3.1. Analysis of tetracycline hydrochloride photodegradation experiment results

Under the condition of simulated visible light, tetracycline hydrochloride was taken as the simulated target degradation substance. By determining the rate at which the manufactured composite samples degraded into tetracycline hydrochloride aqueous solution, the experiment's photocatalytic degradation performance of various samples was examined. The results are depicted in Fig. 1.

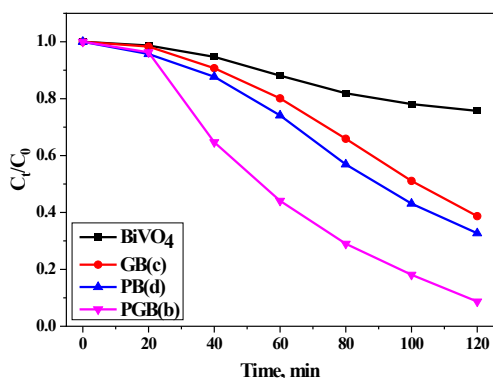


Fig. 1. Curve of tetracycline hydrochloride photocatalytic degradation of samples

After 100 min of photocatalytic reaction, the degradation rate of tetracycline hydrochloride itself was only 4 %, which was negligible, and the degradation rate of BiVO₄ sample on tetracycline hydrochloride was 24.3 %. GB samples degraded at a rate of 61.3 %. PB samples degraded at a rate of 67.3 % whereas PGB samples degraded at a rate of 91.3 %. Therefore, it can be concluded that the degradation of tetracycline hydrochloride in solution was enhanced by composite samples.

3.2. Analysis of the photodegradation results of aureomycin hydrochloride

Aureomycin hydrochloride was used as the simulated target degradation agent, and the photocatalytic degradation results were shown in Fig. 2. After 160 min photocatalytic reaction, there was little photocatalytic activity in the BiVO₄ sample, and only 32.4 % of the aureomycin hydrochloride was broken down. GB samples degraded at a rate of 55.4 %. PB degraded at a rate of 67.2 % whereas PGB degraded at a rate of 76.39 %. The concentration of aureomycin hydrochloride decreased gradually with the effect of light degradation, so the composite catalyst enhanced the elimination of aureomycin hydrochloride in the solution.

3.3. Analysis of photodegradation results of oxytetracycline hydrochloride

Oxytetracycline hydrochloride was used as the simulated target degradation substance to investigate the photodegradation activity of different samples prepared in

the experiment. The photocatalytic degradation results are shown in Fig. 3. The concentration of oxytetracycline hydrochloride decreased gradually with the degradation of light. Therefore, the composite catalyst enhanced the elimination of aureomycin hydrochloride by photocatalyst.

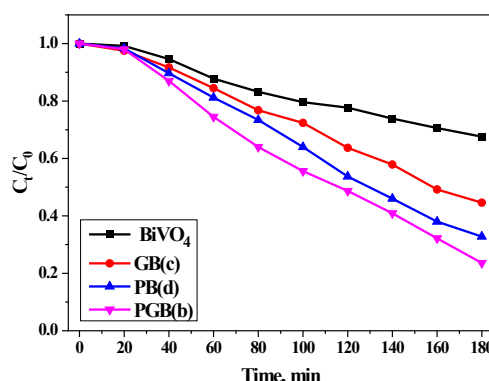


Fig. 2. Curve of the photocatalytic degradation of aureomycin hydrochloride

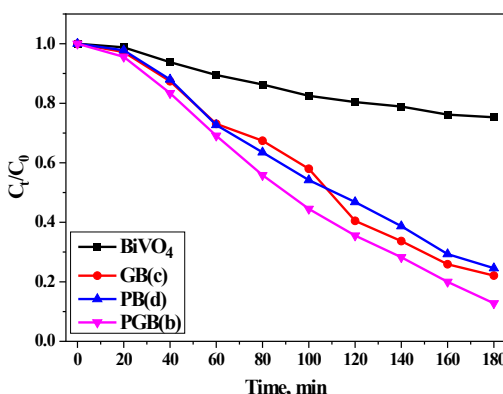


Fig. 3. Curve of photocatalytic degradation of oxytetracycline hydrochloride

3.4. Analysis of kinetic results of tetracycline hydrochloride photodegradation reaction

The sample was dark-reacted in tetracycline hydrochloride solution for 20 min to achieve the adsorption-desorption equilibrium in order to further investigate this experimental finding [37]. Set the end time of the dark reaction and the start time of the light reaction as zero, and analyze the photocatalytic reaction kinetics of each sample, that is, the relationship between $\ln(C_0/C_t)$ and time t , as shown in Fig. 4. The results are shown in Fig. 4. Each correlation coefficient R^2 in Table 1 is more than 0.9, indicating that the oxidation of tetracycline hydrochloride by the catalyst follows the first-order reaction kinetic equation: $\ln(C_0/C_t) = kt$. $\ln(C_t/C_0)$ has a linear connection with the degradation time. The results showed that the degradation rate of PGB was the fastest after 100 min illumination, which was 8 times that of pure BiVO₄. This indicated that PGB composite photocatalyst had a faster photocatalytic reaction rate and higher photocatalytic activity than pure BiVO₄. As a result, the photogenerated carrier of the PGB sample has greater tetracycline hydrochloride breakdown and removal efficiency and stronger REDOX ability. In addition, due to the small size

of the composite sample, the migration distance and time of photogenerated carriers from inside the photocatalyst to the surface will be greatly shortened, and the recombination efficiency of photo-generated carriers will also be reduced.

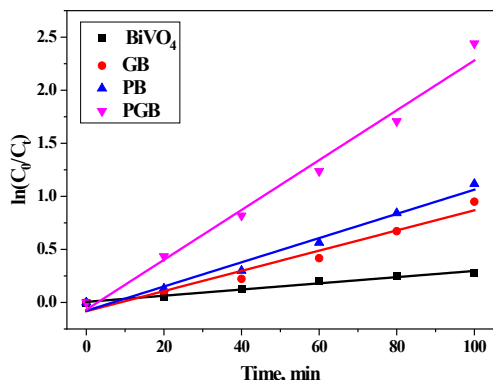


Fig. 4. First-order kinetic study of tetracycline hydrochloride degradation in samples

Fig. 5 shows the UV-visible absorption spectrum of tetracycline hydrochloride degraded by ternary composite PGB(b). The figure shows that as time passes, the intensity of the absorption peak at 356 nm gradually declines, while the peak at 275 nm gradually decreases and shows a certain blue shift. The peaks at 275 nm and 356 nm correspond to the E2 and B bands of the benzene ring respectively, demonstrating that the samples we made can break down the tetracycline hydrochloride's benzene ring and release tiny chemicals from it, and the oxidation capacity of the catalyst is strong [38].

Table 1. The linear fitting data for the kinetics of each sample's photocatalytic process

Sample name	R^2	k	intercept
BiVO ₄	0.9809	0.00292	0.00516
GB	0.95385	0.00952	0.08306
PB	0.97643	0.01141	0.07793
PGB	0.98215	0.02349	0.06794

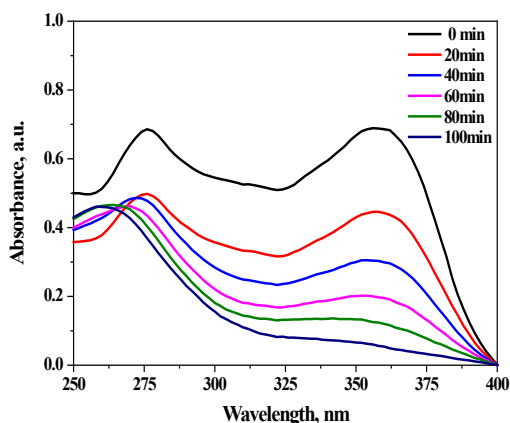


Fig. 5. UV absorption spectra of tetracycline hydrochloride degraded by samples

3.5. Analysis of kinetic results of the photo-degradation reaction of aureomycin hydrochloride

To further study this experimental result, to obtain the adsorption-desorption equilibrium, for 20 minutes, the

material was dark-reacted in an aureomycin hydrochloride solution. Analyze the photocatalytic reaction kinetics of each sample with the end time of the dark reaction and the start time of the light reaction both set to zero, that is, the relationship between $\ln(C_0/C_t)$ and time t [39], as shown in Fig. 6.

The results are shown in Fig. 5. $\ln(C_t/C_0)$ has a linear relationship with the degradation time, and every R^2 correlation coefficient in Table 2 is more than 0.9. It shows that the oxidation reaction of aureomycin hydrochloride in the presence of a catalyst conforms to the first-order kinetic equation $\ln(C_0/C_t) = kt$. This indicated that PGB composite photocatalyst had a faster photocatalytic reaction rate and higher photocatalytic activity than pure BiVO₄.

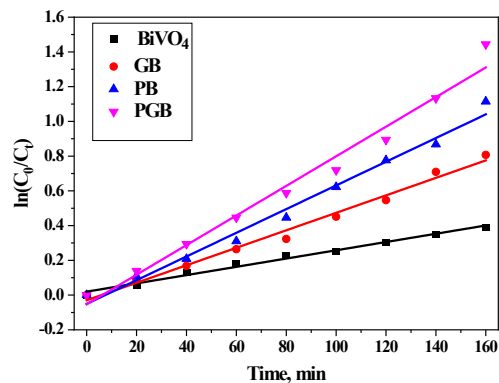


Fig. 6. Effect of reaction kinetics on the degradation of chrysomycin hydrochloride

Table 2. Photocatalytic kinetic curve fitting data for each sample

Sample name	R^2	k	intercept
BiVO ₄	0.98614	0.00238	0.01969
GB	0.98671	0.00503	0.02975
PB	0.98484	0.00682	0.05076
PGB	0.97746	0.00852	0.05338

Fig. 7 shows the UV-visible absorption spectrum of the degradation of aureomycin hydrochloride.

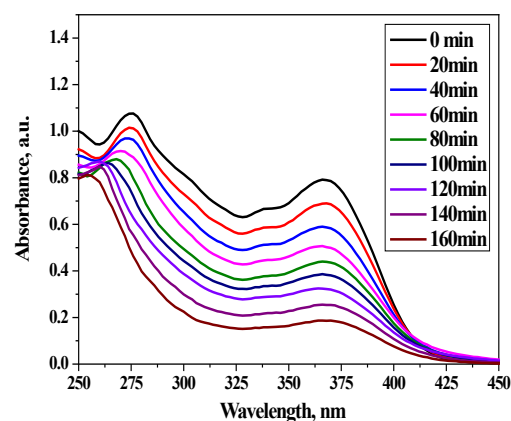


Fig. 7. UV-visible absorption spectrum of degraded aureomycin hydrochloride

From the graph, it can be seen that the intensity of the absorption peak at 366 nm decreases gradually as time goes by, while the peak at 276 nm gradually decreases and appears a certain blue shift. The peaks at 276 nm and 366 nm correspond to the E2 and B bands of the benzene

ring respectively, suggesting that the samples we prepared are degradable and open the benzene ring of aureomycin hydrochloride into small molecules, and the oxidation capacity of the catalyst is strong [40].

3.6. Kinetic study of photolysis of oxytetracycline hydrochloride

To further study this experimental result, the sample was dark reacted in oxytetracycline solution for 20 min to achieve adsorption-desorption equilibrium. The dark reaction termination and light reaction onset times were denoted by 0, and the photocatalytic kinetics of each specimen were analyzed, that is, the relationship between $\ln(C_0/C_t)$ and time t [41], as shown in Fig. 8.

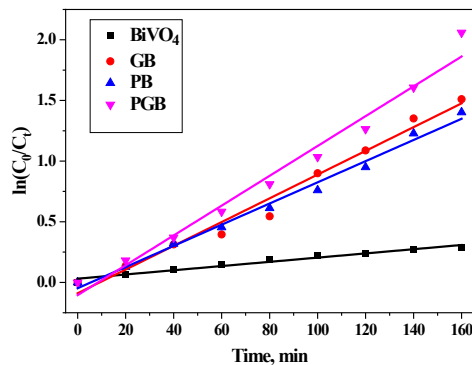


Fig. 8. Primary kinetics of degradation of oxytetracycline hydrochloride in specimens

Table 3. Photocatalytic kinetic curve fitting data for each sample

Sample name	R^2	k	intercept
BiVO ₄	0.96127	0.00174	0.03068
GB	0.97673	0.00979	0.08979
PB	0.98951	0.00873	0.04804
PGB	0.97583	0.01229	0.10487

As shown in Fig. 8, $\ln(C_0/C_t)$ is linearly correlated with degradation time, and the R^2 of each correlation coefficient in Table 3 exceeds 0.9. The results showed that the oxidation process of oxytetracycline hydrochloride followed the first order kinetic equation: $\ln(C_0/C_t) = kt$. According to the experiment, PGB has the fastest degradation rate under 160 minutes of light. The degradation rate of PGB samples is 7 times faster than pure BiVO₄. This indicated that PGB composite photocatalyst had a faster photocatalytic reaction rate and higher photocatalytic activity than pure BiVO₄.

Fig. 9 shows the UV-visible absorption spectrum of the degradation of oxytetracycline hydrochloride. The absorption peak at 354 nm corresponds to the benzene ring B band and decreases in intensity with time, as can be seen from this figure. Meanwhile, the peak at 276 nm corresponds to the E2 band of the benzene ring and gradually decreases with a certain blue shift. The results showed that the sample prepared by us could degrade the benzene ring of oxytetracycline hydrochloride into small molecules, and the catalyst had a strong oxidation ability [42].

3.7. Comparative analysis

Through the above experiments, we can find that BiVO₄ is the fastest degradation for aureomycin hydrochloride,

and the slowest degradation for tetracycline hydrochloride; GB degraded oxytetracycline hydrochloride the fastest and aureomycin hydrochloride the slowest; PB has the fastest degradation rate of oxytetracycline hydrochloride, and the degradation rate of tetracycline hydrochloride and aureomycin hydrochloride is similar; PGB had the fastest degradation rate of tetracycline hydrochloride and the slowest degradation rate of aureomycin hydrochloride.

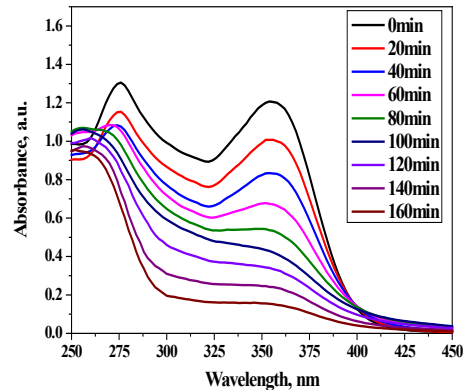


Fig. 9. UV absorption spectra of degraded oxytetracycline hydrochloride

The RGO/gC₃N₄/BiVO₄ Z-scheme heterostructure prepared by Jiang's group [43] showed enhanced photocatalytic activity for the degradation of tetracycline hydrochloride under visible light irradiation, which was about 1.13, 1.16 and 1.41 times higher than that of binary RGO. In this paper, the degradation of tetracycline hydrochloride by PGB was 2.47 times higher than that by GB and 2.06 times higher than that by PB, which was better than that by Jiang's research group.

Zn_{0.75}Mn_{0.75}Fe_{1.5}O₄/ZnFe₂O₄/ZnO photocatalyst was prepared by Fu's research group [44]. The degradation rate of CTC by ZnFe₂O₄/ZnO photocatalyst was 52.86%. Zn_{0.75}Mn_{0.75}Fe_{1.5}O₄/ZnFe₂O₄/ZnO for CTC degradation rate reached 73.04%. The degradation rate of aureomycin hydrochloride in our group was 55.4% for GB sample; The degradation rates of PB and PGB were 67.2% and 76.39%, respectively. It is better than Fu research group. Liu's research group [45] prepared Zn_{0.75}Mn_{0.75}Fe_{1.5}O₄/ZnFe₂O₄ ternary composite to degrade oxytetracycline hydrochloride in mariculture wastewater. It is about three times higher than the pure single product. The degradation effect of PGB in our group was 7 times that of the single product higher than Liu's group [45].

4. CONCLUSIONS

The photodegradation of tetracycline hydrochloride, aureomycin hydrochloride and oxytetracycline hydrochloride simulated target biodegradation was performed by the prepared BiVO₄ and its composite materials. The degradation rates of BiVO₄ were 24.3%, 32.4% and 24.7%, respectively. The degradation rates of GO/BiVO₄ composites were 61.3%, 55.4% and 77.9%, respectively, and the degradation rates of PPy/BiVO₄ composites were 67.3%, 67.2% and 75.4%, respectively. The degradation rates of PPy/GO/BiVO₄ composites were 91.3%, 76.39% and 87.24%, respectively. The degradation rate of PGB composite for tetracycline hydrochloride was 8 times that of

BiVO₄ single product, the degradation rate of aureomycin hydrochloride was 3.6 times that of BiVO₄ single product, and the degradation rate of oxytetracycline hydrochloride was 7 times that of BiVO₄ single product. The results showed that PGB composite photocatalyst had a faster photocatalytic reaction rate and higher photocatalytic activity than pure BiVO₄. This research will make a great contribution to developing new energy sources, improving the ecological environment, and promoting human health.

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