Study on Degradation of Azithromycin Antibiotics by Molybdenum Sulfide Graphene Oxide Composites under Visible Light

Changyan Li, Huihui Jin, Zepeng Hou and Yan Guo*

College of Chemistry and Chemical Engineering, Inner Mongolia University, Huhhot 010021, P. R. China
Email: celicy@imu.edu.cn

Abstract. Waste water including azithromycin antibiotics could cause environment to generate antibiotics bacteria, which heavily damage the ecological balance. It is necessary to study the degradation of azithromycin antibiotics. Molybdenum sulfide graphene oxide composites were synthesized by hydrothermal method. Owing to their better conductivity, the photocatalytic performance of molybdenum sulfide graphene oxide composites for azithromycin was evaluated in the visible-light range. The results show that the degradation rates of molybdenum sulfide and molybdenum sulfide graphene oxide composites to 100 mg/L azithromycin were 87% and 75%, respectively after 180 min of visible light irradiation. Molybdenum sulfide graphene oxide composites show better azithromycin degradation property.

Keywords. Molybdenum sulphide, graphene oxide, azithromycin antibiotics, visible.

1. Introduction

Azithromycin is a macrolide-type antibiotic, which has high antibacterial activity and can remain stable under acidic conditions or alkaline conditions. These characteristics make the wastewater including Azithromycin more harmful. As a drug that can prevent and cure SARS, Azithromycin have antibacterial effects on many pathogenic bacteria and it is now the key drug for research and development. The azithromycin wastewater is also the main macrolide antibiotic wastewater, which is difficult to biodegrade and has large ecotoxicity. The nitrogen is easily nitrosated and entered into the water, which is very harmful to the environment [1]. Therefore, the disposal of this kind of antibiotic wastewater is urgent issue to be solved to ensure that the pollutants in the water meet the standard.

The methods for treating wastewater produced by macrolide antibiotics are now classified into physical methods, chemical methods, biochemical methods, and physicochemical methods [2]. The commonly used physical technologies include adsorption, sedimentation, coagulation, stripping, reverse osmosis, etc. Chemical treatment techniques include redox, electrolysis and neutralization. Biochemical treatment techniques include anaerobic, aerobic and aerobic-anaerobic treatment [3]. Compared with traditional chemical, biochemical and physical methods for treating wastewater, photocatalytic treatment of wastewater has many advantages. And photocatalytic technology has shown great development potential in the field of water environment management. It has the advantages of no secondary pollution, low operating cost and taking use of sunlight as a reaction source. With the deepening of research in photocatalytic oxidation, researchers have continuously put the theoretical results of photocatalytic oxidation in application to treat organic wastewater, and have achieved remarkable effect [4].
Photocatalytic degradation of organic water is a common way of solar energy utilization. It takes advantages of the strong oxidative intermediates generated by solar catalysis to degrade water and atmospheric pollutants. The whole process includes light absorption, generation and separation of photon-generated carrier, carrier transfer, and interface redox. At present, the loss of solar light energy in the photocatalytic process causes a decrease in catalytic efficiency. In view of the good conductivity and low optical band gap of the molybdenum sulfide graphene oxide composite, it is beneficial to the rapid transmission of electrons and photocatalytic degradation [5]. Therefore, hydrothermal synthesis of molybdenum oxide graphene oxide composites is used in this paper. Taking azithromycin antibiotic wastewater as the research object, this paper studied the photocatalytic degradation performance under visible light conditions to explore a new way to degrade azithromycin in the field of photocatalysis.

2. Experimental Section

2.1. Synthesis of Molybdenum Sulfide
0.4840 g of sodium molybdate (Na₂MoO₄·2H₂O) and 0.9016 g of thioacetamide (C₂H₅NS) were added to 70 mL of distilled water, mixed uniformly, and charged into a 100 mL reaction vessel, and reacted at 200 °C for 24 hours. When the reaction was completed, the mixture was cooled to room temperature, centrifuged, and washed with water and absolute ethanol three times. After drying at 80 °C, the obtained black precipitate was protected by N₂ and calcined at 600 °C for 2 h.

2.2. Synthesis of Graphene Oxide
Graphite oxide is prepared using the conventional Hummers method. The specific preparation process is as follows: a 250 mL reaction flask was assembled in an ice water bath, an appropriate amount of concentrated sulfuric acid was added, a solid mixture of 2 g of graphite powder and 1 g of sodium nitrate was added under stirring, and 6 g of potassium permanganate was added in portions. The reaction temperature was controlled under 20 °C for a while and subsequently increased to about 35 °C for 30 min. Then a certain amount of deionized water was slowly added. After mixing for 20 min, the appropriate amount of hydrogen peroxide was added to reduce the residual oxidant, making the solution exhibiting a color of bright yellow. It was filtered while hot and washed with 5% HCl solution and deionized water until no sulfate was detected in the filtrate. Finally, the filter cake was placed in a vacuum oven at 60 °C and dried thoroughly, and stored for later use.

2.3. Synthesis of Molybdenum Sulphide Graphene Oxide Composites
A certain amount of graphene oxide (GO) was uniformly disperse in water, then 0.4840 g of sodium molybdate (Na₂MoO₄·2H₂O) and 0.9016 g of thioacetamide (C₂H₅NS) were added to obtain black deposits with the same hydrothermal synthesis conditions as molybdenum disulfide. When the reaction was completed, the mixture was cooled to room temperature, centrifuged, and washed with water and absolute ethanol three times. After drying at 80 °C, the obtained black precipitate was protected by N₂ and calcined at 600 °C for 2 hours to obtain a composite material of molybdenum sulphide graphite oxide, which is named MoS₂/GO.

2.4. Characterization
PANalytical’s Empyrean X-ray diffractometer, with the incident light source of Cu target, a test voltage of 36kV and a current of 20mA was used. The 2θ measurement range of 5°-80° was selected and scanned for 4.5 min. The scanning electron microscope of the Hitachi S-4800 model uses a S-4800I cold field emission scanning electron microscope main unit with a secondary electron resolution of 1.0 nm (15 kV)/2.0 nm (1 kV) and a magnification of × 20~× 800,000. The FEI Tecnai F20 high-resolution field emission transmission electron microscope with an electron beam acceleration voltage of 80-300 kV was also adopted. The Bruker Tenser 27 infrared spectrometer was adopted to analyse the surface functional groups. The KBr tablet method was used for testing and the measurement range was 400-4000 cm⁻¹.
2.5. Electrocatatalytic Degradation of Azithromycin

0.025 g of catalytic material was placed in a 10 mL quartz tube, and the catalyst was uniformly dispersed in 10 mL of azithromycin solution (100 mg/L) by magnetic stirring. The dark reaction was carried out for 30 min to reach the adsorption-desorption equilibrium. The 350W xenon lamp is used to simulate the sunlight, and the filter is used to filter out the ultraviolet light. Under visible light irradiation, 10 mL of liquid was taken every 30 minutes, and 75% sulfuric acid was used for color development. The absorbance was measured on an ultraviolet-visible spectrophotometer, and the degradation rate was calculated according to \( \frac{c}{c_0} = \frac{(A_0 - A)}{A_0} \times 100\%. \) The Shimadzu UV-Vis spectrophotometer UV-2600 was used with a resolution of 0.1 nm and a measurement wavelength range from 700 to 190 nm. Azithromycin has a maximum absorption peak at 482 nm.

3. Results and Discussions

The samples showed broadening diffraction peaks at 20 = 14.0°, 33.3°, and 58.8° in figure 1a, indicating that the samples should be amorphous. Figure 1b showed that the diffracted peaks of the molybdenum disulfide and molybdenum oxide graphite composites calcined at 600 °C, which are consistent with the standard map of 2H type MoS₂ (JCPDS No. 37-1492), characteristic peaks of 20 = 14.0°, 33.3°, 39.5°, and 58.8° [6] correspond to crystal face (002), (100), (103), (110) of 2H type MoS₂, respectively. The addition of graphene oxide has no effect on the structure of 2H type molybdenum sulfide.

The XRD spectra in figure 2a showed that the (002) characteristic diffraction peak of graphite G appears at 20 = 28.44°. After strong acid oxidation treatment, the diffraction peak of 28.44° disappeared. The (001) characteristic diffraction peak of graphene oxide (GO) appeared at 20 = 9.96° [7]. The Fourier transform infrared (FT-IR) spectra in figure 2b showed that the peak at 3460 cm⁻¹ was belong to the stretching vibration of –OH. The broad absorption peak in the range of 3000-3600 cm⁻¹ was the -OH group of water molecule. The absorption peak at 1715 cm⁻¹ was assigned to C=O stretching vibration peak in GO. The characteristic peak at 1385 cm⁻¹ was the stretching vibration peak of C-O. The peak at 1150 cm⁻¹ was the stretching vibration peak of C-OH. All these results indicated that the graphite powder be oxidized, and oxygen-containing groups were inserted into the sheet [7].

The results of SEM images showed that GO was a lamellar structure in figure 3a. The morphologies of MoS₂ and MoS₂/GO composites displayed flower globular aggregation in figures 3b-3c. In figures 3d-3f, the TEM and HRTEM images demonstrated that graphene oxide and molybdenum sulfide were sheet-like structures with a lattice spacing d of 0.62 nm, which was consistent with the (002) lattice spacing of 2H-MoS₂. And the TEM test results were consistent with that of XRD.

Figure 4 shows the effect of different samples on the photocatalytic degradation of azithromycin. After these samples have been put in dark reaction for 2 h and 30 mins, the absorbance of graphene oxide, molybdenum sulfide and molybdenum sulfide graphene oxide composites decreased significantly. The decrease in absorbance was due to degradation of azithromycin. Graphene oxide, molybdenum sulfide, and molybdenum sulfide graphene oxide composites all showed decreasing absorbance as time increases, which indicated that azithromycin gradually degrade and the content decrease gradually with the increase of irradiation time. Among them, the degradation rate of molybdenum sulfide graphene oxide composite was the highest, reaching 87% in 180min, while the degradation rate of molybdenum sulfide was 75%. The improvement of azithromycin degradation rate was mainly due to the synergistic effect between graphene oxide and molybdenum sulfide, which enhanced the transmission of electrons and reduces the probability of recombination of holes/electrons [8].

4. Conclusions

Graphene is a hexagonal close-packed layered structural material. The band gap width of molybdenum disulfide can be adjustable from 1.2 to 1.9 eV. The upper limit of absorption wavelength is 690-1030 nm. Molybdenum sulfide can absorb photons of visible light frequency, which has good matching with
sunlight and theoretically has high utilization of sunlight. The synergistic effect between GO and molybdenum sulfide enhances the rapid transmission of electrons, which play an important role in azithromycin degradation process.

Figure 1. XRD spectra of MoS₂, MoS₂/GO composites calcined at different temperature: (a) 200°C, (b) 600 °C.

Figure 2. XRD and FT-IR spectra of graphite and graphite oxide: (a) XRD, (b) FT-IR.

Figure 3. SEM images of series samples: (a) GO, (b) MoS₂, (c) MoS₂/GO composites. TEM and HRTEM images of series samples (d-e) MoS₂, (f) MoS₂/GO composites.
**Figure 4.** Azithromycin degradation of MoS\(_2\)/GO composites series under visible light: (a) GO, (b) MoS\(_2\), (c) MoS\(_2\)/GO composites, (d) degradation rate.

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