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Application of the Graphene/ZnO Composites in Treatment of the Simulated Ceftazidime Wastewater

Qiong He

Changzhou Vocational Institute of Engineering, School of Pharmaceutical and Environmental Engineering, Changzhou 213164, China
heqiong@126.com

For study in this paper, nano zinc oxide/graphene composites were prepared at 120 °C with graphene oxide and nano zinc oxide as precursors for the photocatalytic activity of the composites to be tested under 300W xenon lamp in the simulated ceftazidime antibiotic wastewater. Then this paper studies the effects of the pH value on degradation of the ceftazidime solution in treatment by the graphene/ZnO composites as well as the effects of its initial concentration on the degradation time and conducts the kinetic analysis. The results show that the degradation rate of ceftazidime is subject to the pH value, increasing with the pH value. When the pH value is 5, the degradation rate is the highest at 78.8%, so 5 was selected as the pH value of the ceftazidime solution to be degraded. Moreover, it can be seen from the comparison between the pseudo-second-order and pseudo-second-order kinetics models that the former can better simulate the ceftazidime degradation process by the composite materials by further explaining that the degradation process is not a simple diffusion one but a chemistry one.

1. Introduction

1.1 Introduction to the research background

In recent years, the pharmaceutical industry, expanding constantly in China, has hence become the world's largest producer of bulk drugs with the rapid growth of demand. As a consequence, the pharmaceutical wastewater, especially the antibiotic pharmaceutical wastewater, seriously threatens the ecological environment and has resulted in high processing costs due to its unique nature and structure. The production process of the antibiotic drug, being complex with unique manufacturing technique, requires the use of different raw materials, thus resulting in difference in its composition. Moreover, nowadays new products of antibiotics are developed very fast with short replacement cycle, leading to more wastewater discharge due to water quality instability and increased processing difficulty (Xu et al., 2017). The research of antibiotic wastewater treatment, through many years of development, has developed into containing the commonly used methods of adsorption, membrane filtration, biological treatment, advanced oxidation, etc.. However, these methods still have some shortcomings, such as the complexity in the operation process, the difficulty of the degradation effect to stabilize the cost of running large-scale production, etc. Therefore, it is urgent to find out the main factors influencing the wastewater treatment effect in practice as well as the suitable process for treating the wastewater and to improve the production insufficiency through study on the composition of the antibiotic wastewater.
Graphene is a two-dimensional material with only one carbon atom and its carbon atoms are arranged in a sp2 hybrid orbit to form a planar hexagonal lattice film. The two-dimensional graphite material, such as the barbed wire, is arranged in a hexagonal array, and can be regarded as a huge flat fullerene molecule ten times the hardness of steel and showing strong quadratic electric field effect (Huang and Yang, 2015). The structure of graphene is shown in Figure 1.

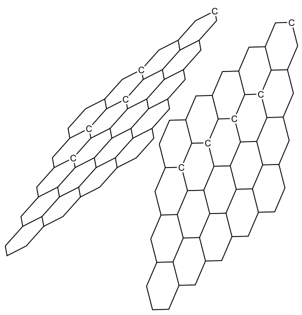

Figure 1: Structure Picture of Grapheme

As the graphene is a honeycomb-like two-dimensional planar carbon nano materials consisting of only one carbon atom with atomic thickness, it has a theoretical specific surface area of over 2600 m^2/g, enabling it to get rid of various substances. Although the synthesis ability of graphene is far from that of a single layer, after ultrasonic treatment, it also has a large specific surface area with the adsorption capacity much larger than that of the general adsorption material (Hung et al., 2014). The precursor (graphene oxide) prepared with conventional methods such as hummers has on its surface a number of functional groups such as carbonyl and epoxy groups which, being hydrophilic, can form with many substances into hydrogen bonds or into an electron- which can introduce other functional groups or new materials by combination, thus further enhancing the water solubility, adsorption capacity and endowing new properties to the graphene. ZnO, being inexpensive, has a wide range of raw materials and is non-toxic at room temperature (Yuan et al., 2014). Therefore, it has been applied in many important fields because of its excellent properties embodied by thermal stability, chemical stability and electrical coupling properties.

1.2 Chemical treatment of the antibiotic wastewater

The antibiotic wastewater owns a wide variety of sources, for example, people taking antibiotics, the leftover of antibiotics after the metabolic effect that is excreted into the city sewer, and the sewage that is drained into the natural river from the treatment plant. The antibiotics used during livestock breeding is absorbed partly by the human body, the rest of which enter the soil or natural water via the metabolic effects. With biological toxicity, the antibiotic wastewater is of high concentration, so treating it chemically has unique advantages. The chemical treatment is mainly to use a certain advanced oxidation technology, such as the ultrasonic, the light Fu shot, the plus electric field, etc., to produce highly oxidized OH for direct oxidation into inorganic with almost no need to select organic pollutants, or for transformation into low-activity biodegradable intermediates (Liu et al., 2016). All those methods can be mainly divided into chemical oxidation, ultrasonic oxidation, photocatalytic oxidation, etc.. The chemical oxidation technology has been paid more and more attention in treatment of high-concentration refractory organic wastewater due to its strong capability to mineralize pollutants and to treat high-concentration wastewater (Ruey and Chin, 2013). As a new type of wastewater treatment, photocatalytic oxidation decomposition technology has been attracting people's attention. This technology, being able to effectively degrade the organic matter in the wastewater, have attractive prospect in organic pollution treatment.

1.3 Study on wastewater treatment mechanism of the graphene/ZnO composites

Since oxygen or water molecules can bind with photogenerated electrons and holes to form free radical groups, most photocatalytic reactions are carried out in air or water. The free radical group is active in its chemical properties and performance. After irradiation in the light source with wavelength less than or equal to 387nm, ZnO is activated to generate electrons and hole pairs in the system and the conduction band electrons and valence band holes in the excited state can transit to the state of exciton, thus converting the light energy into heat or other forms. If there exist a certain suitable surface defects or capture agent for the catalyst, there will be redox reaction on its surface before the recombination of the electrons and holes. The conduction band electrons are good reducing agents while the valence band holes are good oxidizing agents (Zhang et al., 2017). The strong oxidizing property possessed by the holes is made used of in most photocatalytic oxidation reactions either directly or indirectly. And the hole has good reactivity in the photocatalytic semiconductor reaction, being able to form hydroxyl radicals (OH+) of strong oxidizing property with the H2O or OH- ions adsorbed on the surface of the catalyst (Dorival et al., 2012). Meanwhile, obtained through reaction of the electrons with the oxygen molecules adsorbed on the surface of the catalyst, the molecular oxygen is not only required for the reduction reaction but also one of the important sources of surface hydroxyl radicals. Figure 2 shows the antibiotic wastewater treatment mechanism by the graphene/ZnO.

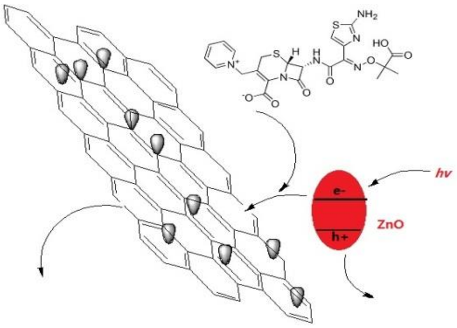

Figure 2: Mechanism of the Treatment of Antibiotic Wastewater by Graphene/ZnO

In terms of adsorption quantity, the Lagergren equation is generally used for the pseudo-first-order kinetic model. The equation assumes that the adsorption process is subject to the diffusion step and is the kinetic equation most widely used for liquid phase adsorption. The model formula is:

$$\frac{\mathrm{d}q_t}{dt} = k_1\left(q_e - q_t\right) \tag{1}$$

Where q_e and q_t are respectively the equilibrium capacity and the adsorption amount at time t (mg.g-1), and k_1 is the pseudo-first-order adsorption rate constant (min-1). Below is the variant of the above formula through the integral shield:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

Based on the above two formulas, the adsorption rate constant and the equilibrium capacity can be obtained respectively via calculation of the straight slope and the intercept of $\log(q_\varepsilon - q_t)$ versus t as well as q_t versus t. And the specific degradation process and the influence of various factors on the chemical reaction rate can be further introduced by analyzing the pseudo-first-order and pseudo-second-order kinetics of the degradation material and comparing those two kinds of dynamic parameters (Wen et al., 2013).
This study on treatment of the antibiotic production wastewater has analyzed the wastewater quality and the main factors influencing its treatment, thus promoting the development of the treatment technology. It is of great significance in meeting the water quality standard to achieve in China the development of the antibiotic wastewater treatment technology at the same time of reducing costs.

2. Preparation of the advanced graphene/ZnO composites

2.1 Test materials and equipment

Test Chemicals: Graphite; Sodium nitrate; Potassium permanganate; Hydrogen peroxide 30%; Hydrate hydrazine 80%; Concentrated hydrochloric acid; Concentrated sulfuric acid; Sodium hydroxide; Ceftazidime standard; Anhydrous ethanol of analytically pure grade.
All those chemicals were purchased on the exploration platform.
Test Equipment: J2200-1 type electronic balance (Beijing Yi Long Technology Co., Ltd.); DF-101S collector-type constant-temperature heating magnetic stirrer (Gongyi City Yuhua Instrument Co., Ltd.); Centrifuges (Shanghai Yi Long Technology Co., Ltd.); UV-5100B UV Spectrophotometer (Shanghai Instrument Co., Ltd.); SHB-3 circulating-water multi-purpose vacuum pump (Jiangsu Jintan Jincheng Guosheng Experimental Instrument Factory); High-pressure hydrothermal reactor & electric blast drying oven (Scientific Instrument Co., Ltd.).

2.2 Test Methods

(1) Synthesis of the graphene
In order to obtain the ideal composite material of high level, the graphene oxide was prepared as its precursor. Firstly, put the concentrated sulfuric acid, flake graphite and potassium permanganate into the polytetrafluoroethylene reactor which were then kept at -2 °C in the refrigerator overnight; Weigh 1.0g graphite and 4.0g potassium permanganate, then put them into the reaction kettle and add 40ml concentrated sulfuric

acid for immediate sealing at -2 °C for 1.5h; Put the reactant into the oven, heating at 100 °C for 1h; After cooling to room temperature, place the reactant into a beaker with the solid being removed; Dilute 500ml purified water into the mixture and maintained strongly; Add hydrogen peroxide 30% drop-wise until the solution became bright yellow; Neutralize the obtained solution with hot hydrochloric acid and purified water, then put it through ultrasonic dispersion for 2 hours and vacuum drying at low temperature, thus obtaining the meat-like graphene oxide solid; Disperse 2.0g graphene oxide solid into 200ml purified water; After 1.5h, add 10ml ammonia drop-wise and stir it for 1h allowing the mixture to mix thoroughly; Then add 6ml water slowly and stir the mixture vigorously for 2 hours; Incubate the mixed system at 95° C and keep the reactant in reflux for 24 h to obtain the black solution (Dias et al., 2014); Filter the filtrate and wash the filter cake, then neutralize the solution with water. Finally the black powdery graphene was obtained by drying the solution at 6 °C for 24h.

(2) Preparation of the graphene composites

Dissolve 0.01g oxidized graphene powder in 10 ml anhydrous ethanol and 20ml distilled water for 30 min; Add 0.1g ZnO powder slowly and stir the mixture magnetically at room temperature for 2h, then put the mixed solution into a 50ml PTFE-lined high-pressure hydrothermal reactor and place it into the oven at 120 °C for 3h; After the incubation, allow the mixture to cool to room temperature, then suction and wash the resulting precipitate several times with ethanol as well as the steamed water, and dry it at 60 °C for 4h. Hence the composite photocatalyst was obtained containing small amount of ZnO.

3. Test results and exploration

3.1 Effect of the pH value on ceftazidime degradation in treatment with graphene/ZnO composites

In order to determinate the effect of the pH value on degradation of the ceftazidime wastewater, 20mg composite catalyst was added into 100ml 20mg/l ceftazidime solution with pH value of 1, 3, 5, 7, 9, 11, 13 respectively (measured solution temperature: 20°C; the initial absorbance: A0 = 0.481), then a magnetic stirrer was used to stir for 30min, and a 300W lamp was used as the light source to conduct the photocatalytic degradation experiment. After 3h, a certain amount of reaction solution was taken for centrifugation before a certain supernatant was collected. Finally, the degradation rate was calculated according to the formula D (degradation rate) = (1 - At / A0) × 100%. The results are shown in Figure 3.

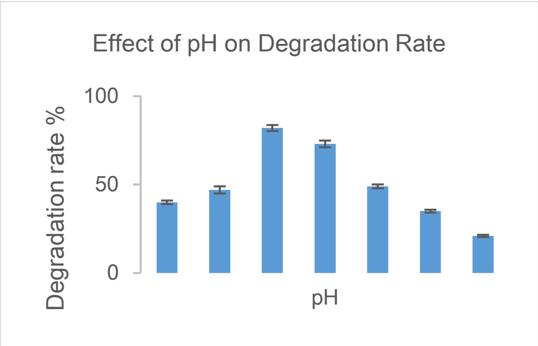

Figure 3: Effect of pH on Degradation Rate

The results show that the degradation rate, subject to the pH value, increases with the pH value. With the pH value of 5, the solution owns the highest degradation rate of 78.8% , so 5 has been selected as the pH value of the degraded ceftazidime solution.

3.2 Impact of the initial concentration on the degradation time and the dynamics analysis

The degradation of the ceftazidime wastewater was studied at three different concentrations of 25, 75 and 100 mg/L respectively and the relationship was explored between the concentration and the degradation time. Figure 4 shows the ability of the composite to degrade the simulated ceftazidime wastewater and the time to reach the degradation equilibrium at the three different concentrations. It can be seen from it that the degradation ability of the composite material increases with the concentration of the ceftazidime wastewater, and that the adsorption capacity of the composite material is much higher at 100mg/l than at 25mg/l, indicating the degradation ability of the composite material is related to the concentration of the simulated ceftazidime wastewater. That is, with constant amount of composite material being input, its active component can react with a certain number of ceftazidime molecules but owns the degradation capacity at different levels. In addition, the degradation equilibrium time also increases with the concentration of the composite material, ranging from 60min at low concentration to 210min at high concentration. This is because the ceftazidime molecules at low concentrations tend to rapidly seize the active components in the composite and interact with them, whereas the density of the ceftazidime molecules increases on the composite at high concentrations, resulting in increased mass transfer resistance in diffusion which makes it difficult to react with the active components, thus extending the time to achieve adsorption equilibrium (Chuang et al., 2015).

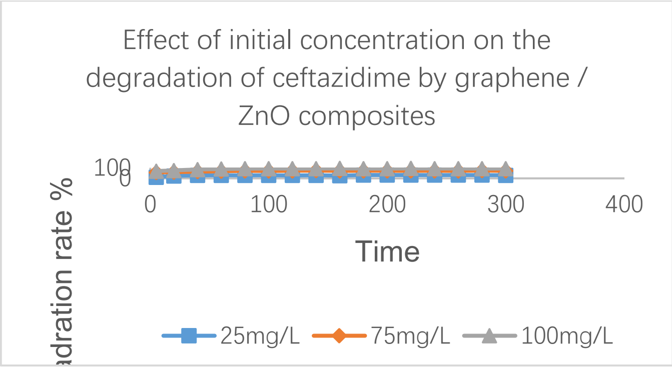

Figure 4: Effect of Initial Concentration on Degradation of Ceftazidime Wastewater by Graphene / ZnO Composites

Meanwhile, the pseudo-first-order and the pseudo-second-order kinetic models were used to further study the degradation mechanism of the cephalosporin. In the pseudo-first-order kinetics, the ceftazidime degradation process is a diffusion controlled one while in the pseudo-second-order kinetic model ceftazidime degradation is a chemically controlled adsorption process. Figure 5 and Table 1 shows the comparison between the fitting curve and parameters of the two kinetic models.

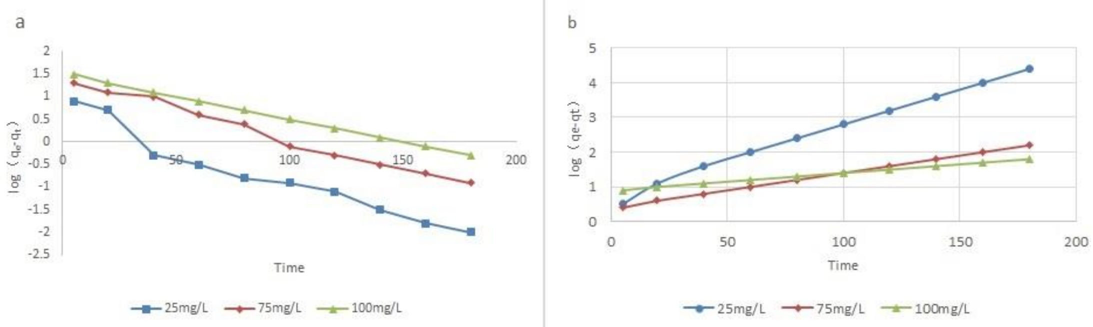

Figure 5: Quasi-first-order Kinetics and Quasi-second-order Kinetics of the Degradation of Ceftazidime by Graphene / ZnO

Table 1: Quasi-first Order Kinetic Model and Quasi-second-order Kinetics Model for the Degradation of Ceftazidime by Graphene/ZnO

Concentration(mg/L)	Quasi - first - order kinetics model			
	$Q_{e.exp}$ (mg/g)	K_1 (min^{-1})	$Q_{e.eal}$ (mg/g)	R^2
25	24.73	0.02391	5.867	0.9450
75	74.91	0.01864	27.25	0.9782
100	99.53	0.01587	34.31	0.9935
Concentration(mg/L)	Quasi - second - order kinetics model			
	$Q_{e.exp}$ (mg/g)	K_1 (min^{-1})	$Q_{e.eal}$ (mg/g)	R^2
25	24.73	0.01418	25.04	0.9999
75	74.91	0.00228	76.89	0.9997
100	99.53	0.00173	101.83	0.9999

It can be known from Figure 5 and Table 1 that the pseudo-second-order kinetic model has a better linear fitting than the pseudo-first-order one at the three initial concentrations, the correlation coefficient of the former being respectively 0.9999, 0.9999 and 0.9999 for 25, 75 and 100 mg/l ceftazidime, and their theoretical adsorption capacities being 25.04, 76.01 and 101.83 mg/g respectively, which is closely connected with the actual measured values. In contrast, the correlation coefficient of the pseudo-first-order kinetics model can reach 94.50, meaning that the theoretic adsorption capacity is far from the actual measured values.

4. Conclusion

The problem of drug residues in water environment has aroused widespread concern both at home and abroad. The drugs or their metabolites not fully absorbed will be drained into the urban or hospital sewage through the urine, fecal excretion or other routes, and can't be fully removed with the existing technology of the sewage treatment plants, probably forming in the water environment the "Pseudo persistent" pollution that threatens the ecological environment and human health. In this paper, nano zinc oxide/graphene composites have been prepared with the graphene oxide and nano zinc oxide as precursors. Then the photocatalytic activity of the composites has been tested under 300W xenon lamp in the simulated ceftazidime antibiotic wastewater. Moreover, this paper studies the effect of the solution pH value on the application of the the graphene/ZnO composites in ceftazidime degradation as well as the effects of the initial wastewater concentration on the degradation time and conducts the kinetic analysis. The results show that the degradation rate of the ceftazidime is subject to the pH value. And at the pH value of 5, the degradation rate is the highest at 78.8%, so 5 has been selected as the pH value of the ceftazidime solution.

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