TiO2-Cu/Ni nanoparticles for photocatalytic reduction of Aminopyrine

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Abstract. In this work, we take the aminopyrine as the model pollutant in order to explore the Cu/Ni ratio effect on the photocatalytic activity of TiO2 nanoparticles. According to some researches, it is the best method to load of 0.1 mol %, the Cu/Ni ratio 1:1, and the photocatalytic activity of TiO2. Under low concentrations of antibiotics, there will be excellent treatment effects.

1. Introduction

Aminopyrine is one of the widely used anti-inflammatory analgesic drugs, which focuses on human healthcare and animals breeding [1]. However, the rate of human body to the antibiotic drug metabolic is low, and most of the drugs' prototypes will be excreted in the urine and stools [2]. In addition, if the antibiotic residues in the environment, it will lead to severe damages to target organs, and do harm to human health, such as having negative impacts on the respiratory function of human body [3].

Recently, the commonly used methods, flocculation, sedimentation, filtration and adsorption of antibiotic wastewater treatment process of amidopyrine drugs are not effective enough, such as removing effect [4]. Nevertheless, Photocatalysis is non-toxic, safe, high efficiency and low energy consumption, It made up for the inadequacy of traditional method and plays an important role in the field of antibiotic wastewater treatment [5.6].

In this report, we will use solvent hot method to load Cu/Ni on the surface of TiO_2. With the model pollutant, we will discuss the TiO_2 load of Cu/Ni alloy in the application of the photocatalytic degradation of amidopyrine pollutants.

2. Experiments

TiO_2-Cu/Ni nanoparticles synthetic drugs are used for the analysis of pure. A typical synthesis methods of TiO_2-Cu/Ni [7]: First, Weigh 160 mg of P25 and disperse it in 25 ml deionized water. Second, add 0.1 ml 0.01 mol/L Cu $(NO_3)_2$ solution and 0.1 ml 0.01 mol/L Ni $(NO_3)_2$ solution in it. Third, after stirring for 1 hour at room temperature, add 0.4 ml 0.05 mol/L hydrazine hydrate solution. Fourth, continue stirring after 10 minus, and use 0.01 mol/L NaOH solution to adjust the above precursor solution pH = 10. Sixth, stir again after 10 minutes, and move the precursor solution into 50 ml in the high-pressure reaction kettle with ptfe lining. Under 150 °C constant temperature solvent, the solution should be dictated for 3 hours. After reaction, natural cooling to room temperature, and collect the white precipitate. Then centrifugal cleaning with deionized water and ethanol for 3 times. Finally, the obtained solid 45 °C vacuum dry for 12 hours. By finishing these steps, the TiO_2 nanoparticles that load 0.1 mol% Cu/Ni (1:1) is prepared.

Photocatalytic reaction was carried out in a sealed quartz reactor (50 mL) at room temperature. Firstly, put a certain concentration of amidopyrine solution into the quartz tube reactor, and add a certain quality of TiO_2. Before the illumination, avoid light stiring 40 minus at room temperature. Secondly, use a condensed water jacket of 500W mercury lamp as light source to photocatalytic degradation reactions. Light source and reactor center distance should be 10 cm with a light filter to remove more than 400 nm wavelength light. Finally, remove solid catalyst by using 0.25 μm membrane filter, and measure it with the UV-vis spectrophotometer.

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3. Results and Discussion

3.1 Characterization of catalysts

According to Figure 1, there is no obvious change by comparing the samples of the XRD diffraction peak and the diffraction peak of P25[8]. It illustrates that the TiO_2 crystal structure did not change. The load of metal Cu and Ni was not into the lattice of TiO_2. However, there is no diffraction peak of Cu and Ni. In my opinion, it may be the load of Cu and Ni is too low, and load on the surface of the metal particle size is too small, which will lead to the ambiguilty.

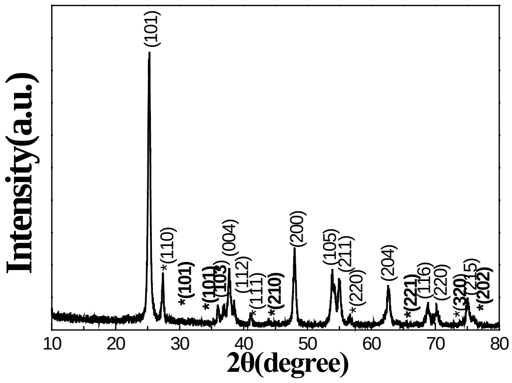

Fig. 1 X-ray diffraction diagram of TiO2-0.1 mol% Cu/Ni (1:1) nanoparticles

Figure 2 shows the EDX analysis of TiO_2-0.1% Cu/Ni (1:1). From figure 2, copper, nickel, titanium and oxygen are observed in the sample. Besides, the atomic ratio of Cu/Ni is about 1:1. This further indicated that copper and nickel were loaded on surfaces of TiO_2 nanoparticles. What's more, from figure 2, Cu and Ni loaded on TiO_2 nanoparticles are found to be alloy which is in accordance with literature report[7].

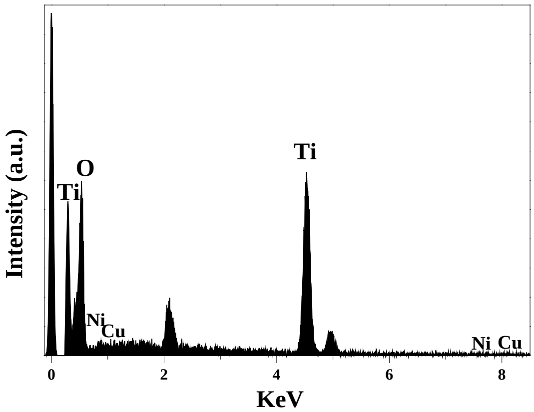

Fig. 2 TiO2-0.1% Cu/Ni (1:1) EDX analysis element

3.2 TiO2-Cu/Ni photocatalytic activity

Figure 3 points the amidopyrine photodegradation kinetics curve on the TiO_2-0.1% Cu/Ni (1:1) under UV irradiation. According to figure 3, under the effect of TiO_2-0.1% Cu/Ni (1:1) catalyst, amidopyrine between 0 to 4 minus photocatalytic degradation speed is very fast. As the reaction to continue, amidopyrine photocatalytic degradation reaction speed is slow down in some extent. After 12 minus' illumination, photocatalytic reaction basic reaches a balance, at this point, the degradation of amidopyrine rate is about 99%. While the use of pure P25 as a photocatalyst, the degradation of amidopyrine rate is only 60% under the same condition. Thus, it can be seen that after loading the Cu/Ni alloy, the photocatalytic activity of TiO_2 nanoparticles is be significantly improved.

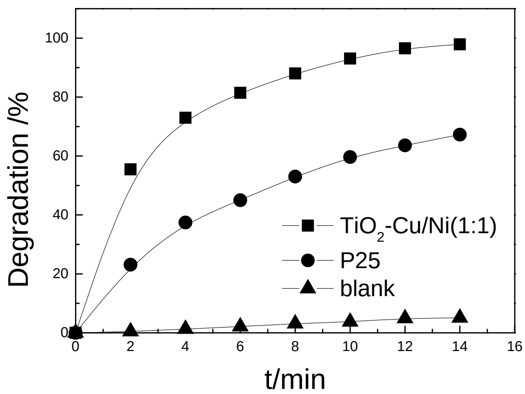

Fig. 3 Amidopyrine photodegradation kinetics curves (Dosage of photocatalysts: 1 g/L, Amidopyrine concentration 5×10-5 mol/L)

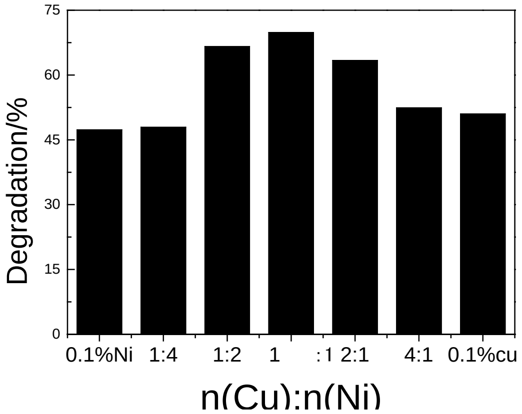

Fig. 4 The proportion of load cocatalyst Cu, Ni impact on the photocatalytic activity of TiO2-Cu/Ni, (Dosage of photocatalysts: 1 g/L, Aminopyrine concentration: 5×10-5 mol/L, irradiation time: 4 min)

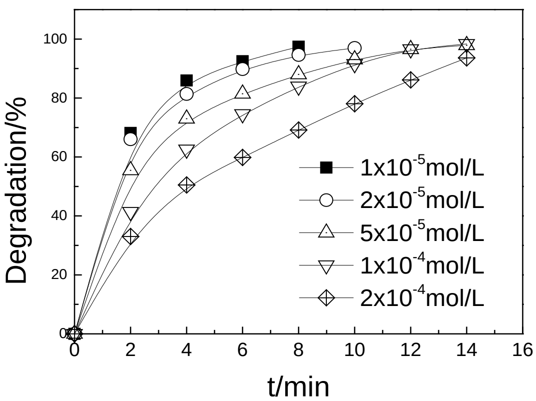

Fig. 5 Amidopyrine the influence of initial concentration of photocatalytic degradation efficiency (Dosage of photocatalysts: 1 g/L)

3.3 The influence of Cu/Ni mole ratio

Figure 4 shows the proportion of load cocatalyst Cu, Ni impact on the photocatalytic activity of TiO_2-Cu/Ni. Experimental results show that after the introduction of Cu/Ni alloy, the photocatalytic activity of t TiO_2 has been significantly improved. In addition, the effects of its catalytic activity is better than single load Cu, Ni's. Moreover, Cu/Ni mole ratio is 1:1, TiO_2-Cu/Ni has the highest photocatalytic activity. It is detrimental to enhance the photocatalytic activity of TiO_2 nanoparticles, if the Cu/Ni mole ratio is too high or too low. The main reason is when the Cu/Ni mole ratio of 1:1, the schottky barrier of the height is advantageous for the separation of the electronic-hole between the metal and titanium dioxide produced [9].

3.4 The influence of the initial concentration of the amidopyrine

The concentration of the antibiotics generally is low in the water, and the treatment on low concentration wastewater is a technical difficulty. The traditional treatment methods have few influences on it. The Fig 5 have shown that above, TiO_2-Cu/Ni for low concentration of antibiotic wastewater has an efficient treatment impacts. Owing to this, we believe that it has a great application potential for treatment the trace antibiotics pollution from water in the future.

4. Summary

Antibiotics is very stable in the water, residual antibiotics in the environment do great harm to ecological environment and human health. Using TiO_2-Cu/Ni photocatalytic oxidation to removal the antibiotic pollutant from water has been reached to good effect. Its preparation method has some characteristics, such as simple, cheap material, and high catalytic activity. However, in the aspect of catalyst recycling and the high concentration, wastewater's treatment remains to be improved. Therefore, it is likely to build a new pollution treatment method by combining with other technologies.

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