Preparation of Catalyst by Phosphating Slag and Its Photocatalytic Performance on Rhodamine B and Methyl Orange

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Abstract. The catalysts are synthesised by hydrothermal reaction of ball-milled phosphating slag with ammonia, ethanol, and oxalic acid respectively. The catalysts are characterized by XRD, SEM and UV-Vis absorption spectra. We studied the photocatalytic degradation efficiency of different catalysts and the amount of catalysts on the organic dye rhodamine B and methyl orange. The results shows that the catalyst prepared by the hydrothermal reaction of 1 mol/L oxalic acid with phosphating slag has a microporous structure after being modified by high temperature, the degradation efficiency of rhodamine B and methyl orange which are carried out for 120 min under the irradiation of 100 w mercury lamp can reach 78% and 81%, and the optimal amount of catalyst is 0.5 g/L. This study provides a new solution for the utilization of phosphating slag.

1. Introduction
Phosphating is a common surface treatment technology and is widely used in the casting and spraying industries [1]. During the phosphating process, a large amount of by-products are generated, its main components are FePO4 and Zn3(PO4)2, and there are some trace heavy metal elements such as Mn, Ni and Cr[2]. Phosphating slag is a kind of hazardous solid waste, but it is also a resource that can be used, phosphating slag contains a large amount of phosphate, iron and zinc, etc, to extract these useful substances from phosphating slag has a wide range of application prospects [3, 4]. At present, there have been many related studies on the utilization of phosphating slag. Fan used iron phosphate slag to prepare iron oxide red paint, which can be used in construction and chemical industry [5]. Ma used iron and calcium in the phosphating slag to prepare iron oxide and tricalcium phosphate [6]. But few studies have been published on the use of phosphating slag for the preparation of photocatalysts. This paper mainly studied on the waste phosphating slag to prepare high-performance photocatalyst through hydrothermal reaction, and studied its photocatalytic degradation ability for rhodamine B and methyl orange under ultraviolet irradiation[7,8].
2. Experimental Procedures

2.1. Ball Grinding Experiment
20 g phosphating slag and 20 mL anhydrous ethanol were added into the utensils, then 10 g, 30 g, 50 g, 70 g, 100 g, 120 g, 150 g and 180 g balls were used respectively, the phosphating slag was milled at 500 r/min for 5 hours \cite{9}, the milled-phosphating slag was mixed with ethanol and water to prepare ferric hydroxy phosphate at 200°C for 8 hours.

2.2. Preparation Of Catalysts
The milled-phosphating slag was mixed with the ammonia, anhydrous ethanol and oxalic acid respectively in the mass ratio of 1:1 to carry out hydrothermal reaction at 200 °C for 8 hours. The resulting sample were filtered, washed and dried at 100 °C, then the dried sample were baked in the nitrogen atmosphere to obtain a series of photocatalysts.

2.3. Photocatalytic Experiment
200 mL of 10 mg/L rhodamine B solution and 100 mg catalyst were added into a quartz tube, then the mixture was stirred for 30 min in the dark room to achieve adsorption equilibrium. Then turned on the power of the photochemical reactor and started the reaction under the irradiation of a 100 W mercury lamp. Took a sample every 10 minutes, the sample was centrifuged and the supernatant liquid was placed in a cuvette, and then measured the absorbance at λ=554 nm with a ultraviolet-visible spectrophotometer. Calculating the concentration of rhodamine B at different time based on the relationship between the concentration and absorbance of rhodamine B, according to the formula D = [(C0-Ct)/C0] ×100%, the degradation rate of rhodamine B was obtained, the D is the degradation rate, C0 is the initial concentration of rhodamine B and Ct is the concentration of rhodamine B at different time.

3. Results and Discussion

3.1. Ball Grinding Effect of Different Quality Balls
The particle size of phosphating slag and ferric hydroxy phosphate reached to the minimal which are 1.6 um and 2.9 um when the mass of ball is 120 g. The particle size of the sample is measured by the Malvern 2000 particle size tester, which is the average particle size and it is a statistical value. As the mass of the ball increases, the phosphating slag is more fully grinded, but when the mass of the ball exceeds a certain limit, the excess ball can’t be fully rotated, so the optimum amount of the ball is 120 g.

![Figure 1. The particle size of phosphating slag and ferric hydroxy phosphate prepared by different ball milling ratios](image-url)
3.2. XRD Characterization of Catalyst Materials

Figure 2 shows the XRD pattern of catalysts prepared by hydrothermal reaction between ball-milled phosphating slag and different solvents. Comparing the diffraction peaks of the samples with iron phosphate, iron oxide and iron hydroxy phosphate standard cards, it can be seen that the main product of hydrothermal reaction between phosphating slag and ammonia water is iron phosphate, the main product of reaction between phosphating slag with ethanol and water is iron hydroxy phosphate, the main product of hydrothermal reaction between phosphating slag with 0.5 mol/L, 1 mol/L and 3 mol/L oxalic acid are iron hydroxy phosphate, the main product of hydrothermal reaction between phosphating slag with 5 mol/L oxalic acid are iron oxide.

![XRD patterns of different catalysts synthesized with different solutions](image)

**Figure 2.** XRD patterns of different catalysts synthesized with different solutions

3.3. SEM Characterization of Catalyst Materials

Figure 3 shows the catalyst prepared by the ball-milled phosphating slag and different solvents. (a) and (b) are prepared by ammonia, ethanol and water with phosphating slag respectively, the particle size are approximately 1 um and the surface are relatively smooth. (c), (d), (e) and (f) are prepared by different concentrations of oxalic acid and phosphating slag, the particle size are approximately 5 um. The surface are rough which has complex pore structure, and the adsorption properties is superior.

![SEM images of different catalysts synthesized with different solutions](image)

**Figure 3.** SEM images of different catalysts synthesized with different solutions, (a)Ammonia (b)Ethanol and water (c)0.5 mol/L Oxalic acid (d)1 mol/L Oxalic acid (e)3 mol/L Oxalic acid (f)5 mol/L Oxalic acid
3.4. UV-Vis Spectroscopy

Figure 4 shows the UV-vis absorption spectra of catalysts prepared by hydrothermal reaction of different solvents and phosphating slags. Phosphating slag has a good absorption effect in the ultraviolet region, after the hydrothermal reaction with ammonia, the wavelength of ultraviolet absorption has undergone a red shift. After the hydrothermal reaction with water and ethanol, the wavelength of ultraviolet absorption shifts red more, but the absorbance in the ultraviolet range decreases. After hydrothermal reaction with oxalic acid, the catalyst has a better absorption effect in the visible light region, but the absorbance in the ultraviolet region has decreased.

![Figure 4. UV-Vis spectra of different catalysts synthesized with different solutions](image)

3.5. Study on Photocatalytic Performance Of Catalysts

Fig. 5 shows the degradation rate of rhodamine B at different time, the degradation rate of rhodamine B is 37% which is under the irradiation of 100 W mercury lamp without catalyst. After adding different catalysts, the degradation rate of rhodamine B is significantly increased, and the catalytic effect of 1 mol/L oxalic acid is the best which reaches 78%. The specific mechanism of photocatalytic degradation of dyes is that under the irradiation of the mercury lamp, the electrons in the catalyst are excited to undergo a transition, thereby generating e⁻ and h⁺, e⁻ can be captured by dissolved oxygen and generate O₂⁻, the protonation of O₂⁻ in the acidic medium produces ·OH, ·OH has strong oxidizing ability and can fully mineralize organic dyes [10, 11]. The speed of photocatalytic degradation of dyes is also related to the adsorption performance of the catalyst [12]. The better the adsorption performance, the faster the photocatalytic degradation[13]. The catalyst prepared by hydrothermal reaction of phosphating slag and 1 mol/L oxalic acid has a rough surface, microporous structure and good adsorption performance, and its photocatalytic degradation rate is relatively good.
Figure 5. Degradation rate of rhodamine B at different time by different catalysts synthesized with different solutions

Figure 6 shows the degradation rate of rhodamine B and methyl orange at different time with the catalyst prepared by hydrothermal reaction of ball-milled phosphating slag and 1 mol/L oxalic acid, the catalyst is modified by high-temperature nitrogen gas. It can be seen from the figure that the catalyst has a good degradation effect on both rhodamine B and methyl orange, and the degradation effect on methyl orange is better than rhodamine B. Compared with the t-test of the degradation effect data, the value is greater than 0.05, so there is no significant difference in the degradation effect of the catalyst on the two dyes, but the degradation effect shows that the catalyst has better selectivity for methyl orange.

Figure 6. Effect of catalyst on the degradation rate of rhodamine B and methyl orange

Figure 7. Effect of catalyst amount on the degradation rate of rhodamine B and methyl orange

Figure 7 shows the effect of the amount of catalyst prepared by hydrothermal preparation of 1 mol/L oxalic acid and phosphating slag on the degradation rate of rhodamine B and methyl orange. It can be clearly seen from the figure that the degradation rates of rhodamine B and methyl orange are
increasing with the increase of the amount of catalyst. When the amount of catalyst is 0.5 g/L, the degradation rate of both dyes reaches the maximum. As the amount of catalyst continues to increase, the degradation rates of both rhodamine B and methyl orange have declined. This is due to the fact that when the amount of catalyst is small, the active sites provided by the catalyst are less, the dye molecules cannot fully contact with the catalyst, the photocatalytic degradation effect is poor. With the increase of the amount of catalyst, the active sites provided by the catalyst increase, the dye molecules can fully contact with the catalyst, the light source is fully utilized, and the photocatalytic degradation effect is significantly increased. However, when the amount of catalyst increases to a certain extent, the excess catalyst will shield the light source and cause light scattering, which will affect the photocatalytic effect and reduce the catalytic degradation rate of the dye.

4. Conclusion
In this study, catalysts are prepared by hydrothermal reaction of ball-milled phosphating slag with different solvents and modified by high-temperature nitrogen calcination. The catalyst prepared by 1 mol/L oxalic acid solvent and ball-milled phosphating slag has a microporous structure, which has good absorption effect of ultraviolet and visible light. Under the irradiation of 100 w mercury lamp, the degradation rate of rhodamine B reaches to the maximum, then based on the catalyst, we studied the degradation rate of methyl orange and rhodamine B and the effect of catalyst amount on degradation rate, the experimental results show that when the amount of catalyst is 0.5 g/L, the degradation rate of rhodamine B and methyl orange reach 78% and 81%. The catalyst has low preparation cost and the surface morphology of the catalyst can be regulated by controlling the concentration of oxalic acid, so that it has excellent adsorption performance. The catalyst can not only be applied to the field of photocatalysis, but also has bright application prospect in adsorption, carrier and targeted drugs [14, 15]. This study provides a new solution for the utilization of phosphate slag.

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