Application of F⁻ modified Fe-SAPO-34 as a New Photocatalyst in Printing and Dyeing Wastewater Treatment

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Abstract. The development of new photocatalysts with a wide range of applications is one of the important challenges in the field of photocatalysis research. In this thesis, ferric phosphate was used as a transition metal salt, and HF was used as a mineralizer to prepare Fe-SAPO-34 photocatalyst, which was applied to the degradation of organic dye wastewater. The materials were characterized by XRD, SEM and other characterization methods. After the photocatalyst is supported on the molecular sieve, it usually exhibits excellent performance in catalyzing the degradation of different dyes, and generally higher than the catalytic efficiency of the unmodified catalyst under the same conditions.

1. Introduction
With the rapid development of industry, the problem of water pollution has become more and more serious in recent years. Traditional technologies of sewage treatment, such as adsorption and coagulation, are costly and easily cause secondary pollution. Nowadays, one of the most promising processing technologies is the photo-Fenton oxidation technology[1], which utilizes transition metals like iron, manganese, etc. as a catalyst, hydrogen peroxide as an oxidant, and strong oxidizing under ultraviolet or visible light. It produces strong oxidizing hydroxyl radicals under ultraviolet or visible light, which can completely oxidize the dye molecules to water and carbon dioxide. It has the characteristics of high processing efficiency, low cost and no secondary pollution[2]. However, its ability to use solar energy is not strong, and only ultraviolet light of λ < 300 nm can be utilized, and most of the visible light area in solar energy is not fully utilized. The porous structure of the molecular sieve gives it a large specific surface area, and this characteristic also makes it an ideal molecular sieve carrier. The contact area between the contaminant and the molecular sieve can be effectively increased if the photocatalyst can be supported on it. Moreover, it can effectively solve the problem of the decrease in the intensity of the optical radiation caused by the suspension of the photocatalyst, thereby improving the catalytic efficiency.

This thesis mainly deals with the preparation of molecular sieve supported photocatalyst and its application in the treatment of printing and dyeing wastewater. Iron-based catalysts have a wide range of applications in the field of photocatalysis[3-5]. The phosphating slag is rich in iron salts. The synthesis of Fe-SAPO-34 molecular sieve catalyst with iron salt in phosphating slag has strong research value for photocatalytic degradation of dye wastewater. In this study, Fe-SAPO-34 was synthesized by
hydrothermal synthesis using iron phosphate as a metal source and HF as a mineralizer. The photocatalytic performance under UV light was studied by degrading rhodamine B.

2. Materials and Methods

2.1. Preparation of Samples
The hydrothermal method was used to synthesize Fe-SAPO-34 molecular sieve. The HF, silicon source, phosphorus source, aluminum source, FePO₄ and appropriate amount of water were mixed uniformly in a certain proportion, then the template reagent diethylamine was added, mixed uniformly and transferred to the reaction kettle. After sealing, it was heated to 180°C, washed and dried to obtain a molecular sieve sample.

2.2. Medicine and Characterization
The morphology of the samples was studied by scanning electron microscopy (SEM) (HITACHI-S4800, Hitachi Corporation, Japan) with the accelerating voltage at 10 kV and current at 10 mA. X-ray diffraction (XRD) (D8-Advance, Bruker Corporation, Germany) measurements were performed to record the phase composition and crystalline structure of the powder samples, operating at 40 kV and 40 mA with a monochromatized Cu/Kα radiation (λ = 0.15418 nm) source. Phosphate residue was supplied by an auto components company in Zhejiang, China, hydrofluoric acid (HF, ≥40%). Other chemicals used in the present work were of analytical grade and used without further purification.

2.3. Photocatalytic Experiment
In this experiment, 50mg/L rhodamine B was used to simulate dye wastewater, 10mmol/L hydrogen peroxide was used as an oxidizing agent. After adding 0.5 g/L of the catalyst, a 500W mercury lamp was used to simulate ultraviolet light. After adding rhodamine B solution and a certain amount of catalyst and H₂O₂ to the reaction vessel, the reaction vessel was placed in a photocatalytic reactor (XPA-7, Xujiang Power Plant, China) to start photocatalytic reaction. Samples were taken every 20 minutes. The sample was filtered through a 0.45 um filter needle, and its absorbance at the maximum absorption wavelength λ = 544 nm was measured by an ultraviolet-visible spectrophotometer (UV-752, Shanghai Yoke Instrument. Co., Ltd., China)[6-8]. The concentration of rhodamine B at different times was calculated according to Lambert Beer's law. The reaction conforms to the first-order degradation kinetics model, and the reaction rate constant K=In(C₀/Cₜ). Where C₀ is the initial concentration of rhodamine B and Ct is the concentration of rhodamine B solution at different times. The reaction time T is plotted on the abscissa and the reaction rate constant K is plotted on the ordinate. Then a straight line is fitted, and the slope K of the straight line is the degradation rate of rhodamine B in different systems.

3. Results and Discussions
The XRD diffraction angular position and intensity are used to identify the phase composition of the unknown sample. Fig.1 shows five peaks at 9.48°, 16.2°, 20.7°, 25° and 31°, corresponding to (101), (211), (104), (401) of SAPO-34 (JCPDS) respectively[9]. The diffraction intensity of Fe-SAPO-34(I) is lower than that of the Fe-SAPO-34(II) sample treated with HF. Except for the addition of HF, the molar ratio of the other components was the same as that of Fe-SAPO-34(I). As a result, the presence of surface HF can significantly promote the growth and dispersion of molecular sieve crystallites on the surface of the support, and improve the structural regularity of the molecular sieve grains[10]. A large number of literatures have shown that the relative crystallinity of Fe-SAPO-34 molecular sieve can be significantly improved under the F ion system, and it also has a certain influence on the introduction of its component Fe.
Figure 1. XRD pattern of SAPO-34, Fe-SAPO-34(I) and Fe-SAPO-34(II)

It can be seen from the Fig.2 that the morphology of Fe-SAPO-34(I) and Fe-SAPO-34(II) molecular sieves are all cubic. Fe-SAPO-34(I) has an average particle size of about 5 microns. The Fe-SAPO-34(II) synthesized by the addition of HF has a particle size of about 1 um. Therefore, the SAPO-34 molecular sieve synthesized by using HF as a mineralizer not only has a regular shape, but also synthesizes SAPO-34 with a small grain size[11].

Figure 2. SEM image of Fe-SAPO-34(I) and Fe-SAPO-34(II)

The photocatalytic performance of the catalyst in different systems was investigated by using rhodamine B simulated dye wastewater and 500W mercury lamp to simulate ultraviolet light. In the UV system, the degradation efficiency of rhodamine B was 7.4% after 20 minutes of mercury lamp irradiation, indicating that UV light can promote the degradation of rhodamine B[12-13]. In the UV/H₂O₂ system (10.2%), H₂O₂ decomposed under ultraviolet light to produce a strong oxidizing hydroxyl radical (E°(·OH/H₂O₂) = 1.9-2.7 V), which can effectively degrade dye molecules. When Fe-SAPO-34(II) was used together with H₂O₂, the degradation efficiency of rhodamine B increased to 30.2%. This indicated that Fe-SAPO-34(II) molecular sieve can catalyze the decomposition of hydrogen peroxide to produce hydroxyl radicals, thereby improving the degradation efficiency of dye molecules. The catalyst captures photons through the surface, which in turn produces photogenerated electrons and holes[14]. The photocatalytic activity of the catalyst is increased, so the degradation rate of rhodamine B is increased. In order to compare the degradation effects of the catalysts, the same quality of Fe-SAPO-34(I) and the modified catalyst Fe-SAPO-34(II) were added to the reaction system under the same conditions. The modified catalyst can completely degrade the dye molecules within 60 min, and its degradation effect is better than that of the unmodified catalyst. Because Fe-SAPO-34(II) has a more complete crystal form and a larger specific surface area, it can effectively capture dye molecules, which has more excellent catalytic degradation performance than Fe-SAPO-34(I). In addition, the kinetics of
the degradation reaction of rhodamine B, which Fe-SAPO-34 molecular sieve catalyst, was also studied. It was found that the reaction was pseudo-first order reaction model, in line with LH kinetic model. In order to quantitatively analyze the degradation effect of Fe-SAPO-34 under ultraviolet light, the degradation rate constant K was fitted.

Figure 3. Degradation rate of rhodamine B at different system

Figure 4. Kinetic equations under different systems

Figure 5. Effects of H₂O₂ dosage on the catalytic degradation of rhodamine B
Furthermore, in order to study the relationship between the reaction conditions and the catalytic degradation effect, the effect of the dosage of $\text{H}_2\text{O}_2$ on the degradation effect was investigated, as shown in Fig. 5. It illustrated the effect of the amount of hydrogen peroxide added on the degradation rate of rhodamine B. Under the catalysis of a sufficient amount of catalyst, as the amount of hydrogen peroxide added increases, the amount of hydroxyl radicals generated increases as well. However, when the amount of hydrogen peroxide added exceeds 12 mmol/L, due to insufficient active sites provided by the catalyst, the system had a considerable amount of hydrogen peroxide which is not reacted with the catalyst exists. This has a certain quenching effect on the hydroxyl radicals that have been produced[15], so the degradation rate of rhodamine B will decrease.

4. Summary and Conclusion
In summary, Fe-SAPO-34 molecular sieves were prepared by using iron phosphate as a transition metal. And HF was used as a mineralizer. The research shows that in the synthesis of molecular sieves, HF can not only play a role in mineralization, but also function as a template to stabilize the molecular sieve structure. After the F$^-$ is added to the initial gel, the synthesized molecular sieve has a higher crystallinity and a smaller average particle diameter. In this paper, the prepared catalyst is used to degrade rhodamine B dye molecules in a heterogeneous Fenton system. As a result, the surface-modified Fe-SAPO-34 catalyst exhibited excellent catalytic activity under ultraviolet light.

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