Photocatalytic degradation of oily wastewater by ZrO$_2$(Er$^{3+}$)/TiO$_2$ composite photocatalyst

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Abstract. Photocatalyst/polypropylene ball which can float on the water is prepared through coupling agent method, and the photocatalyst is the ZrO$_2$(Er$^{3+}$)/TiO$_2$ which is fabricated by co-precipitation. The diesel and crude oil degrading experiments are made with the floating photocatalyst and powder photocatalyst. After 8 hours illuminating in visible light, the removal rate of diesel in float experiment can reach 98%, however the rate in ZrO$_2$(Er$^{3+}$)/TiO$_2$ powder experiment is 68%. The removal rate of crude oil in float experiment is more than 96%, which is much higher than the removal rate of 39% of crude oil in ZrO$_2$(Er$^{3+}$)/TiO$_2$ powder experiment.

1. Introduction
In today's society, rapid economic development requires a large amount of energy to support. Oil as a traditional fossil fuel demand is also increasing year by year [1,2]. An important sign of rapid economic development is the exploitation and utilization of oil [3]. Of course, the process of oil extraction and utilization is accompanied by certain oil pollution. At present, the three methods of physical method, chemical method and biological method are the basic methods for treating oily pollution in wastewater [4]. The physical method is to absorb and recover petroleum by using oil-absorbent materials. The chemical method is to add emulsifiers, oil coagulants, oil collectors, settling agents to the water, or to treat oil pollution through combustion. Biological method refers to the process of biocatalytic degradation of petroleum pollutants in the wastewater to reduce or eliminate petroleum pollutants in water [5]. Very little oil pollution on the surface of water bodies is difficult to clean up by common treatment methods. Therefore, the ideal treatment method is to use solar energy and photocatalytic methods to degrade marine oil pollution and treat a small amount of oil pollution on the water surface. As a photocatalyst, semiconductor TiO$_2$ has been favored by many scholars in the treatment of environmental pollution [6]. TiO$_2$ can use sunlight as a light source for photocatalytic reaction with pollutants, which can degrade pollutants into small molecules of non-toxic substances, avoiding secondary pollution of the environment [7]. Cui et al. used TiO$_2$ powder to treat n-octane, dodecane, tetradecane, hexadecane and 0# diesel in the photocatalytic degradation experiment, and concluded that the photocatalysis effect of aliphatic hydrocarbon Eventually degrades into CO$_2$ [8]. In order to study the photocatalytic degradation of oil-polluted wastewater by photocatalysts, Joanna Grzechulska and others prepared pure TiO$_2$ and modified TiO$_2$. Comparison of the photocatalytic degradation of oil-polluted wastewater by pure TiO$_2$ and modified TiO$_2$ shows that the higher removal rate of oily wastewater is modified TiO$_2$. Past studies on photocatalytic degradation of marine petroleum pollution have found that photocatalytic degradation of petroleum pollution is still insufficient in practical applications [9-10]. We should pay attention to
the following points: (1) To treat oil pollution in water, the mixture required to be treated is more complicated. It is necessary to study the photocatalytic degradation of petroleum and the intermediate products produced in the degradation process. Only by understanding the degradation mechanism can it be better applied and prevent the catalytic process. The generation of secondary pollution. (2) It is necessary to prepare a photocatalyst with high oil pollution treatment efficiency and no secondary pollution by studying the influencing factors of the composite photocatalyst. (3) Applied in reality through experimental research, the catalyst is loaded on a certain carrier to degrade petroleum and the photocatalyst is recovered.

2. Experimental section

2.1. Synthesis of the ZrO2(Er3+)/TiO2-30%

In this paper, the ZrO2(Er3+)/TiO2 composite photocatalyst with a doping ratio of 30% prepared by the co-precipitation method is bonded to a polypropylene polyhedral sphere with a diameter of 40 mm using the coupling agent method. The production method refers to Xu Gaotian, Zhao Jun, The production method of Dongdong and others. The details are as follows: the ZrO2(Er3+)/TiO2 composite photocatalyst powder prepared by the co-precipitation method with a doping ratio of 30% is placed in water and dispersed by ultrasonic to make it uniformly mixed to form liquid A; the polypropylene polyhedral ball is ultrasonicated After cleaning, immerse it in butyl titanate coupling agent and stir slowly for 5 minutes, then take it out and put it in liquid A, and continue to stir it for 5 minutes, then take it out and put it in an oven, and dry it at 80 ℃ 2 h completes the load.

3. Results and discussion

3.1. XRD analysis

It can be clearly seen from Figure 1 that there are obvious peaks at 2θ of 25.3°, 36.9°, 36.269°, 37.7°, 48.0°, 54.1°, 55.1° and 62.7°. The particle size of the photocatalyst can be determined by the Scherrer formula. Seeking, the average size is: (a) 16.15 nm; (b) 24.65 nm; (c) 48.50 nm; (d) 13.45 nm; (e) 48.48 nm and (f) 13.60 nm, which is the same as the TiO2 in the JCPDS card Therefore, the TiO2 in the prepared ZrO2(Er3+)/TiO2 powder belongs to anatase, and its lattice constants a, b and c are 3.7848, 3.7848 and 9.5124 Å, respectively, which is very similar to the XRD pattern of TiO2 similar. In the detection of each peak in the figure below, no obvious diffraction peak of (Er3+) was found, which may be caused by the low content of (Er3+). There are no significant peaks at 2θ of 28.2° and 30.2°. As the doping amount of ZrO2 (Er3+) increases, the intensity of these two peaks also increases. This may be because the peaks here are all composed of ZrO2(Er3+). And this peak is due to ZrO2(Er3+) doping. In addition, compared with the standard card of ZrO2, it can be inferred that this peak may be caused by the generation of the ZrO2 card number (00-007-0343). Compared with the standard card, it can be seen that ZrO2 is mainly monoclinic zirconia (2θ = 28.2°, 30.2°), corresponding to the monoclinic system. According to the (111) diffraction peak, the ZrO2 grain size is about 37.86 nm, so it can be considered that the composite photocatalyst is a mixture of the upconversion material ZrO2 (Er3+) and TiO2 photocatalyst.
3.2. SEM analysis

It can be seen from Figure 2 that the crystallinity of the photocatalyst is better, showing a cubic structure, which is consistent with the anatase mentioned in XRD. The particle size is mostly between 10-50nm. At the same time, it can be seen that the dispersion of the sample is better. The ZrO2 (Er3+) upconversion material particles and TiO2 particles are evenly distributed, and they are not covered with each other. This structure is conducive to the absorption of visible light by the ZrO2 (Er3+) upconversion material, and the ultraviolet light emitted by it will also better transfer to TiO2 particles, so as to achieve the purpose of degrading macromolecular pollutants.
As shown in Figure 3, A are all polygonal spheres without loading, and B are polypropylene polygonal spheres loaded with composite photocatalyst. It can be seen from the figure that the supported polygonal spheres are light yellow. Experiments have shown that the ZrO$_2$(Er$^{3+}$)/TiO$_2$ composite photocatalyst supported on the polypropylene polygonal spheres is relatively strong and not easy to fall off in wastewater.

3.3. Photocatalytic degradation

Under the experimental conditions, 50 mL of wastewater was simulated pollution with diesel oil with initial concentrations of 0.2, 0.4, 0.6, and 0.8 g/L, and a load of 30 % ZrO$_2$(Er$^{3+}$)/TiO$_2$ photocatalyst was carried out. The spheres are placed as a photocatalyst in wastewater that simulates diesel pollution, and the pellets are taken out after 2.0, 4.0, and 8.0 hours of reaction under visible light irradiation. The diesel in the reactor is extracted with n-hexane and the remaining amount is calculated, using the standard curve of diesel. Calculate the total degradation rate of the photocatalyst to diesel, then extract the photocatalyst-loaded pellets with n-hexane, calculate the amount of diesel adsorbed on the pellets, and finally calculate the amount of diesel degraded by the photocatalyst. The effect of the photocatalyst-loaded pellets in degrading diesel oil is divided into two types: photocatalyst degradation and adsorption. The degradation effect is shown in Figure 4. The hollow column represents the efficiency of the composite photocatalyst to degrade diesel fuel, and the mesh column represents the total degradation rate of the diesel fuel by the supported pellets. As shown in Figure 4, after 2.0 hours of visible light, the photocatalyst-loaded pellets with a lower initial diesel concentration have a good degradation effect on diesel, and it is beneficial for the pellets surface to support 30 % ZrO$_2$(Er$^{3+}$)/TiO$_2$ photocatalyst photocatalytic degradation of diesel. When the initial concentration of diesel is 0.2 g/L and 0.4 g/L, the ZrO$_2$(Er$^{3+}$)/TiO$_2$ photocatalyst with 30% doping ratio of polypropylene polygonal ball has the best photocatalytic degradation efficiency for diesel. The removal rate is about 50 %. As the diesel fuel concentration increases, the photocatalytic effect of the catalyst also tends to decrease.

It can be seen from Figure 4 that after 4.0 hours of reaction, the efficiency of photocatalytic degradation increases with the increase of diesel fuel concentration. When the best effect is reached, it
shows a downward trend. From Figure 4 it can be seen from the comparison that with the increase of the light time, the degradation rate of the diesel oil by the ZrO2(Er3+)/TiO2 photocatalyst with a doping ratio of 30% on the polypropylene polygonal ball is also increased. Under the condition of the same diesel fuel concentration, the light time increased by 2 hours, and the photocatalytic degradation efficiency also increased by about 10%. When the initial concentration of diesel oil is 0.4 g/L, the highest photocatalytic degradation rate also reaches 61.9%. It can be seen from Figure 4 that after 8.0 hours of reaction, the total removal rate of diesel does not change much, but with the increase of light time, under the same diesel concentration, the loading ratio of polypropylene polygonal ball The 30 % ZrO2(Er3+)/TiO2 photocatalyst has an increase in the degradation rate of diesel fuel, but it is even less obvious.

Based on the above, it can be seen that the photocatalytic degradation and adsorption of diesel fuel by the photocatalyst-loaded pellets increases with the increase of light time. After visible light irradiates simulated wastewater with an initial diesel concentration of 0.4 g/L for 8.0 h, the photocatalytic degradation of diesel the efficiency is 68.5 %, while the diesel remaining in the wastewater is less than 2%. It can be inferred that the pre-degradation of diesel fuel by the supported photocatalyst is dominated by adsorption. As the reaction time increases, the contact time between the ZrO2(Er3+)/TiO2 photocatalyst supported on the pellets and the adsorbed diesel fuel also increases. Therefore, the electron-hole pairs and hydroxyl radicals generated by the adsorbed diesel oil and the ZrO2(Er3+)/TiO2 photocatalyst with a load doping ratio of 30 % undergo oxidation reaction, which promotes the degradation of diesel by the photocatalyst. The degradation effect gradually becomes the dominant one with the increase of time, and the photocatalytic degradation efficiency is also increasing. Polypropylene polyhedral spheres loaded with photocatalyst have both adsorption and photocatalysis.

4. Conclusions
In this chapter, a ZrO2(Er3+)/TiO2 photocatalyst with a doping ratio of 30 % and polypropylene polygonal spheres were prepared by the co-precipitation method to degrade diesel under visible light. The conclusions are: (1) The ZrO2(Er3+)/TiO2 photocatalyst with a doping ratio of 30 % is loaded on a polypropylene polygonal sphere to form a floating photocatalyst, which has a good adsorption and degradation effect on low-concentration diesel pollution in the ocean; (2) After 8.0 hours of light, the total removal rate of the floating photocatalyst to diesel oil is above 98 %, and the photocatalytic degradation rate of the ZrO2(Er3+)/TiO2 photocatalyst with a doping ratio of 30 % is above 68 %;

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