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Effect of Magnetic Field on the Photocatalytic Degradation Dye of Nano-TiO_2

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In this paper, nano-TiO_2 powder, prepared by liquid deposition method, is investigated by X-ray diffraction and transmission electron microscope. Using acid red B dye as degradation simulation wastewater object, effect of different magnetic field strength under fixed magnetic field strength on nano-TiO_2 photocatalytic degradation performance was studied. The photocatalytic degradation mechanism is also discussed. The results show that the magnetic field strength have great influences on the photocatalytic properties under specific light intensity, ventilation, the amount of catalyst with other factors unchanged. It is found that photocatalytic capability increases with the increase of the magnetic field. At the same time the mechanism of photocatalytic degradation is discussed based on the effects of the magnetic field and the catalyst interface charge distribution.

Keywords: Nanometer TiO_2, Magnetic field, Photo-catalytic degradation, Degradation mechanism.

INTRODUCTION

In recent years. The photocatalytic oxidation technology applied to environmental pollutants has been become the hotspot of environmental sciences research. Especially, the nano-TiO_2 as an important semiconductor inorganic functional material has the unique physical and photochemical properties and it is widely used in many fields, such as wastewater treatment, air purification, solar cells, gas sensors, packing material, painting and so on[1,2].

The nano-TiO_2 theory and practical applications of the photocatalytic oxidation have been made considerable development with the study. In order to expand the photocatalyst absorption of visible light and improve the quantum efficiency and capacity usage rate. On the one hand, researchers devote themselves to research the catalytic adorning means of the particle size modulation, the doping of the transition metal, semiconductor composite, surface load, photosensitive surface, noble metal deposition in the preparation method and process[3,4]. On the other hand, adopt the acidic modulation, the combination of the photocatalyst with oxidant as well as control and promote the photocatalysis with synergistic effect of physics out-field and optical field. Its purpose is to accelerate the interface mobility of the photogenerated carrier, to reduce the recombination rate, to improve the quantum efficiency and capacity usage rate[5,6].

In fact, the process is constituted with the generation,the composition, the capture and the interface migration of the photogenerated electrons and the electron holes in semiconductor, as well as a series of the free radical reactions followed. In the process, there are a lot of charge particles and radicals which are sensitive to the magnetic fields. So these actions of the electrons, holes and radicals can be influenced by magnetic fields and they impact the property of photocatalysis finally. On the other hand, magnetic field research indicates that the magnetic field affects the free radical reaction. It enhanced the generation rate of the photocatalyst surface hydroxyl radicals.

Thereby, it improved its concentration, applied magnetic field extended the useful life of photogenerated carrier, changed the distribution of intermediates and it is contributed to the formation and reaction of radicals and then influenced the intermediates and distribution of productions[7-9]. In recent years, the studies of ultrasonic wave, microwave and electric field assisted photocatalytic have obtained delightful achievements, but the latter researches of physical field are seldom at home and abroad. Therefore, to introduce the magnetic field and to discuss the influence of the photocatalytic degradation have a certain practical significance.

In this paper, nano-TiO_2 powder, prepared by liquid deposition method,is investigated by X-ray diffraction (XRD) and transmission electron microscope (TEM). Using acid red B dye as degradation simulation wastewater object, effect of different magnetic field strength under fixed magnetic field strength on nano-TiO_2 photocatalytic degradation mechanism is discussed and we try to obtain some knowledge regularly. It can give a hand for magnetic field assisted photocatalytic oxidation.

EXPERIMENTAL

Preparation of nano-TiO_2: The nano-TiO_2 photocatalyst is prepared by liquid-phase precipitation method. Add the amount of the titanium tetrachloride solution with the velocity of 1D/s into the deionized water under magnetic stirring. In the process of dropping keep the solution remained clear as far as possible. And then adjust the pH to weak alkaline using aqueous ammonia solution. It can produce a large number of white precipitate. By filtration, washing to remove the Cl^- and drying. Heat to 500 °C by temperature programming in a muffle furnace maintaining 1 h and then anneal. We can obtain the nano-titanium powder after grinding.

Dye experiment of nano-TiO_2 photocatalytic degradation in the action of a magnetic field: 30 mg TiO_2 is measured before put in the beaker filled with 50 mL simulated dye water which the acid red B. The concentration of contained acid red B is 20 mg/L. The beaker is put in the middle of an adjustable permanent magnet. Stir in 20 W UV irradiation fixed inflatable. Fully dispersed nano-TiO_2 and the UV lamp is apart from the liquid 10 cm. When the magnetic field strength is different, at intervals of a certain time put a beaker approximately 5 mL of the solution into a centrifuge tube and centrifuge 15 min with the speed of 2000 rpm. Then take the supernatant to the cuvette and measure the absorbance using TU-1900UV-Visible spectrophotometer in the maximum absorption wavelength of 510 nm. Calculate the decolorization rate by means of this formula: $D = (A_0-A)/A_0 \times 100\ \%$.

Estimate the influence of photocatalytic degradation property of nano-TiO_2 according to the change of decolorization rate. On the formula, D is the decolorization rate and is also the catalysis property of nano-TiO_2; A_0 is the absorbance of simulated waste water before the treatment; A is the one after treatment.

Instrument and characterization: Y-2000X-ray diffractometer (XRD) with CuK_α radiation (λ = 1.54178 Å, 30 kV × 20 mA) (China Dandong ray instrument Co.Ltd.). JEM-1000SX transmission electron microscope (jeol, resolution was 0.34 nm); 200 W rainbow brand ultraviolet lamp (Shanghai Xinxin Lighting Electrical Appliance Co.Ltd. The wavelength was 253.7 nm). KC-70C permanent magnetization (Shanghai JieLing Magnetic Equipment Co.Ltd.); SXG-1B Tesla instrument (ShangDa Electronic Equipment Co.Ltd.); TU-1900UV-visible spectrophotometer (Beijing Purkinje General Instrument Co.Ltd.)

The nano-TiO_2 powder is analyzed by X-ray diffractometer in order to determine the phase structure of nano-TiO_2. Calculate the granularity by the Scherrer formula $Dhkl = k\lambda/\beta\cos\theta$ and estimate the average size of crystal grains. Where D is the average size of crystal grains; K is constant (0.89); λ is the wavelength of X-ray (0.154178 nm); θ is Bragg angle; β is the integral measurement of peak width (in radians). TiO_2 particle size was characterized by TEM. Measured the absorbance by TU-1900UV-Visible spectrophotometer and determine the magnetic field intensity by Tesla meter.

RESULTS AND DISCUSSION

Phase structure and morphology of nano-TiO_2 particle size analysis: Fig. 1 is XRD pattern of nano-TiO_2 prepared by liquid phase method. When 2θ = 25.28°, 37.80°, 48.05°, it appeared the characteristic peak of nano-TiO_2 (PDF standard No. 21-1271). The average size of crystal grains is about 20 nm by Scherrer formula.

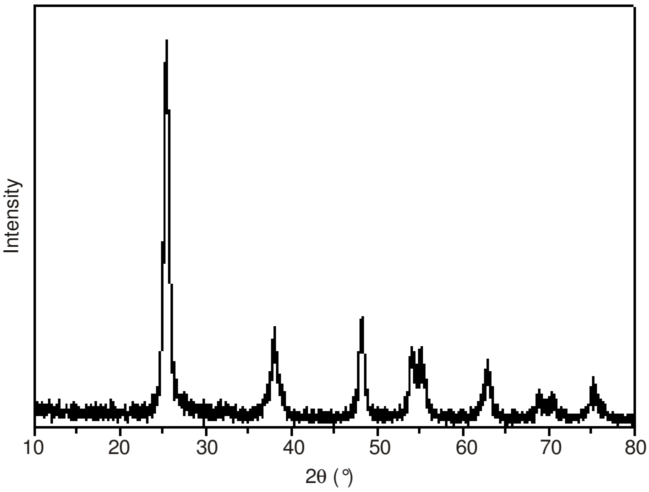

Fig. 1. XRD pattern of TiO_2 powder

Fig. 2 shows the TEM sample, from the chart, we can see that the basic particle is four square, it has a good dispersion and the particle size is about 20 nm. The calculation results are basically consistent with Scherrer formula.

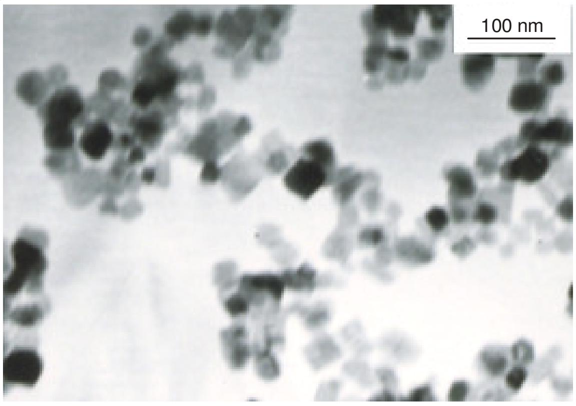

Fig. 2. TEM photograph of TiO_2 powder↵

Effect of magnetic field intensity on the photocatalytic performance: Adjust the pole distance of the permanent magnet from 6 cm to 12 cm. Fig. 3 is a curve of the change in magnetic field strength over the distance between magnetic poles. Fig. 4 is the changing curve of magnetic field strength about decolorization rate in the fixed ventilation and light intensity condition. From this figure, we know that the photocatalytic activity is very low and the decolorization rate is only 22 % (pH = 5) when there is no applied magnetic field. With the increase of magnetic field intensity, the rate increases significantly. It shows that the magnetic field has obvious promoting effect on the photocatalytic reaction. Fig. 5 is a curve of decolorization rate about photocatalytic time when the fixed magnetic field strength is 0.4 T and without magnetic field. From this figure, the rate increases when the time is extended. At the beginning, the influence of magnetic field was obvious. When the time prolonged, the effect on the decolorization rate slowed down.

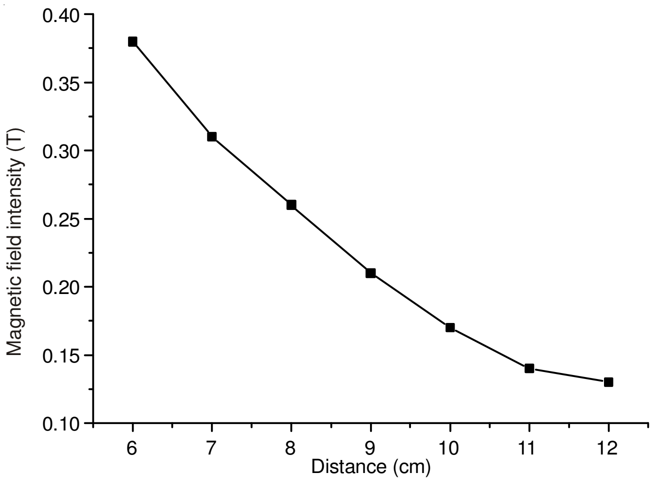

Fig. 3. Relation of magnetic pole distance on magnetic field intensity

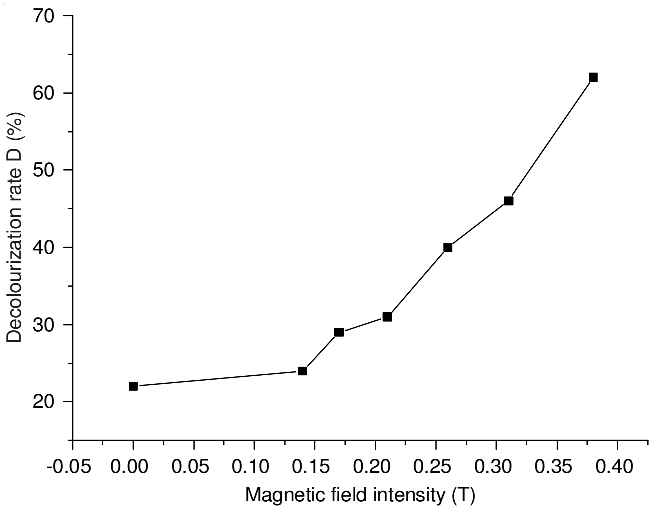

Fig. 4. Effect of magnetic field intensity on decolorzing rate

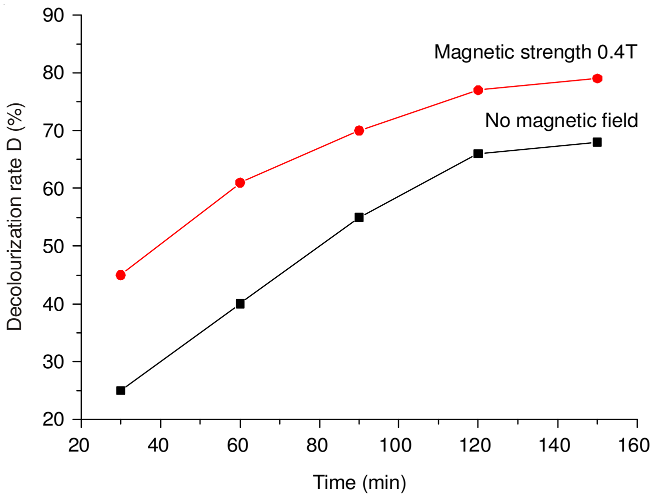

Fig. 5. Effect of photocatalytic time on decolorzing rate

Photocatalytic degradation of organic compounds of TiO_2 is a typical free radical reaction. When the photoenergy is larger than or equal to TiO_2 band gap light radiated to TiO_2 semiconductor surface, the valence electrons were excited into the conduction band, generating electron-hole pairs, migrating to the TiO_2 surface. In the aqueous system, it occurs a series of reactions on the surface, with strong oxidation ability of $^{\bullet}OH$ and O_2^{-}. Hence, how to reduce the recombination of electron-hole pairs and how to increase the strong oxidation ability of $^{\bullet}OH$ and the yield of O_2^{-} are the main factors[10-12]. From the experimental results, the magnetic field has a significant effect on this system. It can improve the efficiency of photocatalytic degradation. We consider that it is determined by a variety of magnetic field effect.

On the one hand, in this system, different materials have different magnetic properties and they have different magnetic field on the magnetization. In the presence of external magnetic field, the magnetic moment of the atoms and molecules and molecular radical, bond angle and bond length, all of these can change the intrinsic energy. (It presented the paramagnetism, diamagnetism, ferromagnetism and the improper fluctuations of the chemical reaction on the macro.) On the basis of atomic absorption theory, when the ultraviolet light beam is perpendicular to the direction of the magnetic field, the transverse Zeeman effect will occur. Then it will affect the system of free radical transition. Under the action of an applied magnetic field, we can control the intersystem transition, maintaining the radicals on the triplet state as much as possible. Then the radical life can be extended from 10^{-8}-10^{-9} s to10^{-6}s. In the process of degradation reaction, $OH^{\bullet}$ radicals play a decisive role. The magnetic field extends the useful life of the photogenerated carriers, changes the intermediate distribution, improves the production rate of surface hydroxyl radical and then increases the concentration. It contributes to promote the deepening of the reaction and ultimately improve the property of the photocatalytic reaction and the quantum efficiency of this process[13-16]. With the enhancement of the magnetic field strength, its role is more obvious and the final performance in the macro is the increasing of the decolorization rate. Furthermore, because that there is a host of different charge anion and cation in the system, magnetic field effect is bound to have an effect on these charged particles. Thereby influence the surface of the catalyst charge distribution. The charge distribution on the surface affects the nanoparticles dispersion directly. They disperse better under the action of magnetic field. The surface area of catalyst increases in the light of the excitation. It directly impacts on the photogenerated carrier recombination and trapping between the catalytic agent and solution interface, as well as the total quantum yield of the charge transfer. It dissociated easily into R^+ and O_2^{-} radicals in acidic or alkaline environments. So accelerate the photocatalytic degradation of organic matter.

On the other hand, as a result of the magnetization, the aqueous environment can reduce the molecular association hydrogen generated. It declines the surface tension of the solution, increases the solubility of the oxygen. The magnetic particularity of the oxygen molecule inevitably leads to be probable activated in the magnetic field. Release a certain number of a single oxygen atom or produce ozone molecules.

In the interface between TiO_2 and aqueous solution, it produces more O_2^- in favour of photocatalytic degradation reaction. Consequently, promote the oxidative degradation of organic pollutants.

The impact of magnetic field involves a series of physical and chemical processes. Its influence mechanism is still in the exploring stage, especially, the photocatalytic degradation of different organic. The formation mechanism of $^{\bullet}OH$ in magnetic field assisted photocatalysis system as well as reaction mechanism and reaction kinetics between $^{\bullet}OH$ and pollutants need to study and discussion in-depth.

Conclusion

The magnetic field has an obvious effect on the photocatalytic degradation reaction. With the increase of magnetic field intensity, the degradation rate was improved significantly. In a fixed magnetic field strength and the other conditions remain unchanged, compared with no magnetic field. When achieve the same decolorization rate, the applied magnetic field takes short time and the rapid rate.

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