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Bisphenol A photocatalytic degradation by magnetic nano-Fe$_3$0$_4$

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Bisphenol A photocatalytic degradation by magnetic nano-Fe$_3$O$_4$

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Abstract. Bisphenol A (BPA) is a typical environmental endocrine disrupting chemicals. Photodegradation of BPA was catalyzed by magnetic nano-Fe$_3$O$_4$ under irradiation of medium pressure mercury lamp (500W, $\lambda \geq$ 290nm). Effects of pH value, initial concentration of BPA and magnetic Fe$_3$O$_4$ dosage were discussed respectively. The research results show that the photodegradation of BPA can be enhanced by Fe$_3$O$_4$. The removal rate decreased with the increase of initial concentration of BPA, and the reaction was in accordance with the first-order reaction kinetics. The removal rate is over 98% under acidic (pH $\leq$ 3) and alkaline (pH $\geq$ 9) conditions. The removal rate of BPA increased with the increase of magnetic nano-Fe$_3$O$_4$ dosage at the beginning of the reaction, and when the removal rate of BPA was more than 95% after 60min irradiation, the effects of dosage were small.

1. Introduction

Bisphenol A (BPA), as an important organic chemical raw material, is widely used in the production of epoxy resin, polycarbonate and other polymer materials, but also used in the production of flame retardants, plasticizes, coatings and other consumer products [1]. BPA can be migrated into the environment through a variety of ways, so which has been detected in water environment, soil environment all over the world and also found in the air and food [2-4]. Studies confirm that BPA is a typical environmental endocrine disruptor with estrogen-like effects [5,6]. The influences of BPA on environmental ecology and human health are gradually appearing. Therefore, the study of its degradation and environmental risk has become a hot spot [7, 8].

Nano-Fe$_3$O$_4$ is characterized by small particle size, large specific surface area, strong adsorption capacity, superparamagnetism, easy separation and collection under the action of external magnetic field. Therefore, magnetic nano-Fe$_3$O$_4$ has been widely used in the adsorption and catalytic degradation of organic pollutants and the removal of heavy metals in water environmental [9]. The research shows that nano-Fe$_3$O$_4$ has both photocatalytic activity and mechanical catalytic activity. Chlorpyrifos were degraded by nano-Fe$_3$O$_4$ and converted into nontoxic inorganic small molecules, which reduced the effective concentration of pesticides and reduced virulence [10]. In the Fe$_3$O$_4$/H$_2$O$_2$ system, H$_2$O$_2$ and Fe^{2+} are composed of Fenton system, which has strong oxidation ability and can completely oxidize many organic pollutants to CO$_2$ and H$_2$O [11].Furthermore, the remarkable reusability of the Fe$_3$O$_4$ nanocomposite during both photocatalytic and photo-Fenton degradation properties is of great importance for environment remediation application [12-14].

Photodegradation technology is widely used in the removal of organic pollutants in water. In these experiments, the effects of the initial concentration of pH value and the dosage of magnetic nano-Fe_3O_4 on the degradation of BPA were studied, and the rules of photocatalytic degradation of BPA by magnetic nano-Fe_3O_4 were discussed. These results provide a reference for the application of magnetic nano-Fe_3O_4 to remove BPA from water.

2. Materials and methods

2.1. Materials and instruments
Bisphenol A (> 99.0%) and nano-Fe_3O_4 (> 99.5%) are purchased from Shanghai Aladdin Reagent Co., Ltd. Methanol, acetonitrile, ethanol are chromatographic pure. HCl and NaOH are all analytical purity. The experimental water is ultra pure water.

P680 HPLC (DIONEX Company, USA); XPA photochemical reactor (Nanjing Xujiang Power Plant China).

2.2. Experimental methods
The mixture of 250 mL magnetic nano-Fe_3O_4 and BPA was prepared and placed in the photochemical reactor, then turn on the 500 W medium pressure mercury lamp. The reaction conditions, such as the initial concentration of BPA and pH value, the dosage of nano-Fe_3O_4 were changed under irradiation. Samples were collected in the 0 min, 10 min, 20 min, 30 min, 45 min, and 60 min respectively. The concentrations of BPA in the samples were determined by HPLC after separation using a magnet.

2.3. HPLC Analysis of BPA
The concentration of BPA was analyzed by HPLC with a C18 column (5 μm, 4.6 mm×150 mm). The mobile phase was methanol/water =70/30 (V/V), the flow rate was 1 mL/min, the column temperature was 30°C, the UV detection wavelength was 276 nm, and the injection volume was 20 μL.

3. Results and discussions

3.1. Control experiment of BPA removal
In order to study the effect of nano-Fe_3O_4 on the photocatalytic degradation of BPA, the direct photolysis of BPA and the removal of BPA under dark reaction conditions were carried when the initial concentration of BPA was 10 mg/L and the dosage of nano-Fe_3O_4 was 1g/L. The results are shown in Figure 1. From the figure, the removal rate of BPA at 120 min is only 9% in dark reaction, which indicates that there is a small amount of adsorption of BPA on the particles. BPA can be photolysis directly under irradiation, but the degradation rate is small. However, the removal rate of BPA can reach 100% in 120min irradiation after the addition of nano-Fe_3O_4. These are due to the surface reaction of nano-Fe_3O_4 crystalline to form Fe^{3+} and Fe^{2+} in acidic solution. These active ions in the solution can produce some OH radicals under irradiation. In addition, the surface electrons of magnetic Fe_3O_4 can be excited by illumination, which makes it easier to adsorb BPA and catalyze its' degradation [15].

3.2. Effect of initial concentration of BPA
The effect of initial concentration of BPA on the photocatalytic degradation by nano-Fe_3O_4 was studied under the condition of pH = 3 and the dosage of nano-Fe_3O_4 as 1g/L. The results are shown in Figure 2.The results show that the catalytic reaction of BPA can fit the kinetic model of first-order reaction (*Eq*.(1) [16]), and the apparent reaction rate constants (k_{obs}) are -0.06466 min^{-1}, -0.06298 min^{-1}, -0.05178 min^{-1}, -0.03931 min^{-1}, -0.0205 min^{-1} when the initial concentrations of BPA range from 5 mg/L to 100 mg/L.
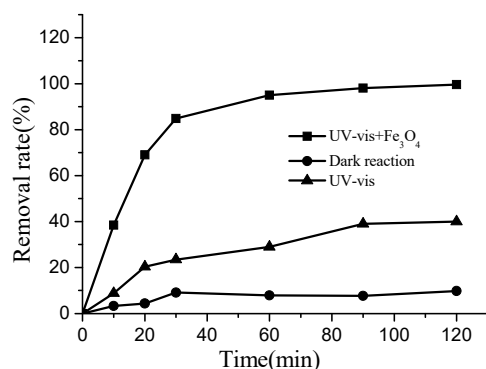
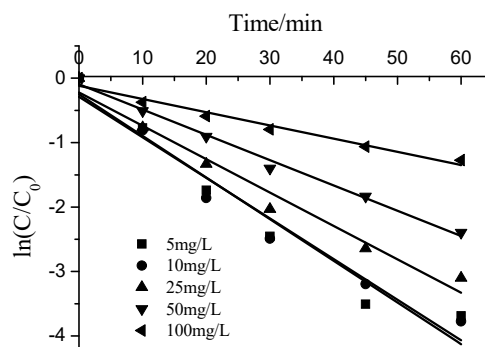**Figure 1.** Control experiment of BPA removal.

Figure 2. Kinetic models of BPA photocatalytic degradation by nano-Fe_3O_4.

$$\ln(C/C_0)=k_{obs}\,t+b \tag{1}$$

Where C_0 is the initial concentration of BPA; C is the concentration of BPA at t time; k_{obs} is an apparent reaction rate constant; b is a constant.

The fitting results show that the reaction rate constant k_{obs} decreases with the increase of initial concentration of BPA when the initial concentrations of BPA are in the range of 5-100 mg/L. These are due to the high initial concentration of BPA, there are more BPA molecules can be adsorbed on the surface of nano-Fe_3O_4, resulting in a lack of enough electrons on the surface of nano-Fe_3O_4 to oxidize BPA.

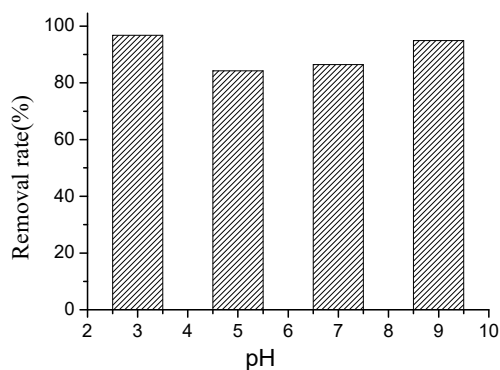*3.3. Effect of pH value on photocatalytic degradation of BPA*

Figure 3. Effects of pH value on photocatalytic degradation of BPA.
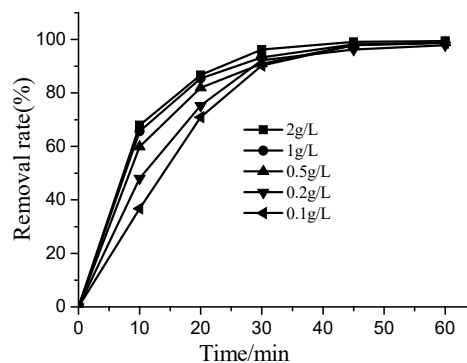

Figure 4. Effects of dosage of nano-Fe_3O_4 on photocatalytic degradation of BPA.

The pH values of the system was controlled at 3, 7, 9 when the initial concentration of BPA is 10 mg/L and the dosage of the nano-Fe_3O_4 is 1g/L. Effects of pH values on photocatalytic degradation of BPA in 60 min are showed in Figure 3. The results showed that the effects of pH on the photocatalytic degradation of BPA were complex. The removal rate of BPA was higher in acidic condition (pH ≤ 3) and in alkaline condition (pH ≥ 9), but the removal rate was lower in neutral condition (pH = 5-7). It is well known that the pH value of the PZC of nano-Fe_3O_4 in aqueous solution is 7. When the pH value is less than 7, the surface potential of nano-Fe_3O_4 is positive, and it is easy to adsorb the negatively charged BPA, which is favorable to the photocatalytic degradation of BPA. Therefore, the lower the acidity, the higher the catalytic degradation rate. When pH > 7, the photodegradation of BPA increases

with the increase of pH value. Therefore, the removal rate of BPA was also higher under alkaline condition [17].

3.4. Effect of dosage of nano - Fe_3O_4 on photocatalytic degradation of BPA
The effects of the dosage of nano-Fe_3O_4 on the degradation of BPA were studied when the initial concentration of BPA is 10 mg/L and pH is at 3.The results are shown in Figure 4. The degradation rate of BPA increases slightly with the increase of Fe_3O_4 dosage within 30 min. The reaction reached equilibrium and the removal rate of BPA was above 98% after 60 min.

4. Conclusions
(1) BPA can be photocalytic degradation rapidly with nano-Fe_3O_4 under the irradiation of 500W medium pressure mercury lamp ($\lambda \geq 290$ nm). The removal rate of BPA reached 100% after 120 min reaction.

(2) BPA degradation rate decreased with the increase of the initial concentration of BPA, and the reaction rate fitted to the first-order reaction in the range of the concentration of 5-100 mg/L.

(3) At pH = 3 and 9, the removal rate of BPA was higher and the removal rate was more than 98% after 60 min irradiation.

(4) The removal rate of BPA increased with the increase of nano-Fe_3O_4 dosage, and the removal rate of BPA was more than 95% in the end.

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