Photocatalytic Degradation of Selective Herbicides Using $Ag/AgCl/Ag_3PO_4$ Plasmonic Nanocatalyst under Visible Irradiation

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Abstract. $Ag/AgCl/Ag_3PO_4$ plasmonic nanocatalysts were prepared through the ion exchange and subsequently light-induced process. The obtained samples showed a high photodegradation capacity for prometryn, bentazone and metribuzin under visible light irradiation. Effects of reduction time (RT) and Cl/P in the synthesis process on the photocatalytic activity of $Ag/AgCl/Ag_3PO_4$ were explored in this study. When RT was 30 min, the RE of prometryn, metribuzin and bentazone reached the maxima of 99.86%, 98.20% and 97.12%, respectively. As Cl/P was 1.5, prometryn, bentazone and metribuzin were decomposed completely within 15, 30 and 20 min, respectively. The stability of $Ag/AgCl/Ag_3PO_4$ photocatalysts was investigated and confirmed with 5-cycling experiments.

Introduction

The modern agricultural production depends on using large numbers of pesticides, about 80% of which directly leach into groundwater and cause water environmental pollution. This problem has been considered as a major environmental issue and received increasing attention all over the world.

Most pesticides and some herbicides are endocrine disrupting chemicals, which are not facile to be excreted from the body and may bring about adverse effects on the endocrine system, reproductive system and immunologic system of human and animal after enrichment[1]. Curbing environmental endocrine disruptors has become the national environmental science research focus in twenty-first century[2,3]. The European Directive 2000/60/EC concerning domestic water establishes maximum concentrations for pesticides and herbicides for the sake of ensuring human health[3]. Besides the usage increase, the frequent occurrence of these contaminants in drinking waters is the result that they are not removed by conventional water treatment processes efficiently due to the low biodegradability.

Recently, water pollution problems have prompted the research of advanced oxidation processes (AOPs) that can overcome the disadvantage of poor degradation rate and easily destroy organic contaminants exhaustively or lower the concentration to reach the standard[1,4]. Among AOPs, heterogeneous photocatalysis has attracted extensive attention for the last a few decades and been proven to be a potential alternative to such currently usual methods as O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV and photo-Fenton for high-performance, energy efficient technology (can use sunlight), possibilities for recycle, eco-friendly property and complete mineralization[5-7]. Photocatalysis is based on the irradiation of semiconductor photocatalysts to generate electrons and holes, which can recombine on the surface or be trapped in surface states to form reactive oxygen species (e.g. •OH radical, $•O_2^-$) to oxidize contaminants[1,8]. The photocatalytic degradation is greatly depended on a few factors, especially composition and type of photocatalyst.

TiO_2 has been known as a prevailing semiconductor photocatalyst. However, it is activated only in the ultraviolet region, which restricted its application in a natural light condition[2]. Thus, there have been many researchers making great efforts to use visible light responded photocatalysts in water and wastewater treatment, which can be activated by the solar and possess advantage of energy saving[4,9-11]. Ag_3PO_4 was reported as a semiconductor with extremely high photocatalytic activities for the degradation of organic contaminants under visible irradiation. However, the studies about Ag_3PO_4 showed that it always exhibited low structural stability and photocorrosion characteristic because the photogenerated electrons combined with interstitial silver ions, which restrained it from being used widely. Bi et al.[12,13] prepared the heterogenous photocatalysts of $AgCl/Ag_3PO_4$ by ion-exchange method to enhance the photocatalytic activity and increase the stability, which were proved through the photocatalytic degradation of dyes. The research by Huang et al.[6,14] indicated that the Ag^0 species on the surface of a series of silver salts can enhance the electron-hole separation and improve the photocatalytic activity due to the localized surface plasmon resonance, such as Ag/AgCl, Ag/AgBr, Ag/AgI, Ag/Ag_3PO_4 et al.

In this paper, we synthesized composite materials modifying Ag_3PO_4 photocatalysts by Ag/AgCl. Selective herbicides, such as metribuzin, prometryn and bentazone, were chosen as pollutants to investigate the removal efficiency (RE) and the degradation kinetics by $Ag/AgCl/Ag_3PO_4$ nanoparticles under visible irradiation.

Experimental

Preparation of Composite Photocatalysts. It is a simple method to synthesize $Ag/AgCl/Ag_3PO_4$ nanoparticles through the ion-exchange and subsequently light-induced process using NaCl, $AgNO_3$, Na_2HPO_4 and Xe lamp. Ordinarily, 20 mL dilute aqueous solution of Na_2HPO_4 (0.1 $mol\cdot L^{-1}$) was dropwise added into 30 mL $AgNO_3$ (0.1 $mol\cdot L^{-1}$) aqueous solution with violent stirring, and then certain amount aqueous solution of NaCl (0.1 $mol\cdot L^{-1}$) was sequentially titrated into it slowly. After the end of adding process, the mixed suspension was continued to be stirred violently for 30 min till to yellow precipitates were obtained. The amount of the NaCl aqueous solution was 10, 20 and 30 mL, respectively. The precipitates were separated from the suspension through vacuum filtration and washed for several times by distilled water repeatedly. The cleaned precipitates were dried at 65℃ for 1h and then the dried samples were dispersed into a solution of methylene blue (MB) and irradiated with a xenon lamp for 0.5, 3 and 30 min respectively. During irradiation procedure, silver appeared on the surface of precipitates and the color of samples changed into black, which indicated that $Ag/AgCl/Ag_3PO_4$ powders were yielded.

Photocatalytic degradation experiments. The photocatalytic degradation experiments were performed in a photochemical glass reactor under visible irradiation. $Ag/AgCl/Ag_3PO_4$ samples (dosage of 200 $mg\cdot L^{-1}$) were dipped into the three types of herbicide solutions (2 $mg\cdot L^{-1}$), which was put into the reactor positioned under 300 W xenon lamp with a cutoff filter of 400 nm in order to filter the ultraviolet light. Before the lamp was switched on to start the degradation process, the suspension had to be stirred magnetically for 30 min in the darkness to establish adsorption and desorption equilibrium between photocatalysts and herbicides. No oxidants or no aerated conditions were used for the photocatalytic degradation experiments. During the light irradiation, the suspension was kept being stirred by magnetic rotor as well and preserved in a constant temperature of 25℃ through a cooling-water system around the outside wall of the reactor. At a 5 or 10 min interval, aliquots of the solution were sequentially extracted by a set of disposable syringes, filtered through 0.45 μm cellulose acetate membrane filters for analysis with a high performance liquid chromatograph (HPLC). The concentration of herbicides was obtained according to the standard curve of concentrations and integral areas of chromatographic peaks. RE was calculated by Eq. 1.

$$RE=(C_0-C)/C_0\times100\%. \quad (1)$$

Where, C_0 and C are concentrations of herbicides at illumination time 0 and t, respectively.

Analytical Method. The concentrations of herbicides were determined using a HPLC system (Agilent series1200, USA). The analysis was carried out by means of a ZORBAX Eclipse Plus C18 chromatographic column (100 mm×4.6 mm, 5 μm, USA).

Results and Discussion

Effects of light-induced process on removal efficiency. During the preparation procedure of Ag/AgCl/Ag_3PO_4 composite photocatalysts, the light-induced process is a crucial step to make Ag^+ be reduced into Ag^0 on the surface of photocatalysts and form the localized surface plasmon resonance [15,16]. The irradiation time (or reduction time, RT) of the light-induced process would affect the amount of Ag nanoparticles, which has a relatively large impact on photocatalytic activity. The RE of three types of herbicides using Ag/AgCl/Ag_3PO_4 powders with different RT under visible light irradiation for 30 min was showed in Fig. 1. In these three types of herbicides, prometryn and metribuzin were degraded over 95% within 30 min using Ag/AgCl/Ag_3PO_4 samples with diverse RT, which indicated that Ag/AgCl/Ag_3PO_4 composite photocatalyst had a very high photocatalytic activity on them. The effect of reduction time was not significant for prometryn and metribuzin. However, there was a different result for bentazone due to the difficult degradation property. The RE of bentazone was obviously enhanced with the increase of RT. When RT was 30 min, the RE of prometryn, metribuzin and bentazone reached the maxima of 99.86%, 98.20% and 97.12%, respectively.

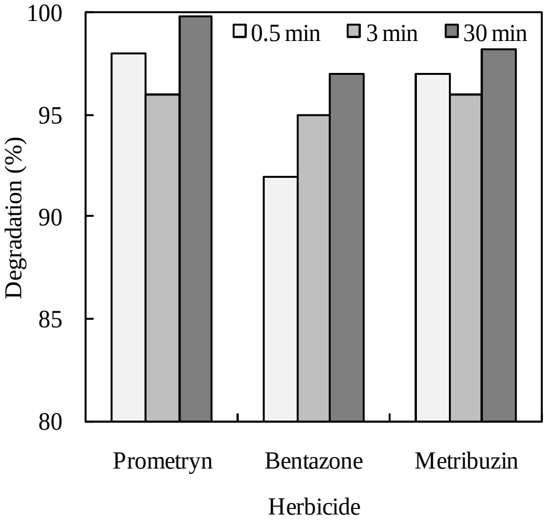

Fig. 1 RE of herbicides using Ag/AgCl/Ag_3PO_4 plasmonic photocatalysts at different RTs

Photocatalytic Performances Affected by Proportion of Cl^- and PO_4^{3-}. It was expected to further improve the photocatalytic activity of Ag_3PO_4 making full use of the synergistic effect formed by Ag^0, AgCl and Ag_3PO_4. Silver nanoparticles deposited on the surface of photocatalysts induced the plasmonic effect, and meanwhile h^+ generated in the photocatalytic process reacted with Cl^- to produce Cl^0 free radicals with a strong oxidation activity[10]. Ag/AgCl/Ag_3PO_4 samples demonstrated discrepant photocatalytic performances for herbicides with varying the proportion of Cl^- and PO_4^{3-} (Cl/P), which was displayed in Fig. 2. In the initial dark adsorption experiment for 30 min, C/C_0 of bentazone and metribuzin declined negligibly, which indicated that Ag/AgCl/Ag_3PO_4 samples showed low adsorption capacity for them in darkness. In contrast, prometryn was facile to be adsorbed in the dark and degraded using Ag/AgCl/Ag_3PO_4 under visible light irradiation. The experiment results revealed that about 25-36% prometryn molecules were adsorbed within 30 min and 66-90% could be decomposed under visible irradiation within 5 min. In the synthesis procedures, the photocatalytic oxidation capacity of Ag/AgCl/Ag_3PO_4 could be improved with the increase of Cl/P. As Cl/P was 1.5, prometryn, bentazone and metribuzin were decomposed completely within 15, 30 and 20 min, respectively.

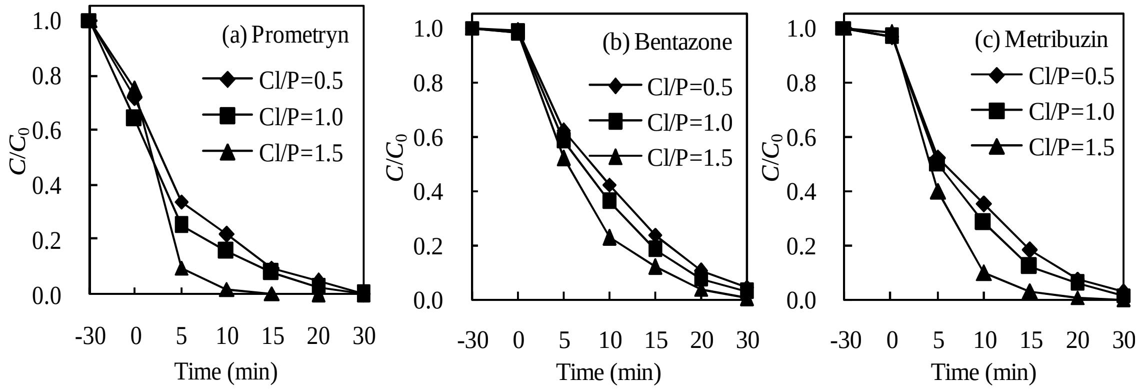

Fig. 2 Photocatalytic performances for herbicides using Ag/AgCl/Ag_3PO_4 plasmonic photocatalysts at different Cl/P ratios

Photodegradation Kinetics. Fig. 3 shows the photodegradation kinetics of prometry, bentazone and metribuzin aqueous solution by Ag/AgCl/Ag_3PO_4 samples under the same experimental condition, which were prepared with the same process except for Cl/P. It was illustrated that the photocatalytic degradation of herbicides followed a pseudo-first-order kinetics. The rate constants, R^2 and RE within 10 min were calculated and displayed as Table 1. It was clear that degradation rate of Cl/P=1.5 was highest due to preferable visible light photocatalytic activity. For prometry and metribuzin, the efficiency of Ag/AgCl/Ag_3PO_4 photocatalysts was enhanced by twice as Cl/P increased from 0.5 to 1.5. The efficiency of Ag/AgCl/Ag_3PO_4 photocatalysts for degradation of bentazone increased ca. 1.5 times. The RE of photodegradation for prometry, bentazone and metribuzin under visible irradiation within 10 min were 97.85%, 77.36% and 90.56%, respectively. These results indicated that Ag/AgCl/Ag_3PO_4 materials with Cl/P=1.5 could be used as efficient visible-light-driven plasmonic photocatalysts for the photodegradation of herbicide pollutants.

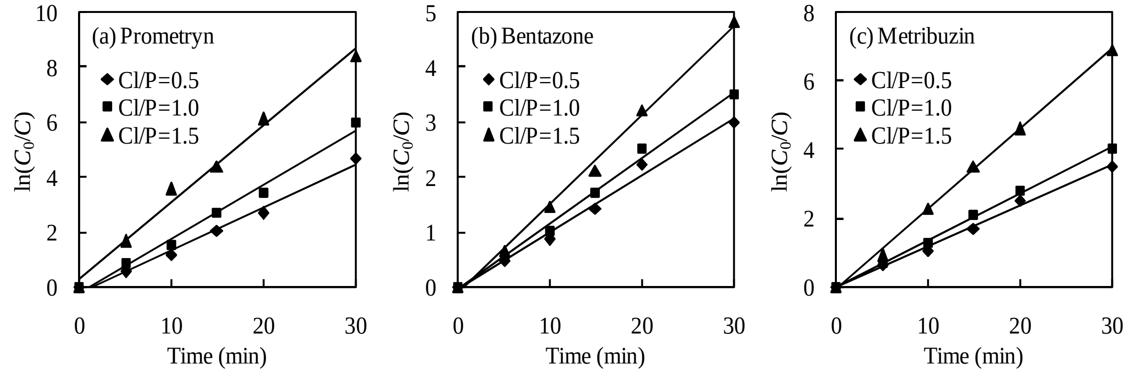

Fig.3 The relation between $\ln C_0/C$ and time (min) of photodegradation for herbiciedes under visible irradiation by Ag/AgCl/Ag_3PO_4 samples at different Cl/P ratios

Table 1 Kinetic constants of photodegradation for herbiciedes using Ag/AgCl/Ag_3PO_4 photocatalysts

Herbicides	Cl/P	equation	R^2	10 min RE [%]
Prometryn	0.5	y=0.115x-0.215	0.987	78.16
	1	y=0.197x-0.206	0.987	84.42
	1.5	y=0.278x+0.301	0.990	97.85
Bentazone	0.5	y=0.103x-0.050	0.989	57.66
	1	y=0.120x-0.052	0.993	64.12
	1.5	y=0.163x-0.125	0.995	77.36
Metribuzin	0.5	y=0.118x-0.006	0.993	65.24
	1	y=0.135x+0.008	0.997	72.38
	1.5	y=0.233x-0.077	0.998	90.56

Cycling Experiments. The stability of photocatalysts is important as well besides the photocatalytic activity in the practical application. Cycling experiments of photodegradation for herbicides were implemented to further investigate the stability of Ag/AgCl/Ag_3PO_4 plasmonic photocatalysts prepared at RT of 30 min and Cl/P of 1.5. Fig. 4 shows the results of the RE of herbicides in five-cycle experiments under the same conditions. It was obvious that $Ag/AgCl/Ag_3PO_4$ maintained a high photocatalytic activity even after five cycles. Especially for prometryn, the decrease of RE was almost negligible. It was demonstrated that the stability of photocatalysts was improved greatly in comparision to the pure Ag_3PO_4, which had been confirmed to be unstable by researchers [15].

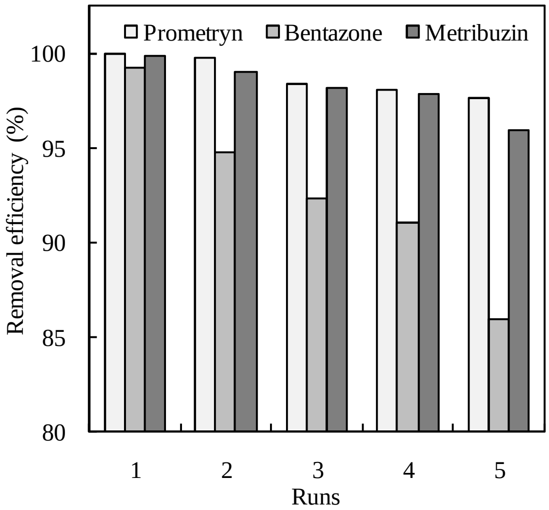

Fig. 4 Cycling runs of $Ag/AgCl/Ag_3PO_4$ for photodegradation of herbiciedes under visible irradiation within 30 min

Conclusions

$Ag/AgCl/Ag_3PO_4$ nanoparticles synthesized through the ion-exchange and subsequently light-induced process performed a relatively high photodegradation capacity for prometryn, bentazone and metribuzin under visible light irradiation.

As the reduction time of the light-induced process was 30 min, the RE of all the herbocides reached the highest due to the effect of RT on the amount of Ag nanoparticles on the surface of photocatalysts, which brought about plasmon resonance to enhance photocatalytic activity. The increment of Cl/P was in favor of enhancement of the degradation rate for herbocides as the result of generating Cl^0 free radicals.

The obtained heterogeneous photocatalysts maintained a high photocatalytic activity after five cycles, which indicated the improvement of the stability of them. The photodegradation using $Ag/AgCl/Ag_3PO_4$ may provide a new approach to remove selective herbicides, which will accomplish the resolution of environmental problems by taking advantage of solar energy.

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