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Article

Photocatalytic degradation of dyes by AgBr/Ag₃PO₄ and the ecotoxicities of their degraded products

Pongsaton Amornpitoksuk^{a,c,*}, Sumetha Suwanboon^{b,c}^a Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla, 90112 Thailand^b Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla, 90112 Thailand^c Center of Excellence in Nanotechnology for Energy (CENE), Prince of Songkla University, Hat-Yai, Songkhla, 90112 Thailand

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ABSTRACT

Ag₃PO₄ powders were prepared through a precipitation reaction between AgNO₃ and precipitating agent solutions that were prepared by adjusting the amount of H₃PO₄ in the Na₃PO₄ solutions. The Ag₃PO₄ powders prepared from the precipitation solution with a pH of 6 showed the highest photocatalytic activity for decolorizing the methylene blue and rhodamine B dyes. These Ag₃PO₄ powders were further modified by the addition of KBr solutions to obtain AgBr/Ag₃PO₄ powders and these photocatalysts can decolorize the anionic dyes as reactive orange and methyl orange. The reactive species involved in the photocatalytic degradation process were evaluated for their inhibitory activity using the appropriate scavengers. After photocatalysis, mass spectrometry confirmed that the dyes were degraded to smaller molecules. The ecotoxicities of the dye solutions before and after treatment were evaluated by studying their ability to inhibit the growth of the bioindicator *Chlorella vulgaris*.

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1. Introduction

The semiconductors TiO₂ and ZnO are commonly used as photocatalysts and require activation by short wavelength such as UV-rays [1], which make up only a small portion of available sunlight compared with visible light. Hence, the development of visible-light-driven photocatalysts has received much attention from many research groups and Ag₃PO₄ has been found to possess excellent photocatalytic properties. It has a direct band gap of 2.36 eV and can therefore absorb solar energy with wavelengths shorter than 530 nm [2]. The photocatalytic activity of Ag₃PO₄ is strongly influenced by its morphology, which can be controlled by the precipitation parameters used for its preparation, including: the type of complexing agent [3]; the type of precipitating agent [4]; and the pH of the reaction solu-

tion [5]. Although control of the Ag₃PO₄ particle shape and size can enhance its photocatalytic activity [3–8], it still decomposes to Ag⁰ under illumination with visible light and this leads to a reduction of its photocatalytic performance [6]. Surface modification by coupling with a promoter to give a heterostructure has been shown to reduce the solubility of Ag₃PO₄ and also inhibit charge recombination that leads to increase photocatalytic activity [9,10]. It has been reported that combining photosensitive AgBr with Ag₃PO₄ facilitates its photocatalytic properties, increases particle stability, and requires relatively simple preparation techniques [9–11]. AgBr/Ag₃PO₄ is usually synthesized using a two-step ion-exchange method, by first preparing Ag₃PO₄ and then transferring into a Br[−] solution. In AgBr/Ag₃PO₄ system, photogenerated holes (h⁺) in the Ag₃PO₄ can be transferred to the AgBr, whilst the photogenerated elec-

* Corresponding author. Tel: +66-74288438; Fax: +66-74558841; E-mail: ampongsa@yahoo.com, pongsaton.a@psu.ac.th

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trons in the AgBr can be transferred to Ag_3PO_4 , inhibiting the electron-hole pair recombination [9]. Therefore, the amount of AgBr formed at the Ag_3PO_4 surfaces and the particle morphology of Ag_3PO_4 before exchange with Br^- ion strongly influence the photocatalytic activity of AgBr/ Ag_3PO_4 .

Altering the pH of precipitation solution is one of the effective parameters that is simple and easy to handle but there have been few reports describing the effect of precipitation pH on the photocatalytic activity of Ag_3PO_4 . Wang et al. [5] studied the pH dependence of Ag_3PO_4 growth by using hexamethylenetetramine (HMT) to increase the pH of the reaction system. In this work, the Ag_3PO_4 particles were grown in solutions containing Na_3PO_4 and H_3PO_4 . Furthermore, the number of preparation steps for AgBr/ Ag_3PO_4 was reduced by using a one-pot synthesis. The photocatalytic activities of AgBr/ Ag_3PO_4 powders were investigated through the degradation of methylene blue (MB), rhodamine B (RhB), reactive orange (RO) and methyl orange (MO) dyes and the presence of the reactive species $\text{OH}^\bullet$, $\text{O}_2^{\bullet-}$, and h^+ was determined using appropriate scavengers. Finally, the ecotoxicity of the treated and untreated dye solutions were studied by testing their inhibition of the growth of the bioindicator *Chlorella vulgaris*.

2. Experimental

2.1. Synthesis

Ag_3PO_4 was prepared by a precipitation method between Ag^+ and PO_4^{3-} ions. The pH of precipitation solution was adjusted by addition of H_3PO_4 into Na_3PO_4 solution. Precipitation solutions were prepared with pH values of 5–10 because the formation of Ag_2O was observed when the pH of the solution was more than 10 [4]. Upon addition of aqueous AgNO_3 solution to the precipitation solutions, a yellow precipitate formed immediately and the mixture was stirred at room temperature for 1 h. The solids were filtered off, rinsed with distilled water, and dried at 100 °C in a hot air oven for 1 h.

AgBr/ Ag_3PO_4 powders were prepared using a one-pot synthesis. Aqueous AgNO_3 solution was added to the precipitation solution at pH = 6 and this mixture was stirred at room temperature for 30 min. Aqueous KBr solution was added to the mixture and the resulting solution was stirred at room temperature for a further 30 min. The solids were filtered off, rinsed with distilled water, and dried at 100 °C in a hot air oven for 1 h.

2.2. Characterization

The identification of crystalline phases and morphological studies on the synthesized powders were carried out using an X-ray diffractometer (XRD, X'Pert MPD, Philips) with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) and a scanning electron microscope (SEM, QUANTA 400, FEI), respectively. Elemental analysis of the AgBr/ Ag_3PO_4 powders was performed using an energy dispersive X-ray spectrometer (EDS, Oxford) operating in a point scan mode coupled with the SEM. The surface areas of samples were evaluated by the Brunauer-Emmett-Teller (BET)

method using a surface area analyzer (Autosorb 1 MP, Quantachrome). X-ray photoelectron spectroscopy (XPS) was performed on an AXIS Ultra DLD (Kratos Analytical Ltd.) electron spectrometer and all binding energies were calibrated to the C 1s line at 284.8 eV.

2.3. Photocatalytic activity tests

The photocatalytic activities were investigated through the degradation of the cationic dyes MB and RhB and the anionic dyes RO and MO. In a typical procedure, the photocatalyst (0.1 g) was dispersed in an aqueous dye solution (10^{-5} mol/L , 150 mL) for 30 min to study the adsorption of dye and ensure that the system had reached equilibrium. After this period, the suspension was irradiated with visible light by three parallel fluorescent tubes (15 W) with a long pass filter ($\lambda > 420 \text{ nm}$, Edmund) and 3 mL of the dye solution were removed at 10 min intervals during the irradiation. The remaining dye concentration after irradiation was determined by the absorption technique using a UV-vis spectrophotometer (UV-2600, Shimadzu) and the decolorization was calculated using the following equation:

$$\text{Decolorization (\%)} = [(C_0 - C_t)/C_0] \times 100\% \\ = [(A_0 - A_t)/A_0] \times 100\%$$

where C_0 and A_0 are the concentration and absorbance of the dye before irradiation, respectively, and C_t and A_t are the corresponding concentration and absorbance of the dye after irradiation, respectively, for time t .

The reactive species involved in the photocatalytic degradation of dyes over AgBr/ Ag_3PO_4 powder were determined using appropriate scavengers. The disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA), benzoquinone (BQ), and *t*-butyl alcohol (TBA) were used as effective trapping agents for h^+ , $\text{O}_2^{\bullet-}$ and $\text{OH}^\bullet$, respectively. In a typical procedure, the scavenger (1 mmol) was added to aqueous RhB and RO solutions (dye concentration = 10^{-5} mol/L , 150 mL) containing the AgBr/ Ag_3PO_4 photocatalyst.

2.4. Dye mineralization and ecotoxicity tests

The total carbon content of the dye solutions before and after irradiation was analyzed by a CHNO analyzer (Flash 1112 EA Series EA, Thermoquest). The degradation products were detected by liquid chromatograph-mass spectrometry (LC-MS, 2690-LCT, Waters, Micromass) coupled with an electrospray ionizer operating in the positive mode (ESI^+) for the cationic dyes and in the negative mode (ESI^-) for the anionic dyes. Ecotoxicity was determined by growth inhibition of the unicellular green algae *Chlorella vulgaris* (*C. vulgaris*) using a previously reported method [12].

3. Results and discussion

3.1. Effects of the pH of precipitation solutions

Na_3PO_4 produces OH^- when dissolved in water and this can result in solution with pH value more than 12. In this work, the

Fig. 1. XRD patterns of the Ag_3PO_4 powders prepared from the precipitation solutions with various pH values.

pH of the precipitation solution was reduced by the addition of H_3PO_4 into the Na_3PO_4 solution. Fig. 1 shows the XRD patterns of the products using the precipitation solutions with different pH values (pH = 5–10). It was observed that all diffraction patterns matched well with the JCPDS NO. 06-0505 with no additional impurity peaks; thus, it was concluded that all the prepared powders were pure Ag_3PO_4 . The lattice parameters of all the prepared Ag_3PO_4 powders are shown in Table 1.

The morphologies of the Ag_3PO_4 particles prepared from the precipitation solutions with pH values between 5 and 10 are shown in Fig. 2. This indicated that the particles of Ag_3PO_4 prepared from the precipitation solution of pH 5 had the biggest size, while the Ag_3PO_4 particles prepared from the precipitation solutions of pH 7–10 were all similar in size. The product yield was very low in acidic solution (Table 1) because PO_4^{3-} is a strong base that reacts with H^+ to form the HPO_4^{2-} , thereby increasing the solubility of Ag_3PO_4 in acidic solution. In general, when the Ag^+ ions reacted with the PO_4^{3-} ions, it produced the Ag_3PO_4 nuclei that become suspended in the reaction solutions. In the case of acidic precipitation solutions, some of these nuclei can dissolve and this suppresses the overall rate of nucleation and growth. So, the prepared Ag_3PO_4 in an acidic condition has a larger sizes and a low-yield. The dissolution rate is negligible in basic precipitation solution so more Ag_3PO_4 nuclei form rapidly, leading to smaller particles and high yield.

The band gap energies for all the prepared Ag_3PO_4 powders were determined as the interceptions at the $h\nu$ axis from the

Fig. 2. SEM images of the Ag_3PO_4 powders prepared from the precipitation solutions with various pH values.

linear portion of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) plots as shown in Fig. 3 and their values are shown in Table 1. The particle sizes of all samples were larger than the Bohr radius so the changes in band gap energies with the sizes of the Ag_3PO_4 particles cannot be explained by quantum size effects. However, the changes could result from the lattice contraction as the lattice parameters of the Ag_3PO_4 powders trended to decrease with increasing pH values of the precipitation solutions as shown in Table 1.

The photocatalytic decolorization of MB and RhB dyes by the Ag_3PO_4 powders prepared from precipitation solutions with different pH values are shown in Fig. 4. It was clearly observed that the Ag_3PO_4 prepared at pH 6 showed the best activity for decolorization of MB and RhB. The efficiency of semiconductor-based photocatalysts has traditionally been correlated to their surface area; however, this was not observed in this case because the photocatalytic activities of the prepared Ag_3PO_4 powders were not related to their surface areas, as shown in Table 1. The results of Indra et al. [13] have shown that the photocatalytic activity of Ag_3PO_4 particles with well-defined multifaceted morphologies, larger particle sizes, and lower surface areas were better than particles with an irregular shape and a correspondingly high surface area. Furthermore, Dong et al. [14] reported that irregular sphere-like Ag_3PO_4 particles had the worst photocatalytic activity when

Table 1

Yields, lattice parameters (a), band gap energies (E_g) and surface areas (S_{BET}) evaluated using the BET method for Ag_3PO_4 powders prepared using precipitation solutions with different pH values.

pH of precipitation solution	Yield (%)	a (Å)	E_g (eV)	S_{BET} (m^2/g)
5	8.36	6.01386(5)	2.417	2.04
6	18.01	6.01357(3)	2.417	2.56
7	26.45	6.01282(4)	2.425	3.95
8	38.14	6.01275(4)	2.425	4.01
9	41.36	6.01273(5)	2.425	4.03
10	43.80	6.01273(5)	2.425	4.03

Fig. 3. Evolution of the band gap energies of the Ag_3PO_4 powders prepared from the precipitation solutions with various pH values.

compared with Ag_3PO_4 with other shapes. As the Ag_3PO_4 powders prepared from the precipitation solutions of pH 7–10 had irregular sphere-like shapes and the particles prepared from the precipitation solution of pH 5 did not possess a well-defined multifaceted structure, these Ag_3PO_4 particles had lower photocatalytic activities than those prepared from the precipitation solution of pH 6.

3.2. Effect of Br^- concentration

Fig. 5 shows the XRD patterns of $\text{AgBr}/\text{Ag}_3\text{PO}_4$ powders prepared at pH = 6 after stirring for 30 min in solutions containing different amounts of dissolved KBr. When the concentration of Br^- ions in the solution was increased, the products changed from being yellow to chartreuse in color and additional diffraction peaks corresponding to AgBr were present. The intensities of these diffraction peaks increased with the amount of KBr added to the reaction solutions, while these assigned to Ag_3PO_4 decreased. This resulted from the exchange of Br^- ions for the PO_4^{3-} ions at the surface of the Ag_3PO_4 to produce $\text{AgBr}/\text{Ag}_3\text{PO}_4$. If the product was formed through the co-precipitation of Ag_3PO_4 and AgBr, the diffraction peaks of

Fig. 5. XRD patterns of $\text{AgBr}/\text{Ag}_3\text{PO}_4$ powders prepared using KBr concentrations of 0 (1), 0.001 (2), 0.005 (3), 0.01 (4), 0.03 (5), and 0.05 mol (6). The indexed peaks correspond to the AgBr phase.

Ag_3PO_4 would not be expected to disappear at a high Br^- concentrations and the XRD should demonstrate the co-existence of Ag_3PO_4 and AgBr. Fig. 6 shows the EDS spectra of Ag_3PO_4 and AgBr present in a synthesized powder and this confirmed the heterostructure of $\text{AgBr}/\text{Ag}_3\text{PO}_4$.

When the concentration of KBr in the preparation solution was increased, the morphologies of the photocatalysts changed from a rhombic dodecahedral-like shape (pure Ag_3PO_4 at pH 6), to more irregular shapes initially and then to large sphere-like shapes (pure AgBr) as shown in Fig. 7.

The diffuse reflectance absorption spectra of the $\text{AgBr}/\text{Ag}_3\text{PO}_4$ powders are shown in Fig. 8(a). The intensity of the characteristic peak corresponding to the direct band gap of Ag_3PO_4 at 455 nm decreased as the amount of KBr in the preparation solution was increased. This was in agreement with the XRD results, which showed that the number of Ag_3PO_4 phases decreased as the amount of KBr added increased. Moreover, the band gap energy also increased with the amount of KBr added as shown in Fig. 8(b).

The effect of AgBr on the photocatalytic decolorization of dyes over $\text{AgBr}/\text{Ag}_3\text{PO}_4$ powders is shown in Fig. 9. Pure

Fig. 4. Photocatalytic decolorization percentages of MB (a) and RhB (b) dyes by Ag_3PO_4 powders prepared from the precipitation solutions with various pH values as a function of irradiation time.

Fig. 6. SEM image of the AgBr/Ag₃PO₄ prepared using a 0.001 mol KBr solution with the EDS patterns from the corresponding locations that comprised Ag₃PO₄ (1) and AgBr (2).

Ag₃PO₄ did not degrade the anionic dyes RO and MO because of the repulsion between the anionic dye and the negatively charged Ag₃PO₄ surface [15]. The presence of AgBr on the surface of Ag₃PO₄ enabled the photocatalyst to decolorize the anionic dyes as shown in Fig. 9. The photocatalytic degradations of the anionic dyes increased as the KBr concentrations in the preparation solutions were increased from 0 to 0.005 mol, but their activities for degradation of the cationic dyes became lower than that of pure Ag₃PO₄ powder (KBr < 0.005 mol). The presence of small amounts of AgBr on the surface of Ag₃PO₄ (KBr < 0.005 mol) clearly inhibited the photocatalytic degradation of the cationic dyes. When the KBr concentration in the preparation solution was 0.005 mol, the prepared photocatalyst showed the best photodegradation efficiency for all four dyes. At higher KBr concentrations, the decolorization efficiency for the four dyes also continuously decreased with the amounts of KBr added because the excess of AgBr would also

reduce the photocatalytic efficiency of the AgBr/Ag₃PO₄ powders. The oxidation states of AgBr/Ag₃PO₄ (pH = 6, KBr = 0.005 mol) before and after photocatalysis were analyzed by XPS as shown in Fig. 10 and this indicated partial decomposition of Ag⁺ to Ag⁰ during the photocatalytic process.

3.3. Evolution of reactive species

During photocatalysis the dye molecules are degraded by photogenerated reactive species. Hydroxyl radicals (OH[•]), superoxide radical anions (O₂^{•-}), and photogenerated holes (h⁺) have been identified as playing an important role in the degra-

Fig. 7. SEM images of AgBr/Ag₃PO₄ particles prepared using KBr concentrations of 0.001 (a), 0.005 (b), 0.01 (c), 0.03 (d), and 0.05 mol (e).

Fig. 8. Absorption spectra (a) and the evolution of band gap energies (b) of the AgBr/Ag₃PO₄ powders prepared using KBr concentrations of 0 (1), 0.001 (2), 0.005 (3), 0.01 (4), 0.03 (5), and 0.05 mol (6).

Fig. 9. Photocatalytic decolorization of MB, RhB, RO, and MO dyes by AgBr/Ag₃PO₄ powders prepared using various KBr concentrations of 0 (1), 0.0005 (2), 0.001 (3), 0.005 (4), 0.01 (5), 0.03 (6) and 0.05 mol (7).

Fig. 10. Ag 3d XPS spectra of AgBr/Ag₃PO₄ powder prepared using a KBr concentration of 0.005 mol before (a) and after (b) photocatalytic dye degradation.

degradation of dye molecules by AgX/Ag₃PO₄ (X = Cl, Br and I) powders [16,17]. Fig. 11 shows the decolorization activity of AgBr/Ag₃PO₄ (KBr = 0.005 mol) towards RhB and RO dyes in the presence of Na₂EDTA, BQ and TBA. It was observed that the addition of TBA did not affect the decolorization activity towards the cationic dye RhB and the anionic dye RO and this indicated that OH• was not the main reactive species in this process. In contrast, the photocatalytic activity was strongly suppressed by the addition of Na₂EDTA and BQ so both h⁺ and O₂^{•−} were main reactive species involved in the photocatalytic decolorization of RhB and RO dyes by AgBr/Ag₃PO₄ (KBr = 0.005 mol) powder under illumination with visible light.

3.4. Mineralization of the dye and the ecotoxicity of the treated dye solutions

Table 2 shows the total carbon content (TCC) values of the dye solutions before and after photocatalysis using AgBr/Ag₃PO₄ powder (KBr = 0.005 mol) as the photocatalyst. The observed TCCs of the treated dye solutions were significantly lower than those of the corresponding untreated dye solutions. This implied that the carbon compounds were probably converted to CO₂ that was lost from the system. However, the dyes did not completely degrade to CO₂ after photocatalysis and some residual organic compounds were present in the

Fig. 11. Photocatalytic degradation of dyes by AgBr/Ag₃PO₄ powder (KBr = 0.005 mole) in the presence of different scavengers.

Table 2

Comparison of total carbon content (TCC) values (%) of dye solutions before and after photocatalysis.

Sample type	MB	RhB	MO	RO
Untreated solution	0.96	1.51	0.89	0.91
Treated solution	0.30	0.32	0.29	0.30

treated solutions. The degraded products after photocatalysis were investigated by electrospray ionization mass spectrometry (ESI-MS) and the mass spectra of the treated dye solutions are presented in Fig. 12.

Because most of the detected products were aromatic compounds that may be toxic, the ecotoxicities of the treated and untreated solutions were further evaluated. The ecotoxicities were determined through growth inhibition of *C. vulgaris* used as an ecological indicator and the results were also presented in Fig. 13. This showed that the MB dye strongly inhibited the

Fig. 13. Individual *C. vulgaris* cell counts in dye solutions before and after (denoted as T-[dye]) photocatalysis and in deionized water (D.I.).

growth of *C. vulgaris* when compared with the three other dyes. Fig. 14 shows microphotographs of *C. vulgaris* after 5 days of incubation. It indicated that only MB diffused into the *C. vulgaris* cells as the pigment of the algae changed color from green to blue. From Fig. 13, the number of individual *C. vulgaris* cells in all of the treated dye solutions was greater than for their corresponding untreated solutions but these solutions were more toxic than the deionized water (D.I.) used as a control. It cannot be concluded that the degraded products were less toxic than their parent dye molecules because the concentrations of these species were not the same. However, by comparing *C. vulgaris* growth in the same solution volume before and after photocatalysis, it was possible to conclude that the overall toxicity of the solution containing the degraded products after photocatalysis was lower.

Fig. 12. Mass spectra of the treated dye solutions. Positive ionization mode ESI⁺ was used for the cationic dyes (MB and RhB) and negative ionization mode ESI⁻ was used for the anionic dyes (RO and MO).

Fig. 14. Light microscopic observations of *C. vulgaris* after 5 days for incubation in untreated dye solutions and D.I.

4. Conclusions

Ag_3PO_4 powders prepared from the precipitation solution at pH 6 had a multi-faceted structure and showed the best activity for decolorizing MB and RhB solutions under irradiation by visible light. $\text{AgBr}/\text{Ag}_3\text{PO}_4$ powders were successfully synthesized using a one-pot ion-exchange method. The photocatalyst prepared from the precipitation solution with a KBr concentration of 0.005 mole showed the best photocatalytic degradation activity for all of the dyes tested under visible light. Using appropriate scavengers, it was concluded that the photodegradation was most likely due to the generation of h^+ and $\text{O}_2^{\bullet-}$ by the $\text{AgBr}/\text{Ag}_3\text{PO}_4$ photocatalyst. These reactive species degraded the dyes into smaller organic molecules during the photocatalytic process and some aromatic compounds remained in the treated dye solution after photocatalysis. Although the dyes were not completely converted to CO_2 , the overall ecotoxicities of the degradation products in the treated dye solutions were shown to be much lower than the corresponding untreated dye solutions using *C. vulgaris* as a bioindicator.

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Graphical Abstract

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Photocatalytic degradation of dyes by $\text{AgBr}/\text{Ag}_3\text{PO}_4$ and the ecotoxicities of their degraded products

Pongsaton Amornpitoksuk*, Sumetha Suwanboon
Prince of Songkla University, Thailand

$\text{AgBr}/\text{Ag}_3\text{PO}_4$ powders were successfully synthesized using a one-pot ion-exchange method and showed promising photocatalytic activity for organic dye degradation under visible light.

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AgBr/Ag₃PO₄光催化降解染料的性能及其降解产物的生态毒性

Pongsaton Amornpitoksuk^{a,c,*}, Sumetha Suwanboon^{b,c}

^a宋卡王子大学理学院化学系和化学杰出创新中心, 合艾, 宋卡, 90112, 泰国

^b宋卡王子大学理学院材料科学与技术系, 合艾, 宋卡, 90112, 泰国

^c宋卡王子大学能源纳米技术杰出中心, 合艾, 宋卡, 90112, 泰国

摘要: 通过调节Na₃PO₄溶液中H₃PO₄的含量制得沉淀剂, AgNO₃与此沉淀剂反应制得Ag₃PO₄粉末. 当沉淀剂pH = 6时, 所制得的Ag₃PO₄粉末表现出最高的光催化降解甲基蓝和罗丹明B活性. 进一步添加KBr溶液修饰Ag₃PO₄可制得AgBr/Ag₃PO₄粉末. 该光催化剂可使阴离子染料 (如活性橙和甲基橙) 脱色. 采用适当的捕获剂考察了参与光催化降解过程的活性物种的抑制活性. 光催化反应之后, 质谱检测证实染料降解为更小的分子. 以*Chlorella vulgaris*为生物指示剂考察了处理前后染料的生态毒性.

关键词: 磷酸银; 溴化银; 光催化降解; 一步合成; 生态毒性

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*通讯联系人. 电话: +66-74288438; 传真: +66-74558841; 电子信箱: ampongsa@yahoo.com, pongsaton.a@psu.ac.th

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