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Effects of Cu(Ⅱ) or Zn(Ⅱ) on photodegradation of some toxic organic compounds in wastewater by using TiO_2 as catalyst①

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[Abstract] The effects of Cu(Ⅱ) or Zn(Ⅱ) on the photo-catalytic degradation of some organic chemicals in water, such as acetone, phenol, dyes, and tea saponin were studied. Dyes in wastewater from a textile factory can be effectively degraded by photo-catalysis with TiO_2 and ultraviolet light or sunshine, but the reaction rate could be slowed down if copper or zinc salt exists in the solution.

[Key words] photo-catalytic degradation; titanium dioxide; dye wastewater; acetone; phenol; tea saponin
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1 INTRODUCTION

Oxidation, reduction, and adsorption usually are good methods to remove organic compounds in water, and the combination of these methods is also very often used. Chlorinating oxidation was only used in a small scale due to the fact that chlorine is a hazard material and the products of chlorination may be carcinogenic. Oxidation and reduction can also be achieved with biodegradation. Bio-technique is usually an environmentally friendly way with low cost but it is very much dependent on the conditions for bacteria to grow, and it usually takes a very long time if the ambient condition is not so good and sometimes even cannot be employed if some substances in wastewater are toxic for bacteria to grow. In adsorption way solid adsorbents, such as activated carbon or activated mud, are often used. In this case the organic substances then are transferred from liquid to solid phases, which makes things even harder to handle. Therefore scientists and engineers have been looking for a new way to treat toxic components in water. The way should be environmentally friendly and economically acceptable. Ozone is a good oxidant, very effective and friendly to environment, but the production of it is an energy consuming process and ozone is very unstable.

Photo-degradation with TiO_2 as catalyst has been studied for more than 20 years and many interesting results have been recently reported for water treatment[1]. TiO_2 is nontoxic material and produced in a large scale either in metallurgy or in chemistry and pigments. It is a very promising technology from the view of resources and the environment influences. So far this technology has not been used in a large scale. More work in both laboratory and pilot scale is still needed since the catalyst processes is not fully understood especially in the case of coexistence of inorganic substances. The purpose of this work is to study the treatment of some common organic substances by the photo-catalytic technique with TiO_2. These organic substances are often environmentally toxic but not acute toxic, such as acetone, a common solvent; phenol, a common chemical met in metallurgy and is also responsible for water pollution near the iron and steel making industry; saponin, a common organic additive used often in shampoo now; and colorful wastewater from textile industry. Since metallic salts are often met together with these organic materials, their influence on the treatment of these organic materials should be studied.

2 EXPERIMENTAL

The wastewater of dyes was taken from the effluents of a textile factory, and the composition varies from day to day. Table 1 was only an example of the water.

Tea saponin is usually extracted from tea saponin

Table 1 An effluent from a textile factory

COD	BOD	SS	pH	Color	Oil	Total N	Total P
500	140	500	5	110	50	160	3.6

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seeds, which were crushed and dried in a thermo-box with the temperature being controlled at 120 ℃ till the water content was less than 10%. The dried powder was extracted with ethanol. The oil part was separated and only the water-soluble part was used for our experiments. The tea seeds were local products in Hunan Province, China, and bought from a farmer. The saponin has a hemolytic property and can kill small loaches in a few minutes. The other chemicals were bought as chemical reagent without further treatment.

The analyses of all organic substances were carried out on the bases of their ultraviolet spectra (UVSP). The UVSP were recorded with the UV spectrum meter(Model 751) made by Optical Instrument Factory, Beijing, China. The UVSP of tea saponin showed that the peak at 270 nm could be used for the analysis. The metallic salts, $Cu(Cl)_2$ and $Zn(Cl)_2$, were used as examples to study the influences of metallic salts. The Cu^{2+} has blue color and is easily analyzed at the peak of 840 nm at pH= 6. The zinc salt was analyzed by atomic adsorption spectrum. The concentrations of Cu (Ⅱ) and Zn (Ⅱ) in experimental solutions were changed from 10^{-2} g/L to 1 g/L. A reactive dye 3bx with the concentration 20 mg/L was first used to test the influence of copper and zinc salts on the photo-degradation using TiO_2 as a catalyst. The concentration of 3bx was determined by UVSP at 305 nm.

One of the two medium pressure mercury lamps with power of 300 W and 500 W was used as the sources of ultraviolet lights (UV). The advantage of this type of mercury lamp is that their wavelengths are rather close to that of the sunlight. The equipment is showed in Fig. 1. The water cooling system keeps the temperature at 40 ℃. The sampling tube can take aliquots at required time intervals.

3 RESULTS AND DISCUSSION

From Table 2 we can see that with the help of TiO_2 there is no doubt that all of the organic chemicals mentioned above were degraded very effectively. Phenol is one of the examples that it is difficult to decompose with biotechnological methods, but it can easily decomposed by photo-catalytic degradation. It also confirmed the results of the others[2, 3].

Table 2 Degraded ratio of some organic substances under UV (500 W) with H_2O_2(0.005 mol) and TiO_2(50 mg/L)

Substance	Initial concentration	Degraded ratio/%
Acetone	1 g/L	85
Phenol	25×10^{-6}	90
Dyes	COD 310	90
Saponin	50 g/L*	60

* Solution from 50 g of dried seeds

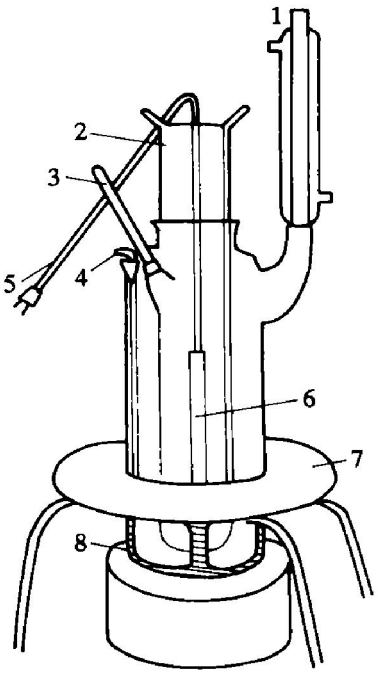

Fig. 1 Reactor system for photodegradation
1—Condenser; 2—Cooling net; 3—Thermometer; 4—Inlet for gas; 5—Plug-in for UV lamp; 6—Mercury lamp; 7—Standing; 8—Stirrer system

Acetone was also photo-catalytically oxidized to CO_2 and H_2O, via the intermediates of formic acid, which was confirmed with permanganate salt. Without the help of TiO_2, acetone can not be easily mineralized to CO_2 and H_2O[4].

Dye wastewater is usually very complicated in composition and often treated by combination of several methods[5, 6]. The dye wastewater for our research was a mixture of several dyes, so the UVSP shows a large wide peak. From the experimental results it can also be mineralized. The present treatment in a factory, Changsha, China, consists of solid adsorption by the ashes from a power generation, something like the way reported in Ref. [7]. As mentioned above it is only a transferring way and may cause additional environmental problems.

Tea saponin treated with photodegradation may be the first attempt in the literatures. It is also of interest, because it is a by-product of oil production from tea seeds and is not useful due to its toxicity. Getting rid of the poisonous components, the residues of the tea seeds can be used for animal food. Our controlled experiments with loaches showed that the tea saponin in solution (refer to Table 2) can kill all loaches in 5 min. With the photo-catalytic treatment from 20 min to 1 h the loaches survived from 20 min to as long as that in the tap water.

The metallic salts under study exert big influences on the photo-catalytic degradation of organic compounds. The degradation of organic substances

was greatly slowed down. For example, from one of our experiments the data showed that the degradation of dyes was considerably retarded, if Cu^{2+} or Zn^{2+} existed in the reactive dye 3bx with concentration more than 0. 5 g/L. To compare the decolourization situation of red dye 3bx only with the red dye plus Cu^{2+} or Zn^{2+} several dozen beakers with 100 mL 3bx solution and 20 mg TiO_2 in each were firstly prepared, then put different copper or zinc salt into the solution and make the concentration of these salts vary from zero to 1 g/L. All the beakers were taken in the sun to have sunshine and measure the colority of samples in every 30 min. Since the color for the 3bx is proportional to its concentration (c), so the colourity ratio is also the ratio of concentration expressed by c/c_0, c_0 was the concentration of stock solution 3bx (20m g/L) or the corresponding colority. The data for the dye with Cu^{2+} is listed in Table 3 and also shown in the Fig. 2. For comparison the dye 3bx only and the dye with Zn(II) were tested in the same way and the data are shown in Fig. 2.

Table 3 Colority variation of red dye 3bx with Cu^{2+} concentration and sunned time

Time in sun/min	Concentration of Cu^{2+} /(g·L^{-1})					
	0	0.01	0.1	0.5	0.75	1
0	1	1	1	1	1	1
30	1/2	1/2	1/2	1/2	1/2	1/2
60	1/4	1/4	1/4	1/4	1/4	1/4
90	1/8	1/8	1/8	1/4	1/4	1/4
120	1/32	1/32	1/32	1/4	1/4	1/4

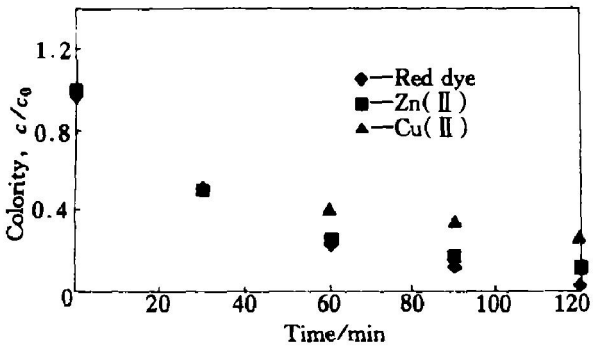

Fig. 2 Influence of Cu^{2+} or Zn^{2+} on photodegradation of red dye 3bx

The curve tendency in Fig. 2 is logarithmic, which is the symptom of first order reaction. A plot $\ln(c_0/c)$ vs reaction time is shown in Fig. 3. The rate constant k is able to get from the slope of a line in Fig. 3. The k values obtained from Fig. 3 are 0.028 min^{-1}, 0.018 min^{-1} and 0.010 min^{-1} for the red dye only, the red dye with Zn(II) and the red dye with Cu(II) respectively. From the rate constants we can see that the photodegradation for the red dye 3bx were slowed down by 2. 8 times by the copper salt and by 1. 8 times by the zinc salt. The reason might be that the catalyst was poisoned by the salts. Not only red dye 3bx but also other organic substances in the paper had their photodegradation reactions slowed down by the copper or zinc salts coexisted with the catalyst TiO_2. Reaction rate constants k values in Table 4 show the evidence of the impact of copper or zinc salt on the catalyst TiO_2.

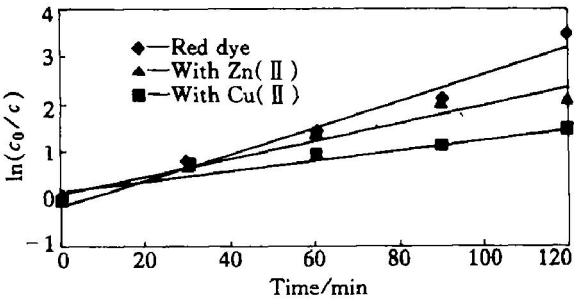

Fig. 3 $\ln(c_0/c)$ vs time in sun

Therefore to remove some salts of heavy metals like copper and zinc from dye wastewater would be helpful for photodegradation of dyes with the catalyst TiO_2.

Theoretically the e-holes produced on TiO_2 surface are responsible for the oxidation of organic substances and at the same time the electrons produced could be used for the reduction of metallic ions, for instance, $Cu^{2+} + 2e = Cu$. Unfortunately the process was not very effective as showed in Table 4. Under dark condition, the adsorption of Cu^{2+} and Zn^{2+} reaches only from 5% to 10 %. With the irradiation of UV the electrons produced could be used for the reduction and it would be expected to have more metallic ions reduced on the TiO_2 particles. It happened to a small extent, only 10 % of ions could be removed from the solution, as listed in Table 5.

Table 4 Influence of copper or zinc salt on reaction rate constant (min^{-1})

Substances	With Cu^{2+}	With Zn^{2+}	Without Cu^{2+} or Zn^{2+}
Red dye 3bx	0.010	0.018	0.028
Acetone	0.008	0.015	0.024
Phenol	0.009	0.014	0.025
Saponin	0.006	0.011	0.017

The reduction of metallic ions could be employed to accelerate the oxidation of the organic substances by the e-holes, since the electrons consumed up, then the e-holes could exist longer and more chances for the organic compounds to be oxidized. But the suspending particles of TiO_2 are very close to cubic and round shape. The oxidation reaction happens on the surface and pushes the electrons to the inside of the

particles. The metallic ions adsorbed on the surfaces could not easily take electrons from inside. Anyhow the separation of the electrons and holes does operate, as showed

Table 5 Adsorption of Cu^{2+} and Zn^{2+} on TiO_2(1 g/L of suspension)*

Initial concentration of Cu^{2+} in solution/ 10^{-6}	Initial concentration of Zn^{2+} in solution/ 10^{-6}	Concentration after adsorption in darkness/ 10^{-6}	Concentration after 1 h irradiation/ 10^{-6}
10		9.5 ±1.0	9.3 ±1.0
100		95 ±2.0	90 ±2.0
500		480 ±10.0	445 ±10.0
	10	9.0 ±0.5	8.8 ±0.5
	100	90 ±1.0	85 ±1.0
	500	490 ±5.0	440 ±10.0

* Adsorption of ions was calculated from differences of concentration under three conditions in table.

by the experiment of a photo-acoustic study[8]. Therefore a creative way to use the separated charges is worth of further study. Recently some advances and problems in such way were reported in Ref. [9, 10] for degradation of aniline via photoelectrocatalysis.

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