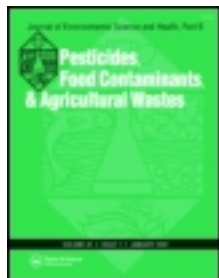


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The influence of metal ions on the photocatalytic oxidation of 2-chlorophenol in aqueous titanium dioxide suspensions

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THE INFLUENCE OF METAL IONS ON THE PHOTOCATALYTIC OXIDATION OF 2-CHLOROPHENOL IN AQUEOUS TITANIUM DIOXIDE SUSPENSIONS

Key Words: Photocatalysis, titanium dioxide, UV light, 2-chlorophenol, metal ions

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ABSTRACT

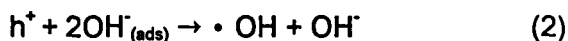
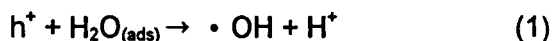
This study investigated the effect of metal ions, such as Fe³⁺, Cu²⁺, Ni²⁺, Cr³⁺ and Zn²⁺, on the photocatalytic oxidation of 2-chlorophenol with illumination of 254 nm and 365 nm UV lights. Different metal ions have individual reduction potentials, and hence, their abilities to capture electrons also differ; the rates of 2-chlorophenol decomposition vary as well. This study was made to explore the relationships between the reduction potentials of different metal ions and their photocatalytic rates of

2-chlorophenol. Results show that when the reduction potential is greater than zero, regardless of illumination wavelength, the reaction rate increases with increasing reduction potentials of the metal ions. When the reduction potential is less than zero, the reaction rates are about the same for illumination of 365 nm or 254 nm UV lights.

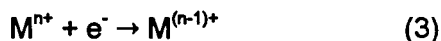
INTRODUCTION

Photocatalytic oxidation is an emergency technology using semiconductor as the catalyst to remove contaminants from polluted waters. This process not only mineralizes organic matter completely but also has the following advantages: (1) organic contaminants are rapidly decomposed by this process, (2) the sun can be used as the light source, and it is an inexhaustible source that will not diminish with use, (3) this technology may be combined with and used prior to biological processes, and (4) heavy-metal ions can be reduced using this process (Prairie et al., 1982; Sclafani et al., 1991; Butler et al., 1993; Herrmann et al., 1993; Lu et al., 1993; Brezova et al., 1995; Bekbolet, 1996).

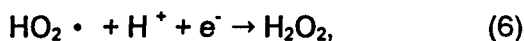
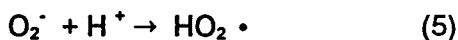
The first step in photocatalytic reaction is to illuminate a TiO_2 surface with UV light. This causes TiO_2 electrons in the valence band to vault into the conduction band leaving holes in the valence band and allowing the electrons to move about freely. Subsequently, the valence band, holes, may then form hydroxyl radicals with water molecules adsorbed on the surface of the TiO_2 , or with hydroxyl ions, as follows (Butler et al., 1993):



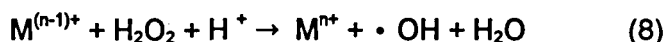
However, recombination of electrons and holes cuts down the chances of forming hydroxyl radicals, and hence reduces the photocatalytic efficiency. Generally, adding some electrophilic species such as oxygen, H_2O_2 , or metal ions such as Fe^{3+} , Cu^{2+} , and Ag^+ , usually are referred to electron scavengers to improve the reaction rate. These species may reduce electron-hole recombination, and enhance photocatalytic efficiency. The role of metal ions is shown below (Sclafani et al., 1991; Butler et al., 1993; Kawagichi et al., 1994).



Electrons are thus captured by the metal ions, and leaving holes free to form hydroxyl radicals through the reactions shown in Equation.(1)-(2), increasing the efficiency of photocatalytic decomposition of organic contaminants. H_2O_2 is also produced in the presence of oxygen through a series of reactions shown below (Sclafani et al., 1991; Butler et al., 1993; ; Brezova et al., 1995).



The reduced-state metal ions may then undergo Fenton reactions with H_2O_2 (Sclafani et al., 1991; Butler et al., 1993; Brezova et al., 1995),



Different metal ions have different reduction potentials, and their electron-scavenging abilities also differ. The rates at which organic chemicals decomposed also vary. This study discusses the relationships between the reduction potentials of different metal ions (E°) and the oxidation rates of 2-chlorophenol. Different light-source wavelengths also produce different degrees of light adsorption, especially since inhibition appears after metal ions in oxidized states adsorbing light and returning to reduced states. However, it should be noted that the process is not a catalytic reaction when metals are plated out onto the photocatalyst because the catalyst surface is being consumed. Many researchers have been reported the influence of metal ions on the photocatalytic oxidation (Sclafani et al., 1991; Butler et al., 1993; Brezova et al., 1995; Kawaguchi et al., 1994; Lu et al., 1994). Nonetheless, there has been little information for the effect of UV light on the wavelength on the photocatalytic oxidation in the presence of different metal ions. Thus, in this study, we present work that explores the influence of dissolved metal ions (Fe^{3+} , Cu^{2+} , Ni^{2+} , Cr^{3+} and Zn^{2+}) and UV wavelengths (254 nm and 365 nm) on the rate of 2-chlorophenol oxidation.

MATERIAL AND METHODS

2-Chlorophenol obtained from the Merck Company was used without further purification. The photocatalyst, TiO_2 , used in this study was

Degussa P25, 50 m²/g, with 30 nm mean particle size obtained from the Degussa Company (Germany). Metal nitrates, Fe(NO₃)₃·7H₂O, Cu(NO₃)₂·3H₂O, Ni(NO₃)₂·3H₂O, Cr(NO₃)₃·9H₂O, and Zn(NO₃)₂·9H₂O were applied to the metal solution preparation. The water used for experiments was purified using a Milli-Q/RO system (Millipore) and had a resistivity greater than 18 MΩ/cm. All other chemicals used in these experiments were of reagent grade and no further purification was performed.

The reactions were conducted in a 1.2 liter double-jacked vessel (i.d. 11cm) with a quartz cover; the reaction mixture was 1 liter in volume. Quartz cover was required for the shorter UV light wavelengths. The cut-off wavelengths by quartz is less than 200 nm, therefore, 254 nm light can pass through the cover to excite the TiO₂. The UV radiators located above the reactor consisted of two sets of UV lights, a low- pressure mercury UV lamp whose main wavelength was 365 nm (Osram, USA), and a low-pressure mercury UV lamp but with a main wavelength of 254nm (Sankyo, Japan).

For all experimental runs performed in this study, the pH of the reaction mixtures was adjusted initially. During experiments, the reaction solutions were agitated continuously with a magnetic stirrer and oxygen (99.9 % purity) was bubbled into the solutions at a constant flow rate of 50 ml/min to insure oxygen saturation, and they were kept at a constant temperature (30°C) during the reaction period. The reaction solutions

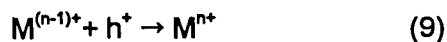
containing [2-CP]= 3.89×10^{-4} M, pH=3, $\text{TiO}_2=1$ g/L, [NaClO_4]=0.1M and [Metal ion]=1mg/L, were stirred for 1 hour before the reaction was started.

Samples were taken from the solutions at certain intervals after turning on the UV light. 2-Chlorophenol was analyzed using a gas chromatograph (HP 5890 II) equipped with an electron-capture detector and a 0.53 mmx30m DB5 column (Supelco). Potassium ferrioxalate solution was used to measure the photon flux in the reactor. The quantum yield (QY) can be defined as the ratio of the number of molecules reacting to number of the photons supplied. Based on reaction with TiO_2 - free actinometry solutions for the reactor, the flux rates were 7.2×10^{-4} einstein/min for the 365 nm UV lamp and 5.25×10^{-5} einstein/min for the 254 nm UV lamp, respectively (Demas *et al.*, 1981).

RESULTS AND DISCUSSION

Photocatalytic Oxidation of 2-Chlorophenol in the presence of Metal Ions

When electrons/holes are formed during the photocatalytic reactions, in the presence of metal ions, the oxidization and reduction of metal ions must be considered. As shown in Equation.(3), metal ions are reduced by electron acceptance. Metal ions are also oxidized by electron-donation to holes as shown below (Butler *et al.*, 1993; Brezova *et al.*, 1995).



Brezova *et al.* (1995) pointed out that when the reduction potential (E°) is less than zero, there is no obvious influence on photocatalytic

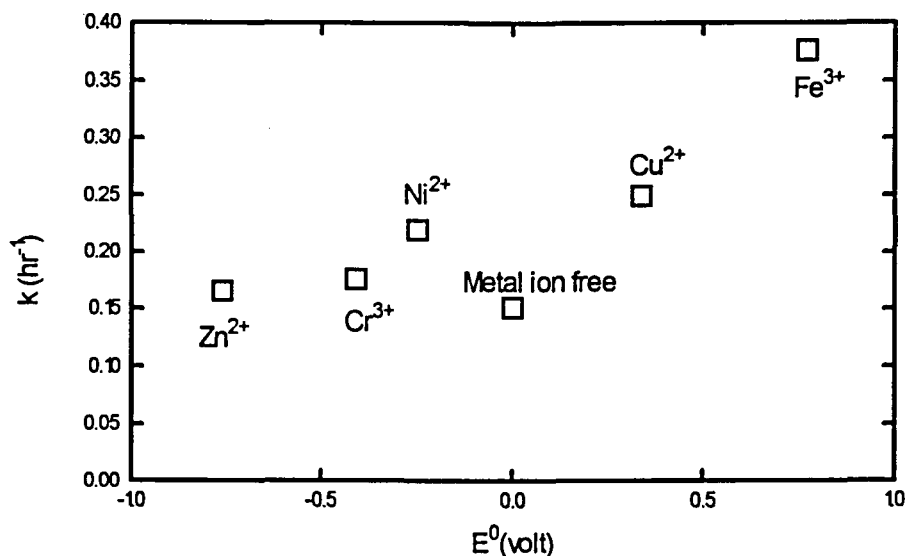


FIGURE 1

Rate constants for 2-chlorophenol decomposition versus standard reduction potentials for each metal in the 254 nm system.

oxidation. However, when the E^0 value is greater than zero, there may be positive and negative effects on photocatalytic oxidation of organic chemicals. When the amount of metal ions added in the solution is too high, photocatalytic reactions will be reversed. In addition, when the metal ions added are in a reduced state, there will also be reversal such as Mn^{2+} , Co^{2+} , Fe^{2+} (Prairie et al., 1982; Sclafani et al., 1991; Butler et al., 1993; Brezova et al., 1995; Lu et al., 1994). This may be explained in Equation (1), (2) and (9) by $M^{(n-1)+}$ exhausting h^+ , and reducing the formation of hydroxyl radicals.

As shown in Figure 1, the rate constants of 2-chlorophenol oxidation with illumination of 254 nm UV light in the presence of metal ions follow

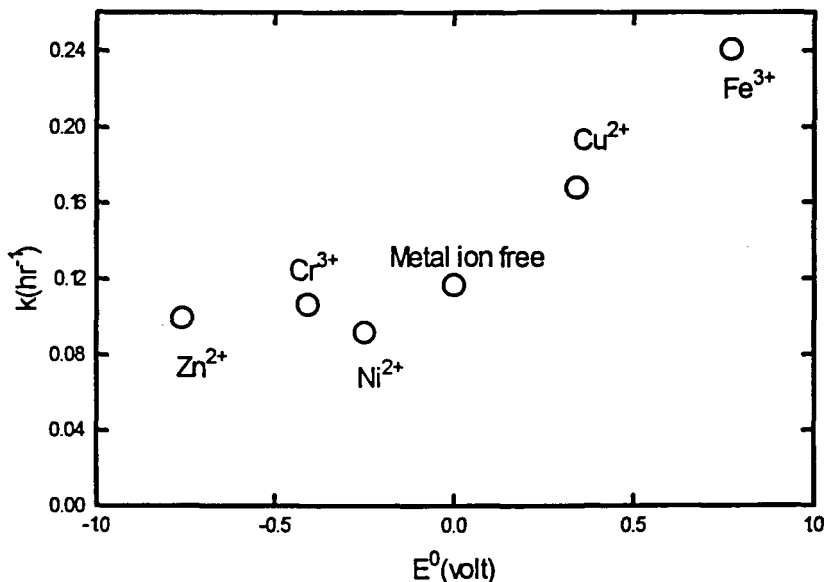


FIGURE 2

Rate constants for 2-chlorophenol decomposition versus standard reduction potentials for each metal in the 365 nm system.

the order: $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cr}^{3+} \cong \text{Zn}^{2+} \cong \text{metal ion free}$. Except for Ni^{2+} , when the reduction potentials of the metal ions are less than zero, the rate of 2-chlorophenol oxidation in the presence of metal ions is similar to that with no metal ions present. When reduction potentials are greater than zero, the reaction rate increases with increasing the reduction potentials of metal ions.

$$k = 0.2919E^0 + 0.1511 \quad (10)$$

r : rate constant of first-order kinetics (hr^{-1})

E^0 : reduction potential (volt)

Figure 2 shows the rate constants for 2-chlorophenol oxidation under 365 nm UV light illumination in the presence of metal ions. The rate of 2-chlorophenol oxidation in the presence of metal ions follows the sequence: $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{metal ion free} > \text{Cr}^{3+} \cong \text{Zn}^{2+} \cong \text{Ni}^{2+}$. When the reduction potentials of metal ions are less than zero, the rates of 2-chlorophenol oxidation in the presence of metal ions are slightly less than those in the absence of metal ions. The figure also shows that when the reduction potential is greater than zero, systems show the positively proportioned linear relationship,

$$k = 0.1601E^0 + 0.1158 \quad (11)$$

r : rate constant of first-order kinetics (hr^{-1})

E^0 : reduction potential (volt)

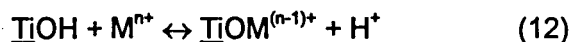
Butler et al. (1993) found that in the presence of TiO_2 , Fe^{3+} promotes the reaction rate only at pH 3. Fe^{3+} has no effect on photocatalytic degradation when the pH is greater than 5. Sclafani *et al.* (1991) pointed out that wavelengths between 200 and 600 nm are adsorbed by Fe^{2+} and Fe^{3+} , and the shorter the wavelength, the higher the light adsorption. Oxygen dissolved in the reaction solution also accepts electrons to form hydrogen peroxide through a chain of reactions titanium dioxide surface electrons. Therefore, Fenton reactions occur between Fe^{2+} and hydrogen peroxide to form hydroxyl radicals, which increases the rate of 2-chlorophenol decomposition.

However, the formation of Fe^{2+} may also cause a reaction suppression because Fe^{2+} exhausts h^+ , reducing the chances of hydroxyl radical formation. These reactions impede the photocatalytic oxidation. But in the two wavelength systems investigated in this study, Fe^{3+} received electrons, reducing the recombination of electrons with holes, and promoting the formation of hydroxyl radicals. The effect of the hydroxyl radicals formed by Fenton reactions between Fe^{2+} and hydrogen peroxide was far greater than the effect of Fe^{2+} hole-exhaustion. Thus, Fe^{3+} was generally beneficial to photocatalytic decomposition.

The reduction potential of Cu^{2+} is 0.34V, like Fe^{3+} , it can receive electrons but its ability of receiving electrons is somewhat poorer than Fe^{3+} . Hence, Cu^{2+} produced fewer hydroxyl radicals than Fe^{3+} . It can also be seen in Figure 1 and Figure 2 that the reaction rate constant in the presence of Cu^{2+} is smaller than that in the presence of Fe^{3+} . Butler *et al.* (1993) found that when TiO_2 is present, Cu^{2+} shows an obvious ability to increase the efficiency of photocatalytic decomposition only at pH value being lower than 5, but when pH is higher than 7, Cu^{2+} does not benefit photocatalytic decomposition in any way. Under these experimental conditions, Cu^{2+} may form complexes with organic matter as well so that these ions are not available to increase the oxidation reaction. Cu^{2+} also impedes the photocatalytic decomposition of phenol, especially when the concentration of Cu^{2+} is high. This is mainly because Cu^0 is deposited and adsorbed on the TiO_2 , creating a shielding effect and reducing the

ability of TiO_2 to adsorb light to form electrons and holes. This effect impedes the efficiency of photocatalytic decomposition of 2-chlorophenol.

The reduction potentials of Cr^{3+} , Ni^{2+} and Zn^{2+} are -0.41, -0.25 and -0.761V, respectively. These metal ions cannot promote the reaction efficiency by the way of increasing the efficiency of electrons/holes separation. Figure 1 and Figure 2 clearly show that the reaction rate constants of photocatalytic decomposition in the presence of Cr^{3+} , Ni^{2+} and Zn^{2+} were similar to those in the absence of metal ion. Brezova et al. (1995) found that the photocatalytic decomposition of phenol is almost at a standstill when the concentration of Cr^{3+} is high. This can be explained by the competitive adsorption between cations and phenol; when Cr^{3+} is added, the solution pH decreases with the increase in the added amount of Cr^{3+} , as shown below,



Strong adsorption occurs between the TiO_2 surface and Cr^{3+} , reducing the amount of 2-chlorophenol adsorbed on the TiO_2 surface. Thus, the photocatalytic decomposition of 2-chlorophenol is slowed down by the addition of Cr^{3+} . However, the concentration of Cr^{3+} in the present study was not so high as to induce the suppression effect.

Effect of UV Wavelength

As mentioned above, when the reduction potentials of metal ions are greater than zero, the initial rates of 2-chlorophenol decomposition will increase as reduction potentials increase. The initial rates of 2-

chlorophenol decomposition in the presence of metal ions having the reduction potentials smaller than zero are similar to those in the absence of metal ions. There are usually positive effects when reduction potentials are greater than zero, and the photocatalytic effect is enhanced with increasing in reduction potentials. The 254 nm wavelength illumination improves the photocatalytic reaction, irrespective of metal ion influence because the 254nm wavelength illumination has more energy than 365 nm wavelength. The 254 nm wavelength system also works faster, irrespective of metal ion influence perhaps because of the greater energy of the 254 nm wavelength illumination.

Figure 3 shows comparison of the initial rates of 2-chlorophenol decomposition in the presence of metal ions under 254nm and 365 nm UV light illumination, and the rate constants are listed in Table 1. The initial 2-chlorophenol decomposition quantum yields for the 254 nm and 365 nm system without metal ions were 1.88% and 0.11%, respectively. Matthews et al. (1992) also reported that the shorter-wavelength 254 illumination is more effective in increasing photocatalytic reactions than 350 nm illumination. In this case, free electrons and holes were produced closer to the TiO_2 surface since the penetration distance of photons into the photocatalyst surface is shorter for 254 nm light than that for 360 nm light.

Therefore, electrons/holes take less time in migrating to the photocatalyst surface resulting in having less time to take part in the recombination reaction before surface or near-surface reaction occurs⁽¹⁰⁾

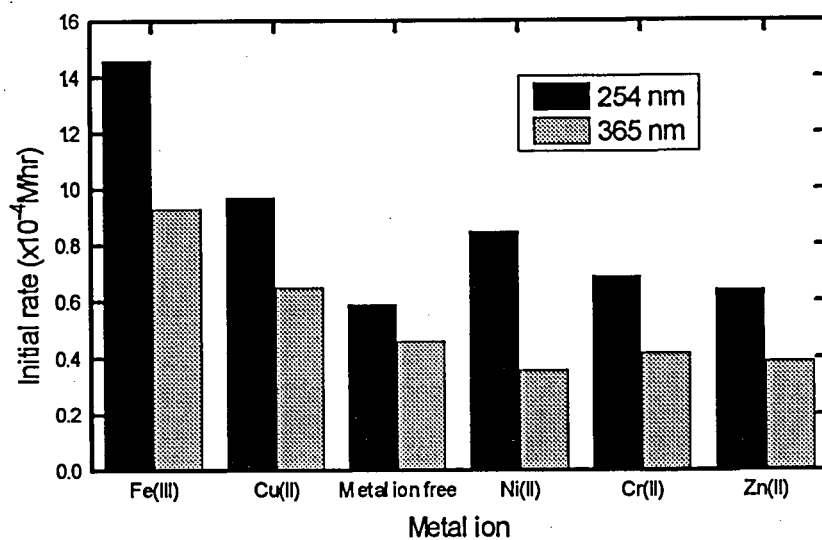


FIGURE 3

Initial rates of 2-chlorophenol decomposition in the presence of various metal ions.

TABLE 1
Rate Constants of Photocatalytic Oxidation Under Illumination of 254 Metal nm and 365 nm UV Light Illumination in the Presence of Ions

Metal ion	E^0 (volt)	k (hr^{-1})	
		254 nm	365 nm
Fe^{3+}	0.77	0.376	0.241
Cu^{2+}	0.34	0.250	0.168
Metal ion free	-	0.152	0.117
Ni^{2+}	-0.25	0.219	0.092
Cr^{3+}	-0.41	0.176	0.107
Zn^{2+}	-0.761	0.165	0.100

Light scattering is greater at wavelength 254 nm than at 365 nm, which induces an increase in photon retention time and promotes photocatalytic efficiency.

CONCLUSIONS

For the technical applications of the photocatalytic systems to the purification of water contaminated with organic pollutants, no metal ions can be added to the water. However, these ions may already be present in the waters. Thus, it is necessary to understand the effects of metal ions on the photocatalytic reaction.

In this study, when reduction potentials were greater than zero, rates of 2-chlorophenol decomposition increased with increasing the reduction potential of metal ions. However, when reduction potentials were less than zero, 2-chlorophenol decomposition rates in the presence of metal ions did not differ greatly from those observed in the absence of metal ion. The presence of electron scavengers may lessen the chances that electrons and holes will recombine to increase the concentration of hydroxyl radicals, increasing the rates of 2-chlorophenol decomposition. Metal ions also impede the photocatalytic decomposition of organic pollutants, especially when the metal ion concentrations are high. The reason is that metals are deposited and adsorbed onto TiO_2 surface, creating a shielding effect and reducing the ability of TiO_2 to adsorb light to form holes by releasing electrons. However, the concentrations of metal

ions in the present study were not so high as to induce this suppression effect. Additionally, the energy of 254nm wavelength illumination is higher than that of 360nm wavelength illumination, when using UV/TiO₂ to decompose 2-chlorophenol, better efficiencies are obtained with 254nm wavelength UV illumination.

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