行政院國家科學委員會補助專題研究計畫成果報告

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本成果報告包括以下應繳交之附件：
　　✓赴國外出差或研習心得報告一份
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　　□國際合作研究計畫國外研究報告書一份

執行單位：國立交通大學環境工程研究所

中　華　民　國　九十　年　七　月　三十一　日

行政院國家科學委員會專題研究計畫成果報告
光催化程序去除金屬離子及危害有機物(3/3)
Preparation of NSC Project Reports

中文摘要

　　本研究針對 pH3 的環境下，金屬離子 Mn^{2+}, Co^{2+}, Ni^{2+} 與 Cu^{2+} 對於光催化二氧化鈦分解 2-氯酚反應動力的影響。結果顯示，當金屬離子存在於光催化氧化分解 2-氯酚系統中，其分解動力符合 Langmuir-Hinshelwood 模式，且其中間產物對於反應速率具有抑制的作用。由理論分析可解釋初始濃度與反應速率之相關性。催化劑表面對 2-氯酚的氧化速率與金屬離子的標準氧化還原電位相關，研究結果顯示較高電位的金屬離子具有較高的表面反應速率。由 2-氯酚分解的礦化分析，推論過渡金屬與有機物分解的中間產物產生選擇性的錯合物，而表面特性與金屬離子及有機錯合物相關。由於選擇性的金屬-有機錯合物與原始有機物 2-氯酚相競爭，因此提昇起始反應有機物濃度將抑制反應速率。

關鍵詞：2-氯酚、Langmuir-Hinshelwood 動力模式、金屬離子、光催化分解、二氧化鈦

Abstract

　　The influence of transition metal ions, Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, on the rate of photocatalytic oxidation of 2-chlorophenol was studied at pH 3. The results shown that the photocatalytic oxidation of 2-chlorophenol presenting in metal ions follows the Langmuir-Hinshelwood type behavior and the reaction byproducts display an inhibiting effect on degradation rate. Results of the theoretical analysis can be used to explain the inverse initial concentration effect of 2-chlorophenol in the apparent degradation rate constant. The surface oxidation rate of 2-chlorophenol was related with the oxidation and reduction potential of metal's standard potential. The higher electron voltage of metal ion the higher reaction rate of the surface oxidative was observed. From the analysis of mineralization of 2-chlorophenol, the transition metals ions generate a complex with the 2-chlorophenol oxidizing intermediate was proposed. The surface property was related with complex formation of metal ions and organic. The selectivity formation was relate with the organic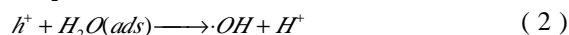-metal-complex competitive with 2-chlorophenol induces the reaction rate when increases the initial 2-chlorophenol concentration.

Keywords: 2-Chlorophenol; Langmuir-Hinshelwood model; Metal ions; Photocatalysis; Titanium dioxide.

Introduction

　　Metal ions are discharged into the ecosystem from natural and industrial sources such as continental dust, forest fires, volcanic eruptions, mining, and metal production [1]. Many hazardous organic compounds can be introduced into the environment because of several man-made activities. Chlorophenols are major pollutants in chemical industrial and should be discharged under a strict effluent limit. To degrade this compound down to a safety level is not easy by traditional wastewater treatment processes. In order to solve the problem caused by hazardous organic, appliance of advanced oxidation processes (AOPs) becomes in evidence and very promising technology, especially using titanium dioxide as a stable and inexpensive photosensitive material [2, 3].
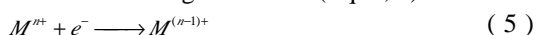
　　Corresponding photogenerate charge carries are involved in the reaction and oxidation processes on the TiO_2 surface [4]. The most important reaction in the oxygenated aqueous suspensions are the oxidation of surface water and hydroxyl groups generating reactive hydroxyl radicals, and the electron capture by oxygen generation superoxide anion- radical O_2^- [5]. These oxidation radicals are widely believed to be the most important oxidizing species in semiconductor photocatalysis system.

$$TiO_2 \xrightarrow{hv} h^+ + e^- \tag{1}$$

$$h^+ + H_2O(ads) \longrightarrow \cdot OH + H^+ \tag{2}$$

$$h^+ + 2OH^-(ads) \longrightarrow \cdot OH + OH^- \tag{3}$$

$$O_2(g) + e^- \longrightarrow O_2^-(ads) \tag{4}$$

　　Several reviews [6-8] have been published recently describing the principal mechanism of photocatalysis and presenting various examples for its applications. The addition of dissolved transition metals has been observed to increase or decrease the rate of TiO_2 photocatalytic oxidation [9-11]. This observed rate increase has been attributed to electron trapping at the semiconductor surface [5]. That will

prevent electron-hole recombination and increase the • OH radical through reactions (Eq. 2, 3).

$$M^{n+} + e^- \longrightarrow M^{(n-1)+} \tag{5}$$

$$M^{(n-1)+} + h^+ \rightarrow M^{n+} \tag{6}$$

$$M^{(n-1)+} + H_2O_2 + H^+ \longrightarrow M^{n+} + \cdot OH + H_2O \tag{7}$$

Many investigators have reported, the transition metal affect on the reaction rate by participating in Fenton's reactions or Fenton's like reaction [12-14]. Producing OH radicals in an alternative pathway for oxidation reactions. That will increase the rate of oxidizing organic compound and its intermediate. When a transition metal compound is present in the solution, a more or less rapid degradation rate of phenols occurs [15]. The photodegradation of phenols has been reported promoted by soluble metal complexes. In addition, the dissolved metal ions present in the natural and wastewater can significantly modify the purification process [10, 16]. Considerable interest is now been focused on the degradation of phenols and phenol derivatives by irradiation of aqueous TiO_2 suspensions [8, 17-19]. A large number of studies have been focused on the photocatalytic reactions promoting by the presence of metal ions. [4, 12, 20, 21]. In the presence of transition metals, a photo-Fenton-type reaction is induced and therefore the oxidation rate can be promoted. The highest phenol degradation rates were obtained in the presence of ferric ions on the photocatalytic oxidation system by previous literature [14]. However the dissolved ions Mn^{2+}, Co^{2+}, and Cu^{2+} inhibited phenol degradation in irradiated TiO_2 suspensions, which were explained by the electron transfer from metal ions to the photogenerated holes in the valence band (Eq. 6). That process probably decreases the yield of hydroxyl radicals. It has been demonstrated that a significant increase in reaction rate was observed in the presence of Cu^{2+}, Fe^{3+}, and Mn^{2+} at pH 3, with decreased rates at higher concentration of metal ions and pH values [5]. It has been observed by a number of investigators that the reaction follows an L-H rate form initial rate of organic removal in TiO_2 photocatalytic systems [2, 5].

$$r = -\frac{dC}{dt} = k_r\theta = \frac{k_r K C_0}{1 + K C_0} \tag{8}$$

Where r : the reaction rate for the oxidation of 2-chlorophenol (mole $l^{-1}min^{-1}$)

t : the reaction time

C : the concentration of organic compound (mole l^{-1})

k_r : the specific reaction rate constant for the oxidation of organic compound observed from L-H kinetics (mole $l^{-1}min^{-1}$)

θ : the fraction of surface covered

K : the equilibrium adsorption constant of organic compound

C_0 : the initial concentration of organic compound

Lu *et al.* [2] used the L-H expression to analyze the heterogeneous kinetics of photocatalytic oxidation. Theoretic deduced (Eq. 9) and observed (Eq. 10) half-life of decomposition reaction has been compared, which assumed that the reaction byproducts displayed an inhibiting effect on degradation rate. Kumar and Davis [18] also observed the inhibition, that the electron-withdrawing characteristics of the nitro group had been explained the decrease of reaction rates with increasing organic concentration.

$$t^*_{1/2} = \frac{0.5 C_0}{k_r} + \frac{\ln 2}{k_r K} \tag{9}$$

$$t_{1/2} = \frac{\ln 2}{k} \tag{10}$$

where $t^*_{1/2}$: half-life deduce form L-H kinetic model

$t_{1/2}$: first order reaction observed half-life

k : first order rate constant

In our antecedent research [22], the theoretical analysis (Eq. 11) of intermediate inference could be used to estimate half-life in different initial concentration of target compound. It could be used to calculate the real reaction rate on the surface.

$$t'_{1/2} = (0.5 + I)\frac{C_0}{k_r} + \frac{\ln 2}{k_r K} \tag{11}$$

where $t'_{1/2}$: the modification half-life deduce form L-H kinetic model

I : the summation of adsorption constant multiple exportation of reaction rate for individually intermediate.

The objective of this research is to show the influence of dissolved metal ions Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} on the L-H kinetics of 2-chlorophenol degradation in the irradiated TiO_2 suspensions by using the modified half-life model. Considering the inference of intermediate, the results of this study may assist to explain how the metal ions affect on the photocatalysis aerated solution with TiO_2.

RESULTS AND DISCUSSION

Dissolved Oxygen and pH Effect

Salvador and Gutierrez [23] have shown that the photocatalytic reaction is strongly dependent on the pH value since the number of basic OH^- sites on the TiO_2 surface is a controlling factor for the generation of $\cdot OH$. In this research, the pH was controlled below pH 3 during reaction time and actually between 3.0 to 2.7. In such narrow range, we assume that the pH has no influence on photocatalytic reaction in this experiment. The average oxygen concentration during reaction was 32 mg l^{-1}. The concentration of oxygen values during reaction times and different organic concentrations were all very close, indicating that the initial rate of 2-chlorophenol removals was not limited by oxygen availability over the range of reaction conditions.

Adsorption of Metals onto TiO_2

There are less of metal ions adsorbed on to the TiO_2 surface under the experimental conditions.

These results have been reported by others [5], whom found little adsorption of Mn^{2+} onto the TiO_2 surface below pH_{pzc}, and little adsorption of Cu^{2+} below pH 3.9. Assuming a hydrated radius of 3.42×10^{-10} M for these divalent cations, 0.1 μ mol M^{-2} amounts to approximately 2 % surface coverage.

Kinetic Influence of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}

Several reviews [5, 6, 24] had found that the presence of metal ions, M^{n+}, may generate electrons and holes in illumination, and then involved in the surface reduction and oxidation processes. The influence of dissolved metal ions on the rate of photocatalytic degradation may be estimated approximately by comparing the standard reduction potential of metal ions to the band edge potentials of TiO_2 [24]. As schematically depicted in Figure 1., the reduction of metal ions can result in the photodeposition of metal on TiO_2 surface, which can significantly change the surface properties [25]. With the changes of metal ions concentration to the photo generated holes (Eq. 3) in the valence band (Fig. 2), this process probably decreases the yield of hydroxyl radical production resulting in the lower 2-chlorophenol degradation rate in these systems.
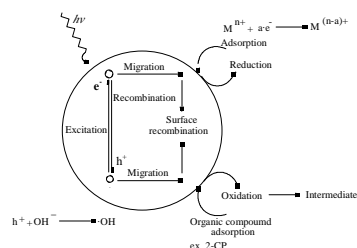

Figure 1. Schematically of metal ion in the photodeposition on TiO_2 surface.

This method could also be applied to prepare metal supported photocatalysts [25]. Both cation species M^{n+} and $M^{(n-1)+}$ may be also dissolved in water(e.g. Fe^{3+}/Fe^{2+}, Co^{3+}/Co^{2+}, Mn^{3+}/Mn^{2+}), and their reaction with generated hydrogen peroxide [5] and surface peroxide groups by the Fenton's like reaction [26], represents the additional source of hydroxyl radicals (Eq. 6, 7)

In the research of Brezová, *et al.* [4], the phenol half-life time in the irradiated TiO_2 suspensions with Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+} additions are strongly dependent on the standard reduction potential of metal, E^0, as illustrated in Table 1. It is interesting to find that in this research the dependence of 2-chlorophenol observed half-life in the applied concentration range ($7.78 \times 10^{-2} \sim 7.78 \times 10^{-1}$ mM) of four metals is only negligible (Table 2). The 2-chlorophenol half-life times in the irradiated TiO_2 systems with dissolved Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} were under given experimental conditions. Results shown that, in the lower 2-chlorophenol concentration the half times were sequence in $Co^{2+} > Cu^{2+} > Mn^{2+} >$ Metal free $> Ni^{2+}$ (7.78×10^{-2}). While the half-life time is in following sequence $Co^{2+} > Cu^{2+} > Ni^{2+} >$ Metal

free $> Mn^{2+}$ (7.78×10^{-1}) with relatively higher 2-chlorophenol concentration. It shows that with lower 2-chlorophenol concentrations ($7.78 \times 10^{-2} \sim 5.83 \times 10^{-1}$ mM), the Ni^{2+} could improve the photocatalysis reaction. Oppositely, with 2-chlorophenol concentrations in 7.78×10^{-1} mM, the Ni^{2+} could inhibit the photocatalysis reaction. The presence of other metals also showed the variant effect for the photocatalysis in different concentration. (Fig. 2.)
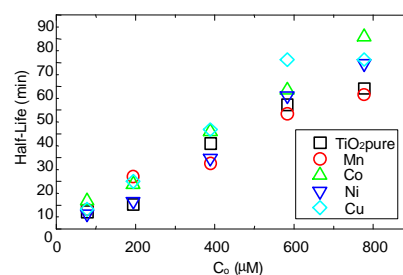

Figure 2. Observed Half-life time on the initial concentration of 2-chlorophenol at Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} ions presented. Experimental conditions: 2g L^{-1} Degussa P25, $7.78 \times 10^{-5} \sim 7.78 \times 10^{-4}$ mole L^{-1} 2-chlorophenol, 4×10^{-5} mole L^{-1} metals ion, 60 mL min^{-1} O_2-stream, 298 K, 10 mmole L^{-1} $NaClO_4$, V = 500 mL , pH = 3.

Table 1. Electron voltage of metal ions [24].

Redox system	E^0(V)
$Mn^{2+} + 2e^- \leftrightarrow Mn$	-1.180
$Ni^{2+} + 2e^- \leftrightarrow Ni$	-0.763
$Co^{2+} + 2e^- \leftrightarrow Co$	-0.277
$Cu^{2+} + e^- \leftrightarrow Cu^+$	0.150
$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.340

Table 2. Half-life of 2-chlorophenol in the photodegradation with TiO_2 presented metal ions.

Con. (mM)	7.78×10^{-2}	1.94×10^{-1}	3.88×10^{-1}	5.83×10^{-1}	7.78×10^{-1}
Metal ions			Half-life time (min)		
Metal free	7.3	26.6	36.1	52.3	59.2
Mn^{2+}	8.2	22.2	27.6	48.5	56.6
Ni^{2+}	6.3	11.6	29.6	56.0	69.5
Co^{2+}	11.8	18.8	40.9	58.4	80.9
Cu^{2+}	8.3	20.0	41.8	71.2	71.3

Verification of L-H Model

Figs. 3 to 6 present the half-life time of four species of metal ions under different initial 2-CP concentration. The points represent the observed value derived from first-order reaction, the solid lines represent the experimental results calculated by theoretical model equation 9, and the dash lines are derived from modified model equation 11. The results from Fig. 4-7 show that the relation-line derived from modified model involved the influence caused by intermediates, therefore is much closer to experimental results. This conclusion is consistent with the antecedent study [22]. By the described above, we can simplify the influence of intermediate and obtain equation 12. The constant *I* thus can account for the general effect caused by intermediates.

4

$$\left[\frac{(0.5+I)}{k_r} - \frac{0.5}{k_r}\right]/\frac{0.5}{k_r} = 2I \qquad (12)$$

Compare the relation-line derived from modified model equation 11 and the relation-line derived from equation 9, we found the increasing slope is proportional to the influence caused by intermediates. The more the deviation the higher the inhibiting effect caused by the intermediates. Table 3 showed that Mn^{2+} is affected most by the inhibiting effect of intermediates, Co^{2+} is less affected than Mn^{2+} by the inhibiting effect of intermediates, and Cu^{2+} shows the lest influence by the intermediates. Derived from the model, the reaction rate on the catalysis surface is in the following sequence: $Mn^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+}$. This tendency shows good correlation with redox potentials but less correspondence with the reaction rate of the overall reaction. This is because the overall reaction rate not only depends on the reaction rate on the catalysis surface but also associates with surface coverage percentage. On the other word, the surface adsorption rate K is related to the initial concentration (Eq. 8). From L-H model, as described above that the effect of degradation rate by the presence of metal ions is strongly depending on the initial concentration. The complex reaction between metal ions and organic compounds has been proposed in previous literature [26].
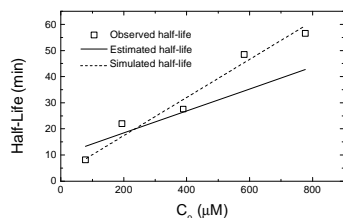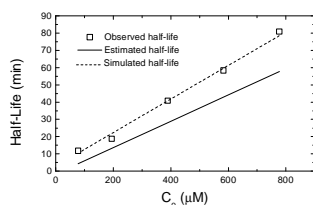

Figure 3. Dependence of observed and estimated Half-life time on initial concentration of 2-chlorophenol at Mn^{2+} ion presented. Experimental conditions: 2g L^{-1} Degussa P25, $7.78 \times 10^{-5} \sim 7.78 \times 10^{-4}$ mole L^{-1} 2-chlorophenol, 4×10^{-5} mole L^{-1} Mn^{2+}, 60 mL min^{-1} O_2-stream, 298 K, 10 mmole L^{-1} $NaClO_4$, V = 500 mL, pH = 3.

Figure 4. Dependence of observed and estimated Half-life time on initial concentration of 2-chlorophenol at Co^{2+} ion presented. Experimental conditions: 2g L^{-1} Degussa P25, $7.78 \times 10^{-5} \sim 7.78 \times 10^{-4}$ mole L^{-1} 2-chlorophenol, 4×10^{-5} mole L^{-1} Co^{2+}, 60 mL min^{-1} O_2-stream, 298 K, 10 mmole L^{-1} $NaClO_4$, V = 500 mL, pH = 3.
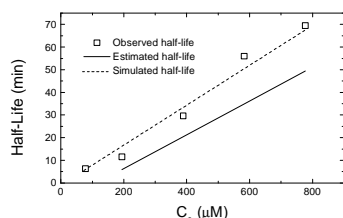

Figure 5. Dependence of observed and estimated Half-life time on

initial concentration of 2-chlorophenol at Ni^{2+} ion presented. Experimental conditions: 2g L^{-1} Degussa P25, $7.78 \times 10^{-5} \sim 7.78 \times 10^{-4}$ mole L^{-1} 2-chlorophenol, 4×10^{-5} mole L^{-1} Ni^{2+}, 60 mL min^{-1} O_2-stream, 298 K, 10 mmole L^{-1} $NaClO_4$, V = 500 mL, pH = 3.
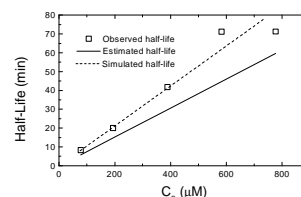

Figure 6. Dependence of observed and estimated Half-life time on initial concentration of 2-chlorophenol at Cu^{2+} ion presented. Experimental conditions: 2g L^{-1} Degussa P25, $7.78 \times 10^{-5} \sim 7.78 \times 10^{-4}$ mole L^{-1} 2-chlorophenol, 4×10^{-5} mole L^{-1} Cu^{2+}, 60 mL min^{-1} O_2-stream, 298 K, 10 mmole L^{-1} $NaClO_4$, V = 500 mL , pH = 3.

Table 3. Slope in the different with real and estimated data, surface reaction constant kr.

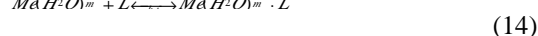| Metal ion	$t'_{1/2}$	$t^*_{1/2}$	kr (mmole min^{-1})
	Slope		
Mn^{2+}	0.069	0.042	11.9
Co^{2+}	0.100	0.076	6.55
Ni^{2+}	0.096	0.075	6.68
Cu^{2+}	0.099	0.077	6.47

Kinetics of Complex Formation

We have generally assumed that the complex reaction is fast and that equilibrium is attained. The classical example of a kinetically inert complex is the hexamine coblt(III) cation in acid solution [27]. According to the large thermodynamic driving force, it takes several days to break down the complex. The reaction rate between a metal ion and a ligand usually is partly dependent on the rate at which water leaves and enters the coordination sphere of the ion, the water exchange. For cations and ligands, this rate decreases from this limit $10^7 \sim 10^9$ per second to the smaller highly charged ions 10^4 per second. (see Table 4)

Table 4. Rate constants for Water Exchange [27].

Metal ion	k_w (s^{-1})
Cu^{2+}	1×10^9
Mn^{2+}	3×10^7
Co^{2+}	2×10^6
Ni^{2+}	3×10^4

Thus the binding of a ligand to a metal ion can generally be written

$$Me(H_2O)_m^{n+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Me(H_2O)_m^{n+} \cdot L \qquad (13)$$

$$Me(H_2O)_m^{n+} \cdot L \underset{k_{-w}}{\overset{k_w}{\rightleftharpoons}} Me(H_2O)_{m-1}L^{n+} + H_2O \qquad (14)$$

The rate of the formation of the complex $Me(H_2O)_{m-1}L^{n+}$ is given by

$$\frac{d[Me(H_2O)_{m-1}L^{n+}]}{dt} = k_{-w}[Me(H_2O)_m^{n+} \cdot L] \qquad (15)$$

The substitution rate of water in the complex $Me(H_2O)_m^{n+} \cdot L$ is similar to that of $Me(H_2O)_m^{n+}$.

The rate of change of $[Me(H_2O)_m^{n+} \cdot L]$, at steady state, is

$$\frac{d[Me(H_2O)_m^{n+} \cdot L]}{dt} = k_1[Me(H_2O)_m^{n+}][L] - (k_{-1} + k_{-w})[Me(H_2O)_m^{n+} \cdot L] = 0 \quad (16)$$

where equation 17 under conditions of $k_{-1} \gg k_{-w}$ gives

$$[Me(H_2O)_m^{n+} \cdot L]_{ss} = \frac{k_1}{k_{-1}}[Me(H_2O)_m^{n+}][L] \quad (17)$$

where $k_1/k_{-1} = K_{os}$ (K_{os} = outer sphere or ion pair complex formation equilibrium constant). Equation 16 can now be rewritten:

$$\frac{d[Me(H_2O)_{m-1}L^{n+}]}{dt} = k_{-w}K_{os}[Me(H_2O)_m^{n+} \cdot L] \quad (18)$$

or in a general notation (aqua ions omitted)

$$\frac{d[MeL]}{dt} = k[Me][L] \quad (19)$$

where $k = k_{-w}K_{os}$. In other words, simple complex formation depends on the energetic of the interaction (ion pair constant, K_{os}) and, above all, on the water exchange rate of the metal ion.

The dissociation rate of a complex is usually inversely proportional to the stability of the complex, K_{ML}:

$$-\frac{d[MeL]}{dt} = \frac{k}{K_{ML}}[MeL] = \frac{k_{-w}K_{os}}{K_{ML}}[MeL] \quad (20)$$

Table 3 showed that among four species of metal ions, Cu^{2+} has highest water exchange rate constant, and Ni^{2+} shows the lowest water exchange rate constant. This phenomenon indicates that Cu^{2+} complex with ligands more than other metal ions. Taken together this phenomenon and the description in the previous section, both of theories help to explain that Cu^{2+} has the lowest reaction rate on the catalysis surface but highest reaction rate on the overall reaction. Therefore we predict that the complex of Cu^{2+} and ligands can enhance the surface adsorption rate.

Degradation of Total Organic Carbon

The photocatalytic degradation of 2-chlorophenol could be described by the following overall reaction stoichemistry.

$$ClC_6H_5OH + 13O_2 \xrightarrow{h\nu} [\text{intermediates}] \xrightarrow{h\nu} 6CO_2 + HCl + 2H_2O \quad (21)$$

Therefore, the mass of intermediates can be gained by deducting the theoretical TOC of 2-CP from the analyzing TOC. And these intermediates may compete with original organic compounds to reduce the reaction rate. From the observed of degradation rate of TOC for the reactions, the residue of intermediate were the objective of the increasing rate for the complex formation (Fig. 7). If the presence of all kinds of metal ions have the similar impact on the photocatalysis reaction, the existing of the intermediates should show inhibiting effect on reaction rate. Nevertheless, our study revealed that there is relatively higher intermediates been produced with Ni^{2+} present in the 2-CP photocatalysis reaction. As described in previous section, the photocatalysis reaction rate received lest effect from intermediates with Ni^{2+} present in the solution. This result apparently conflicts with the previous hypothesis. Accordingly, to explain this phenomenon rationally, we assumed that

in the photocatalysis reaction, metal ions have selectivity reaction with intermediates. Based on this assumption, we predict Mn^{2+} and Cu^{2+} have stronger selectivity reaction with intermediates, therefore the two reactions received more inhibiting effect by intermediates than the reaction with Ni^{2+} present in the solution.
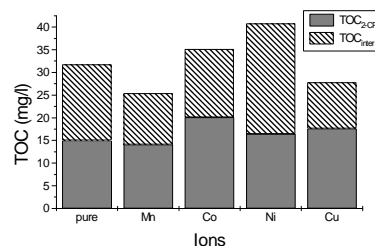

Figure 7. TOC concentrations of intermediate and residual 2-chlorophenol after 90 min reaction time in difference metal ions. Experimental conditions: 2g L^{-1} Degussa P25, 7.78×10^{-4} mole L^{-1} 2-chlorophenol, 4×10^{-5} mole L^{-1} metal ions, 60 mL min^{-1} O_2-stream, 298 K, 10 mmole L^{-1} $NaClO_4$, V = 500 mL , pH = 3.

CONCLSIONS

Under our study circumstance, the reaction of four species of metal ions in photocatalysis reaction for 2-CP in a suspended TiO_2 system can be expressed by first-order equation. Besides, our study showed there is no apparent relationship between reaction rate and metal ions, instead, the reaction rate is strongly related to initial organic concentration. Based on the L-H model and the derived model, we can modify the bias caused by the variance of organic compounds. Also, we predict that the reaction rate on the catalysis surface is associated with the redox potential of metal ions. In our study, The presence of Mn^{2+} ions show the fastest reaction rate in photocatalysis reaction for 2-CP in a suspended TiO_2 system, while Cu^{2+} has the slowest reaction rate. The overall reaction rates not only dependent on the species of metal ions but also related to the catalysis surface characteristic. Thereby, we found the discord effect on the catalysis surface is caused by the presence of different species of metal ions. The different hydroxyl coefficient of metal ions showed different complex characteristics with ligands, thus causing the change of catalysis surface properties. And hence created the selectivity reaction toward organic compounds.

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