1 The mutual influence of speciation and combination of
2 Cu and Pb on the photodegradation of dimethyl
3 o-phthalate
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Abstract

Specific industrial application of dimethyl o-phthalate (DMP) in ore flotation has led to DMP-heavy metals combined pollution, which causes the abiotic degradation of DMP in the environment more complex. This study focused on the effect of Cu and Pb on photodegradation of DMP. The major mechanism of inhibiting effect of Cu and Pb on degradation of DMP involved their speciation and combination. It was found that the Cu (5mg/L, $I=95.4\%$) and Pb (5mg/L, $I=100\%$) could inhibit the photodegradation of DMP. The main species that inhibit the DMP degradation were $\text{Cu}(\text{OH})^+$ and $\text{Pb}(\text{OH})^+$, respectively. The intensity of the UV-Vis absorbance of DMP was obviously related to the concentration of Cu^{2+} ($R^2=0.8655$) or Pb^{2+} ($R^2=0.9019$) ions. Fluorescence quenching effect of Cu^{2+} ($R^2>0.9946$), Pb^{2+} ($R^2>0.6879$) on DMP is strongly correlated with the concentration of ions. And the equilibrium membrane dialysis experiment has also verified the combination of DMP and Cu, Pb. These results are useful to understand the effect mechanism of metal species on the photodegradation of organic chemicals.

1. Introduction

Phthalic acid esters (PAEs) are widely abundant industrial chemicals produced in large quantities for nearly 50 years (Fromme et al., 2002). These chemicals have been used as additives in the production of plastics, polyvinyl acetates, celluloses, polyurethanes, and polyvinyl chloride (Fang et al., 2007). Because they are not chemically bound to the polymeric matrix, PAEs can unintentionally enter the environment during the manufacturing processes or by leaching from final products (Chi and Gao, 2015). In addition, as an important ester-foaming agent, which has been widely used for decades in China and the former Soviet Union, PAEs can improve the recovery efficiency of copper during the flotation of copper silicate (Zhu, 1993). Different PAEs flotation reagents include 1,2-Benzenedicarboxylic acid, 1,2-bis(3-methoxypropyl) ester, dimethyl o-phthalate (DMP), 1,2-Benzenedicarboxylic acid, 1,2-bis(2-ethoxyethyl) ester and others. Specific industrial application in ore flotation has led to PAEs-heavy metals combined pollution in the environment (Li et al., 2009). PAEs have been etiologically associated with several human diseases, including disorders of the neuroendocrine system, and skeletal dysfunction (Eriksen et al., 1988).

DMP is a typical PAEs flotation reagent for lead and zinc sulphide ore flotation (Zhu, 1993). Xu et al. (2010) found that DMP could hardly be degraded by sunlight without catalyst. Many researchers also find that the DMP can be degraded by UV-photodegradation and various catalytic degradation (Feng et al., 2012; Zhao et al.,

2004). Nevertheless, these studies have not considered the influence of the metal elements on degradation of DMP. And some studies have shown that metal ions have the dominating effect on the degradation of compounds. The imazapyr degradation rate decreases with the increasing concentration of Cu^{2+} (Quivet et al., 2006). Sancho et al. found that lead and copper can stabilise metamitron by complexation, thus increasing the residence time of the pesticide in the environment, and hence its toxicity (Sancho, 1997, 1999). Cr, Co, Mo, Cu were found to exert inhibition effects on aquatic photodegradation of organophosphorous pesticides sensitized by humic acid (Mamoru and Katsura, 2001). In addition, in aquatic environment, speciation of metal ions varies with the pH of aquatic environment (Florence, 1983). DMP exists as DMP-metal ion complexes rather than independent chemical in the environment (Li et al., 2009). Therefore, it is necessary to investigate the effect of heavy metal ions on DMP photodegradation.

The present work examines the mechanism of copper and lead effects on the photodegradation of DMP. The effect of pH and concentration of Cu^{2+} and Pb^{2+} on DMP photodegradation were evaluated respectively using reaction kinetic models. The influence of different metal species of Cu and Pb on DMP photodegradation was examined as well. In addition, the effect of adding metal ions (Cu^{2+} and Pb^{2+}) on the emission properties (fluorescence quenching measurements) and absorbance properties (UV-Vis absorbance spectra) of DMP have been studied in water, which indicate the combination of DMP and heavy metal. Also, an equilibrium membrane dialysis experiment was conducted and the difference of metal ions' concentration

inside and outside the membrane verified that the combination of DMP and heavy metals.

2. Methodology

2.1. Chemicals and preparation of samples

Dimethyl o-phthalate (DMP) (99.5% purity, CAS: 131-11-3) was obtained from Beijing Chemical Reagents Company (Beijing, China). All solutions were prepared using 18 MΩ deionized distilled water. For pH adjustment, 0.1 mol/L HCl and 0.1 mol/L NaOH were used. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and PbCl_2 were used for preparation of Cu^{2+} and Pb^{2+} solutions. All experiments were carried out in triplicate.

2.2. UV-photo degradation

Ultraviolet degradation simulation experiments were carried out in Photochemical Reactors BL-GHX-II with a 500W UV-A mercury lamp at stable 30°C. Five different pH values of the solution were used ranging from 4.0 to 10 for the kinetic studies at the initial DMP concentration of 100 mg/L. The Dark control tests at different pH without UV-radiation indicated no volatilization or other major decay of DMP in the laboratory. The nominal concentrations of Cu^{2+} and Pb^{2+} were used 0.5, 1.0, and 5.0 mg/L to study the influence of these heavy metals on photodegradation of DMP. Adjusting the pH of the DMP solutions with 5 mg/L metal ions to retain one major species of Cu(II) or Pb(II) to examine the influence of different speciations. The concentration of DMP was carried out with a Shimadzu LC-20A

(chromatographic column: Athena C18-wp 100A 4.6 × 150 mm, 5 μm). The mobile phase was methanol/water (9:1, v/v) at a flow rate of 0.7 mL/min. The UV detecting wavelength was 224 nm (Vega and Bastide, 2003).

2.3. UV-Vis absorbance spectra

The UV-Vis absorption spectra of DMP (100 mg/L) solution with a series of concentration of Cu²⁺ and Pb²⁺ (0.5, 1.0, 10, 100, and 200 mg/L) were also measured from 200 to 400 nm at room temperature.

2.4. Fluorescence quenching measurements

Fluorescence measurements were performed with a Hitachi Spectrofluorimeter Model F-2700 (700 V) equipped with a 150 W xenon lamp and a thermostat bath, using a 1.0 cm quartz cell. The widths of both the excitation and emission slits were set at 2.5 nm. The fluorescence emission spectra were then measured at room temperature from 290 to 450 nm, using an excitation wavelength at 282 nm. The concentration gradient of Cu²⁺ and Pb²⁺ was 0.5, 1.0, 10, 100, and 200 mg/L, and concentration of DMP is 100 mg/L in solution. Solutions were diluted 10-times before measurement. The appropriate blank corresponding to the buffer solution was subtracted to correct for background fluorescence.

2.5. Equilibrium membrane dialysis

Equilibrium membrane dialysis which has been described earlier (Chen et al., 2006) is a common method used to research combination properties of compound or

organic matter. It was employed to verify the combination between DMP and heavy metals in this study. A dialysis bag having a molecular weight cut off of 100 Daltons was placed in boiling water for 10 min. 3 mL DMP solutions that have been photodegraded for different periods were added into dialysis bags, respectively. Put the dialysis bags into a beaker filled with 1 mg/L Cu^{2+} or Pb^{2+} solution. And then sealed the beaker with a membrane and oscillated for 24 h.

Determinations of heavy metal concentrations inside and outside of the dialysis bag were carried out using an ICP spectrometer (Thermo iCAP 7000 SERIES, USA).

3. Results and discussion

3.1. Rate constants for the degradation of DMP and the associated effects of pH

The photolysis of DMP followed pseudo-first-order kinetics ($C_T = C_0 e^{-kt}$) in three general stages (Fig. 1), of which the second stage played a major role in DMP photodegradation. The influence of pH on DMP degradation during the three stages was evident, particularly during the second-stage (Table 1). The pH value of the mixture did not change during the experimental period.

During the first stage, the rate constants ranged from 0.00 to 0.43 min^{-1} . The rate constant in the first stage was the greatest at pH 8.5, and was higher at pH 4.0 than at pH 7.0. The decay rate is suppressed at pH 5.5 and pH 10. It is believed that the degradation of DMP during the first stage represents a mixed process including hydrolysis, direct photolysis and acid-base catalyst photolysis (Lau et al., 2005). Both acidic and alkaline environments can promote the hydrolysis of DMP (Lertsirisopon

et al., 2009). An alkaline solution, however, can inhibit the photodegradation of DMP, as discussed below.

During the second stage, DMP is probably transferred to its corresponding excited states (singlet or triplet) upon UV absorption at 365 nm (Grossmann et al., 2001) which is then dominated by either direct photolysis or acid-base catalyst photolysis. DMP degradation rates decreased with increasing initial pH values. Under the strong alkaline conditions (e.g., pH 10), DMP was hardly degraded. The possible causes for the decreased DMP degradation rate at increasing pH values are: (a) the decreasing oxidation potential of OH with increasing pH (Buxton et al., 1988), (b) the rapid consumption of OH in alkaline solution according to reaction 1 (shown below), in which $k_{\text{forward}} = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ and $k_{\text{back}} = 9.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ (Hamdaoui and Naffrechoux, 2008); Also, the consumption of OH happened in reaction 2, owing to the presence of the conjugate base of H_2O_2 , HO_2^- , in alkaline conditions ($\text{pK}_a = 11.6$), in which the rate constant, $k_{\text{HO}_2^-}$ is $7.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (cf. $k_{\text{H}_2} = 2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) (Buxton et al., 1988):

However, the decay rate of DMP increased in acidic solutions, which may be due to the involvement of indirect photolysis via the acid catalyzed photo-hydrolysis, analogous to the traditional hydrolysis processes that can be catalyzed in acidic

solutions (Lau et al., 2005). The workers found that the highest rate of dibutyl phthalate decay was at the lowest initial pH level which is 3. In this study, the highest rate of DMP decay was at pH 4.

During the third stage, the DMP degradation rate significantly reduced. The rate retardation attributed to the combined mechanisms as follows. (i) The generation of intermediates in the solution will compete for the photons which retards the further degradation of DMP. Theoretically, this effect will become more and more dominant as the intermediates accumulate to higher levels. (ii) Some of the intermediates and/or photolysis end products may absorb light, thereby attenuating the incident UV intensity available for photodegradation (Chu and Jafvert, 1994).

Fig. 1 here

Table. 1 here

3.2. The influence of heavy metals for DMP photodegradation

Figure 2 shows that the degradation of DMP at natural pH can be inhibited by the presence of either Cu^{2+} or Pb^{2+} . Kinetic studies showed that the DMP degradation was retarded by increasing the concentrations of these heavy metal ions. In fact, the effect of Pb was more apparent in comparison with Cu (Table 2), as evidenced by the higher inhibitory rate. The inhibition mechanism of heavy metal ions for the photodegradation of organics (such as DMP) probably involves more than one

complex reaction.

Fig. 2 here

Table. 2 here

Addition of Cu^{2+} or Pb^{2+} decreases the reduction of O_2 by decreasing the conduction of electrons, subsequently blocks the formation of reactive oxygen species ($\text{O}_2^{\cdot-}$, $\cdot\text{OOH}$, $\cdot\text{OH}$), and hence suppresses the photodegradation of organic compounds under irradiation (Chen et al., 2002). In addition, Quivet et al. (2006) also reported that metal complexation inhibited the degradation of imazapyr, increase the durability of organic compounds in the environment. And results of analog computation indicated that the structures of complex (imidazole and copper(II)) were stable five-membered ring. In the complex formation process, electrons transferred from imidazole compounds to copper(II) (Ang, 2013). Still, exciplex were formed with metals and excited state organic compounds. In this formation process electron or energy transferred from organic compounds to metal ions. So the photodegradation of organic matter are suppressed (Hoffman et al., 1989; Linschitz and Pekkarinen, 1960). However in previous studies (Feng et al., 2012; Navarro et al., 2011), researchers focused on the catalytic effects of heavy metals on photodegradation of DMP under certain conditions. So we conducted further studies to investigate the influencing mechanism of Cu and Pb on photodegradation of DMP.

3.3. The inhibiting mechanism of heavy metals for DMP photodegradation

3.3.1 The influence of metal speciation on photodegradation of DMP

The quantity of the free ions of Cu or Pb in de-ionized water with increasing pH were predicted with the Visual MINTEQ software (Fig. 3). Results indicate that metal specie changes under various pH conditions (Jensen et al., 1999).

There is only one form in copper or lead solution by adjusting the pH to 3, 8, 10, 12. The effect of different species of Cu and Pb on DMP degradation are shown in Supporting Information Fig. S1 and Fig. S2, respectively. The degradation rate constant and the inhibition rate were summarized in Table 3. It shows that inhibition rate of Cu(OH)^+ is 51.7%, while Cu^{2+} and $\text{Cu(OH)}_2(\text{aq})$ is -17.6% and -76.2% respectively. The degradation of DMP can be restrained by Cu(OH)^+ , while Cu^{2+} and $\text{Cu(OH)}_2(\text{aq})$ promote the degradation. It indicates that metal speciation which slows down photodegradation process is Cu(OH)^+ rather than Cu^{2+} . O_2 molecules can transform into H_2O_2 in water (Chen et al., 2002) which consequently can react with Cu^{2+} to generate $\cdot\text{OH}$ efficiently (Litter, 1999). Therefore, Cu(OH)^+ hinders the consumption of O_2 molecules by conducting electrons, thus inhibiting the formation of H_2O_2 . This reaction further blocks the formation of reactive oxygen species ($\text{O}_2^{\cdot-}/\cdot\text{OOH}$, $\cdot\text{OH}$) to inhibit the photodegradation of DMP. Literature has reported that the major inorganic copper group divided into fresh water is Cu^{2+} , Cu(OH)^+ , $\text{Cu(OH)}_2(\text{aq})$ and $\text{Cu(CO}_3)_2^{2-}$ (Wang et al., 2014). So Cu(OH)^+ is likely to increase the stability of the DMP in nature. Pb shows the same phenomenon with Cu. Pb^{2+} and $\text{Pb(OH)}_2(\text{aq})$ promote the decay of DMP. While, Pb(OH)^+ retards the degradation of

DMP. Therefore, it is safe to conclude that metal species that retard the photodegradation of DMP in water are $M(OH)^+$ such as $Cu(OH)^+$, $Pb(OH)^+$. As for $Cu(OH)_3^-$ and $Pb(OH)_3^-$, they only exist in the alkaline solution. Relative to the inhibitory of alkali solution without metal ions, they did not show a special role.

But inhibition rates of $Cu(OH)^+$ (51.7%), $Pb(OH)^+$ (11.6%) are less than that of Cu (95.4%), Pb (100%), respectively. It indicates that the inhibition of degradation is not only caused by $Cu(OH)^+$. Other reasons maybe involve the reactions.

Fig. 3 here

Table. 3 here

3.3.2 The influence of heavy metals on UV-Vis absorbance of DMP

The UV-Vis titration data suggested that the intensity of the absorbance at λ_{max} 230 nm increased gradually with the increase of Cu^{2+} or Pb^{2+} concentration (0-200 mg/L) in DMP solution (100 mg/L) (Fig. 4). Plotting of $1/(A-A_0)$ versus $1/[Cu^{2+}]$ showed a linear relationship (Fig. 5). The binding constant of the DMP with Cu^{2+} and Pb^{2+} were calculated with Benesi-Hildebrand equation (Navarro et al., 2011).

$$1/(A-A_0) = 1/(A_{max}-A_0) + 1/(A_{max}-A_0) K[C] \quad [3]$$

Here, A_0 , A , and A_{max} is the absorbance of DMP, measured with excess amount of

Cu^{2+} or Pb^{2+} at 230 nm, K is the complexing constant and $[C]$ is the concentration of Cu^{2+} or Pb^{2+} ions. The intensity of the UV-Vis absorbance is obviously related to the concentration of Cu^{2+} ($R^2=0.8655$) or Pb^{2+} ($R^2=0.9019$) ions. The complexing constant of Cu^{2+} and Pb^{2+} are 454.8 and 38.77, respectively. It is concluded that the inhibitory effect of Cu^{2+} or Pb^{2+} on DMP photodegradation may be associated with the structure of DMP complex. In a complex form, DMP may be more resistant to photodegradation. DMP, as a kind of lead and zinc sulfide ore foaming agent, is widely used in mining areas in China and the Former Soviet Union (Zhu, 1993). Therefore, in the mining area, such as tailings and the surrounding environment, DMP can combine with Cu^{2+} or Pb^{2+} , which reduces the photodegradation rate of DMP and consequently promote its persistence in the environment.

Fig. 4 here

Fig. 5 here

3.3.3 Fluorescence quenching effect of metals

Fluorescence spectroscopy is one of the important physical properties of excited state chemical compound (Fu et al., 2007). The effect of metal ions act on DMP was studied by fluorescence emission (Fig. 6). The fluorescence quenching process is expressed by Stern-Volmer equation (Shiraishi et al., 2007).

$$F_0/F = 1 + K_s[Q] \quad [4]$$

Here, K_s is the Stern-Volmer quenching constant, F_0 is DMP monomer fluorescence intensity, F is fluorescence intensity measured with excess amount of Cu^{2+} or Pb^{2+} at 340 nm and $[Q]$ is the concentration of Cu^{2+} or Pb^{2+} ions. Fluorescence intensity declined gradually with the increasing concentration of Cu^{2+} or Pb^{2+} , as shown in Fig. 6. The data explicitly showed that Cu^{2+} and Pb^{2+} have fluorescence quenching effect on DMP. The effect of Cu^{2+} ($K_{s1}=0.923 \times 10^{-2}$, $R^2=0.9946$; $K_{s2}=0.031 \times 10^{-2}$, $R^2=0.9956$) correlated with the concentration of ions is stronger than that of Pb^{2+} ($K_{s1}=0.564 \times 10^{-2}$, $R^2=0.7686$; $K_{s2}=0.004 \times 10^{-2}$, $R^2=0.6879$). The quenching effect may be due to the complexation between DMP and Cu^{2+} or Pb^{2+} , because fluorescence quenching is caused by ground-state complex formation between fluorophores and quenchers (Chen et al., 2015). When the concentration of metal ions was greater than 10 mg/L, K_s were approximate to zero. It suggests that quenching effect reaches balance after the concentration of metal ions reaches to a certain level.

Fig. 6 here

3.4. The effect of the photodegradation of DMP on the combination between DMP and heavy metals

Fig. 7 is the change trend in the concentration of heavy metal ions in and out of dialysis bag with the photodegradation of DMP. It shows that Cu^{2+} and Pb^{2+} could

freely pass 100 Daltons membranes. For both Cu^{2+} and Pb^{2+} , the concentration in the dialysis bag is higher than that outside, indicating that Cu^{2+} and Pb^{2+} in the water can be combined with DMP. Some studies have shown that metals can combine with compounds: Cd, Zn, Cu, Ca, Ni can change the different degradations processes of imazaquin (Barkani et al., 2005), dithiocarbamate fungicides (Weissmahr and Sedlak, 2000) and organophosphorus pesticides (Kamiya et al., 2001), such as photodegradation、hydrolysis and biodegradation, through complexing action. Combination between metal ions and compounds maybe induce more heavy metals dissolved in water, so metal ions that absorbed onto suspending particles and sediments maybe less, resulting the metal ions keep the biologic activity (Hirose, 2007).

As the DMP decays, heavy metals combined with the DMP are released ($C_{\text{internal}}/C_{\text{external}}$ diminished after 150 min), which reveals that photochemical process induces the release and migration of heavy metals (Table 4). Photochemical degradation raises a series of results, such as reducing average molecular weight, decreasing functional groups, declining pH values and diminishing absorbency. These results will inevitably lead to the change of the metal-organic interaction, biological availability and toxicity (Monsallier et al., 2001).

Fig. 7 here

Table. 4 here

4. Conclusions

The photodegradation of DMP adjusted to the pseudo-first-order kinetics. The second stage appeared to play a key role among three general stages. Degradation of DMP decreased with increasing initial pH. Under the strong alkaline conditions (e.g., pH 10), after 6 hours, DMP was hardly photodegraded. Cu and Pb inhibited photodegradation of DMP, the higher concentration of metal ions, the stronger inhibition of photodegradation. The inhibition rate of Cu and Pb are 95.4% and 100% respectively at 5 mg/L of metal ions concentration. The inhibition rate of $\text{Cu}(\text{OH})^+$ is 51.7%, while Cu^{2+} and $\text{Cu}(\text{OH})_2(\text{aq})$ is -17.6% and -76.2% respectively. It indicates that $\text{Cu}(\text{OH})^+$ inhibited the photodegradation of DMP rather than Cu^{2+} . The experiment of Pb shows the same rule as Cu. The results of UV-Vis, fluorescence and equilibrium membrane dialysis experiment verified that the combination effect of DMP and Cu^{2+} 、 Pb^{2+} in the photodegradation process. The conclusions would be beneficial for the control of DMP-heavy metals combined pollution in mines.

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452

453 Figure caption

454 Fig.1. Photodegradation of DMP at different pH values

455 Fig.2. The influence of heavy metals for DMP photodegradation at natural pH

456 Fig.3. Percentage distribution among dissolved and adsorbed species of metal ions,
457 Cu^{2+} (CuSO_4), Pb^{2+} (PbCl_2), The percentage was **calculated** by Visual MINTEQ under
458 the concentration of metal ions of 50 mg/L at 25 °C

459 Fig.4. **Sequence of** UV-vis spectra taken during the titration of 100 mg/L DMP with
460 Cu^{2+} or Pb^{2+} ions. Inset: Change in the absorbance of 100 mg/L DMP as a function of
461 Cu^{2+} and Pb^{2+} ion concentration (a. Cu^{2+} ; b. Pb^{2+})

462 Fig.5. Plot of $1/(A-A_0)$ versus $1/[\text{Cu}^{2+}]$ and $1/[\text{Pb}^{2+}]$ showing a linear relationship

463 Fig.6. Plot of F_0/F versus concentration of Cu^{2+} and Pb^{2+} showing a linear relationship.
464 Inset: Fluorescence response of DMP (100 mg/L) on addition of Cu^{2+} or Pb^{2+} ions (λ_{em}
465 340 nm)

466 Fig.7. Photodegradation of DMP on the impact of the combined with heavy metals
467 (a. Cu^{2+} ; b. Pb^{2+})

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533 Table caption

534 Table.1. Pseudo-first-order rate constants of DMP photodegradation at different pHs
535 in three stages.

536 Table.2. Pseudo-first-order rate constant and inhibitory rate in different concentration
537 of heavy metals.

538 Table.3. Pseudo-first-order rate constant in different Cu and Pb species in solution.

539 Table 4. $C_{\text{internal}}/C_{\text{external}}$ of Cu^{2+} and Pb^{2+} .

540

Table.1. Pseudo-first-order rate constants of DMP photodegradation at different pHs in three stages.

pH	$K(\text{min}^{-1})$		
	First-stage	Second-stage	Third-stage
4.0	0.31	1.15	0.04
5.5	0.01	0.89	0.11
7.0	0.29	1.11	0.00
8.5	0.43	0.18	0.39
10	0.01	0.01	0.01

Table.2. Pseudo-first-order rate constant and inhibitory rate in different concentration of heavy metals.

Concentration of heavy metals (mg/L)	$K(\text{min}^{-1})$		$I(\%)$	
	Cu	Pb	Cu	Pb
0.0	1.51×10^{-2}	1.68×10^{-2}	-	-
0.5	0.97×10^{-2}	0.23×10^{-2}	35.8 ± 3.2	86.3 ± 2.1
1.0	0.90×10^{-2}	0.20×10^{-2}	40.4 ± 2.4	86.3 ± 2.6
5.0	0.07×10^{-2}	0.00	95.4 ± 2.9	100 ± 1.2

551

552 Table.3. Pseudo-first-order rate constant in different Cu and Pb species in solution.

pH	species	$K_{\text{Cu}}(\text{min}^{-1})$	$K(\text{min}^{-1})$	$I(\%)$
3.0	Cu^{2+}	0.40×10^{-2}	0.34×10^{-2}	-17.6 ± 2.2
8.0	$\text{Cu}(\text{OH})^+$	0.29×10^{-2}	0.58×10^{-2}	51.7 ± 3.0
10	$\text{Cu}(\text{OH})_2(\text{aq})$	0.37×10^{-2}	0.21×10^{-2}	-76.2 ± 2.5
12	$\text{Cu}(\text{OH})_3^-$	0.00	0.00	-
3.0	Pb^{2+}	0.89×10^{-2}	0.68×10^{-2}	-30.9 ± 2.7
8.0	$\text{Pb}(\text{OH})^+$	0.84×10^{-2}	0.95×10^{-2}	11.6 ± 2.1
10	$\text{Pb}(\text{OH})_2(\text{aq})$	1.04×10^{-2}	0.44×10^{-2}	-57.7 ± 1.2
12	$\text{Pb}(\text{OH})_3^-$	0.00	0.00	-

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Table 4. $C_{\text{internal}}/C_{\text{external}}$ of Cu^{2+} and Pb^{2+} .

	$C_{\text{internal}}/C_{\text{external}}$								
	0min	30min	60min	90min	120min	150min	180min	210min	240min
Cu^{2+}	2.28	2.54	4.14	1.92	2.48	3.26	2.52	2.84	1.77
Pb^{2+}	5.14	0.42	2.54	2.64	3.08	7.21	4.29	2.29	1.53

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