Copper Complexation of Humic Substances Generated in a Landfill Site that is Mainly for Municipal Solid Waste Incineration Residue Disposal

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ABSTRACT
Humic substances are known to have great impact on heavy metal mobility in aquatic environments. Therefore, the complexation of humic substances, which was generated in landfilled municipal solid waste incineration (MSWI) residues, with heavy metals were investigated to evaluate their impact on heavy metal mobility in a landfill body. This study focused on copper complexation with landfill humic substances. Humic substances were extracted from 13-year-old landfilled MSWI residues. They were used for copper complexation experiments with initial copper concentrations ranging from $1.0 \times 10^{-8}$ mol-Cu/L to $1.0 \times 10^{-6}$ mol-Cu/L; humic/fulvic acid concentration of 47.61 mg-C/L; pH range from 6 to 8; and 24-hour contact time. 59.5% to 99.9% of spiked copper was bounded with humic substances at pH 6 to 8. This series of experiments suggested significant impact of humic substance complex on copper mobility in a landfill body. Humic acid had several orders of magnitude larger complexation capacity for copper than that of fulvic acid. Although copper complexation capacities of landfill humic/fulvic acid were much lower than those of generic humic/fulvic acid, landfill fulvic acid had comparable capacity with incubated fulvic acid. This implies similar characteristics of fulvic acid generated in MSWI residues regardless of the humification environment.

Keywords: copper, complexation, landfill site, leachate, humic substance

INTRODUCTION
Owing to the severe lack of landfill sites in Japan, more than 77% of municipal solid wastes (MSW) were incinerated in order to reduce the volume of landfill-disposed wastes (Ministry of the Environment, Japan, 2008). After combustion, almost all of the MSW incineration (MSWI) residues have been landfilled, which accounted to 5.89 Tg in 2006 (Ministry of the Environment, Japan, 2008). Leachate from landfill sites should be monitored and treated during the in-service phase and post-service phase if necessary. In general, leachate usually contains pollutants like COD, NH₃, toxic organic compounds, and heavy metals. Leaching behavior of heavy metals like copper, lead, and zinc depends on many factors such as pH, oxidation-reduction potential (ORP), concentrations of anions, sorption to secondary minerals, and organic compounds that react with heavy metals. Therefore, it is still difficult to describe the heavy metal behavior appropriately inside a landfill body although the leachability of heavy metals from MSWI residues under conditions of wide pH ranges have been investigated well by batch-type leaching tests (Fallman, 1997; Kim et al., 2003; Li et al., 2007; Takahashi et al., 2010). In particular, formation kinetics of secondary minerals, complexation kinetics of heavy metals with organic compounds, sorption kinetics of heavy metal cations and their complexes bound to organic compounds onto secondary minerals should be further investigated for the quantitative description of heavy metal mobility.
This study focuses on the complexation between organic compounds and heavy metals, in particular copper, because it is well known that the mobilization of copper depends strongly on the complexation by humic substances in natural environments (McKnight et al., 1983; Hiraide et al., 1988; Cao et al., 2004). In addition, van Zomeren and Comans (2004) reported that 82 to 100% of copper in the leachate of MSWI bottom ash were bounded with dissolved organic matter (DOM) including fulvic acid between pH 6.6 and 10.6. Although humic substances generated in a landfill body seem to have significant impact on the mobility of heavy metals in a landfill body, the complexation between landfill-derived humic substances and heavy metals is still uncertain. Therefore, the objective of this study is to investigate the complexation of humic substances generated in landfilled MSWI residues with heavy metals. In particular, this study focuses on copper complexation with landfill humic substances.

MATERIALS AND METHODS

MSWI residues
Landfilled MSWI residues were sampled from a landfill site in Northern Kyushu, Japan. The average landfill period of sampled MSWI residues was approximately 13 years. The samples were dried at room temperature for one week, and then sieved to less than 2 mm. All sieved samples were finally crushed to less than 0.25 mm for the extraction of fulvic acid and humic acid.

Humic substance extraction
Fulvic acid and humic acid contained in landfilled MSWI residues were extracted by a standard method, which was suggested by International Humic Substance Society (IHSS). The extraction procedure was illustrated in Fig. 1. Fulvic acid was extracted from MSWI residues using 1.0 mol/L HCl at pH 1.0 to 2.0, and then isolated by adsorption/desorption on Supelite DAX-8 resins (Sigma-Aldrich Inc., USA). Humic acid was extracted from the deposit, which was generated in acid extraction of fulvic acid, using 1.0 mol/L NaOH under neutral pH condition and purified by dialysis. Details of humic substance extraction can be referred to elsewhere (Swift, 1996; Thurman and Malcolm, 1981). Extracted fulvic and humic acid per unit weight of MSWI residues were 2,825 mg/kg and 3,270 mg/kg on the average, respectively. They were used for copper complexation experiments. This study investigated the complexation between copper and extracted fulvic/humic acid in liquid phase. However, extracted fulvic/humic acid should have different solubilities and some of the fulvic/humic acid would likely react with copper and other heavy metals on solid surface, not in liquid phase, in a real landfill body. Therefore, it should be noted that copper complexation experiments in this study just represented interactions only in the liquid phase. The effect of different solubilities of fulvic/humic acid on the complexation with copper is necessary for further study.

Copper complexation experiment
Copper nitrate reagent of more than 99.9% purity (Wako Inc., Japan) was used as the copper cation source. Copper solution was mixed with fulvic acid or humic acid solution at 22 ± 2°C to start the complexation. Initial copper concentrations of mixed solution were $1.0 \times 10^{-8}$, $1.0 \times 10^{-7}$, and $1.0 \times 10^{-6}$ mol-Cu/L. Initial carbon-base concentration of fulvic acid and humic acid was 47.61 mg-C/L, which was a
comparable level to the humic substance concentration in leachate from landfill sites and a previous study (Olsson et al., 2007). Owing to poor consistency between measurements in low pH and high chlorine concentration, it should be noted that the ionic strength in copper complexation experiments (approximately $1.0 \times 10^{-3}$ mol/L) was two or three orders of magnitudes lower than that of the real leachate from landfill sites. The pH of mixed solution was changed from 6.0 to 8.0 using 1.0 mmol/L HNO$_3$ or NaOH solution and kept constant during 24 hours. After the complexation, free copper activity in mixed solution was measured by copper ion-selective electrode (8006-10C, Horiba Inc., Japan). Measurement under the same conditions was conducted several times (2 to 5 times) to confirm data reproducibility. Calibration curves at pH 6, 7, and 8 are illustrated in Fig. 2. Calibration curves were fitted non-linearly and regression equations are also listed in Fig. 2. It should be noted that free copper concentrations at pH 6 - 7 and pH 7 - 8 were calculated using two calibration curves. The pH difference was assumed to be linearly related to the difference between two calibration curves. Therefore, it must be noted that calculated free copper concentrations potentially had large uncertainty with approximately 1 - 3 orders of magnitude difference ranges. Experimental data were compared to the calculated data using the non-ideal competitive adsorption-Donnan (NICA-Donnan) model.
Non-ideal competitive adsorption-Donnan (NICA-Donnan) model

The NICA-Donnan model was referred from Vidali et al. (2011) and this model has been reported in detail by Benedetti at al. (1995), Kinniburgh et al. (1996 and 1999), and Koopal et al. (2005). The NICA-Donnan model assumes competitive adsorption to two types of binding sites, which are considered to represent carboxylic sites and phenolic sites. In addition, NICA-Donnan model takes ion-specific heterogeneity or non-ideality into account. The amount of H\(^+\) and Cu\(^{2+}\) bound to specific binding sites, \(Q_M\) (mol/kg), is expressed by Equation 1,

\[
Q_M = Q_{\text{max}H,1} \cdot n_{H,1} \cdot \frac{(K_{M,1}C_{M,D})^{n_{M,1}}}{(K_{H,1}C_{H,D})^{n_{H,1}} + (K_{M,1}C_{M,D})^{n_{M,1}}} + Q_{\text{max}H,2} \cdot n_{H,2} \cdot \frac{(K_{M,2}C_{M,D})^{n_{M,2}}}{(K_{H,2}C_{H,D})^{n_{H,2}} + (K_{M,2}C_{M,D})^{n_{M,2}}} \\
+ \frac{(K_{H,1}C_{H,D})^{n_{H,2}}}{1 + \left(\frac{(K_{H,1}C_{H,D})^{n_{H,2}}}{(K_{M,1}C_{M,D})^{n_{M,2}}}\right)^{P_1}} + \frac{(K_{H,2}C_{H,D})^{n_{H,2}}}{1 + \left(\frac{(K_{H,2}C_{H,D})^{n_{H,2}}}{(K_{M,2}C_{M,D})^{n_{M,2}}}\right)^{P_2}}
\]

(Eq.1)

where the indices 1 and 2 correspond to the carboxylic and phenolic functional groups, respectively. In addition, \(Q_{\text{max}H,j}\) \((j = 1, 2)\) (mol/kg) is the proton binding capacity of the carboxylic and phenolic functional groups; \(K_{M,j}\) (-) and \(K_{H,j}\) (-) are the median affinity constants of metal cation (Cu\(^{2+}\)) and proton, respectively; and \(C_{M,D}\) (mol/L) and \(C_{H,D}\) (mol/L) are the concentrations of metal cation and proton in Donnan phase, respectively. According to Koopal et al. (2005), the ratio \(n_{M,j}/n_{H,j}\) corresponds to the average stoichiometry of metal cation with respect to the proton binding reaction to carboxylic sites and the ratio \(n_{M,2}/n_{H,2}\) to phenolic functional groups. Exponent \(P_1\) and \(P_2\) account for the intrinsic chemical heterogeneity of carboxylic and phenolic functional groups, which correspond to the width of the affinity distribution. For a simple Donnan model, it is assumed that the overall electroneutrality of the gel phase (Donnan volume) at each
charge is entirely preserved by the penetration of ions in the gel phase. The molar concentration of an ion (Cu\(^{2+}\) or proton) in the Donnan phase of humic substance, \(C_{i,D}\) \((I = \text{Cu}^{2+} \text{ or proton})\) (mol/L), can be correlated to its concentration in the bulk solution \(C_i\) (mol/L) using Donnan potential \((\psi_D \text{ (J/L/C/mol)})\) expressed as Equation 2,

\[
C_{i,D} = C_i \exp \left( -\frac{z_i F \psi_D}{RT} \right)
\]

(Eq.2)

where \(z_i\) is the ionic charge of the ion \(i\) \((i = \text{Cu}^{2+} \text{ or proton})\) (mol/L), \(F\) is the Faraday’s constant (C/mol), \(R\) is the gas constant (J/K/mol), and \(T\) is the absolute temperature (K).

In the Donnan volume, the charge of humic molecule, \(Q\) (C/L), is neutralized by the attraction of counter ions like \(\text{Cu}^{2+}\) and proton and the repulsion of co-ions like \(\text{NO}_3^-\). Therefore, the overall electroneutrality in the Donnan volume \((V_D \text{ (L)})\) is expressed by Equation 3 (Benedetti et al., 1996; Kinniburgh et al., 1996 and 1999).

\[
\frac{Q}{V_D} + \sum_i z_i (C_{i,D} - C_i) = 0
\]

(Eq.3)

If Donnan volume is known, the Donnan potential can be obtained by solving Equation 2 and 3. According to Benedetti et al (1996), the Donnan volume is correlated to ionic strength of the bulk solution and expressed empirically by Equation 4,

\[
\log V_D = b(1 - \log I) - 1
\]

(Eq.4)

where \(I\) is the ionic strength (mol/L); \(b\) (-) is an empirical parameter related to the size of humic molecules and describing how the Donnan volume varies with ionic strength.

All parameters of NICA-Donnan model for generic fulvic and humic acids (Milne et al., 2001) are listed in Table 1. Parameters of fulvic acid extracted from incubated MSWI bottom ash (Olsson et al., 2007) are also listed in Table 1. It was noted that NICA-Donnan model parameters of generic fulvic acid and generic humic acid were optimized using datasets including commercial and site-specific fulvic/humic acids (Milne et al., 2001).

Table 1 - NICA-Donnan model parameters of fulvic and humic acid.

<table>
<thead>
<tr>
<th>Acid-base parameters</th>
<th>Cu complexation</th>
</tr>
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<tbody>
<tr>
<td>(Q_{\text{max}H,1})</td>
<td>(Q_{\text{max}H,2})</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Fulvic acid (generic)*</td>
<td>5.88</td>
</tr>
<tr>
<td>Fulvic acid (Incubated)*</td>
<td>5.95</td>
</tr>
<tr>
<td>Humic acid (generic)***</td>
<td>3.15</td>
</tr>
</tbody>
</table>

* Optimized parameters using datasets including commercial and site-specific fulvic acids (Milne et al., 2001)
** Optimized parameters for fulvic acid extracted from weathered and incubated MSWI bottom ash (Olsson et al., 2007)
*** Optimized parameters using datasets including commercial and site-specific humic acids (Milne et al., 2001)
RESULTS AND DISCUSSION
Copper complexation: landfill fulvic acid vs landfill humic acid

Free copper concentrations after complexation experiments using landfill fulvic acid or landfill humic acid are illustrated in Fig. 3. Although large uncertainty of calculated free copper concentrations should be taken into account, 59.5% to more than 99.9% of spiked copper was bound to landfill fulvic acid and more than 99.9% of initial copper was bound to landfill humic acid. Non-negligible amount of copper seems to be bound to fulvic/humic acid in real landfill leachate although it depends strongly on the molar base ratio of copper cation to fulvic/humic acid. At any pH value and any initial copper concentrations, free copper concentrations with humic acid were one to three orders of magnitude lower than those with fulvic acid. This clearly indicates that humic acid has several orders of magnitude larger complexation capacity than fulvic acid. Lee et al. (2004) reported that landfilled MSWI residues in Japanese landfill sites contained approximately two to four times larger amount of fulvic acid than humic acid. Considering the several orders of magnitude larger complexation capacity of humic acid than that of fulvic acid, humic acid would have more significant impact on copper speciation and mobility in real landfill leachate than fulvic acid. In order to simulate the long-term behavior of copper in a landfill body, the effect of the complexation with humic substances, particularly humic acid, on copper mobility/immobility should be focused on for further study.

Fig. 3 - Copper complexation with landfill fulvic acid and landfill humic acid (initial copper concentrations: (a) $1.0 \times 10^{-6}$ mol/L, (b) $1.0 \times 10^{-7}$ mol/L, (c) $1.0 \times 10^{-8}$ mol/L).
Copper complexation: landfill fulvic acid vs generic/incubated fulvic acid
The complexation of copper with generic fulvic acid was calculated by NICA-Donnan model using the reported parameters of generic fulvic acid (see Table 1). The calculated data were compared with the experimental data and are illustrated in Fig. 4. Olsson et al. (2007) reported optimized parameters for copper complexation of fulvic acid extracted from incubated MSWI bottom ash (incubated fulvic acid). The calculated data using their parameters are also shown in Fig. 4. Free copper concentrations calculated using optimized parameter values for generic fulvic acid were 6 to 7 orders of magnitude lower than the experimental results. This indicates that landfill fulvic acid has several orders of magnitude smaller capacity of copper complexation than generic fulvic acid. On the other hand, there are good agreements between experimental and calculated data using optimized parameter values for incubated fulvic acid (Olsson et al. (2007)). The characteristics of MSWI residues used in this study and used by Olsson et al. (2007) seem to be different owing to different combustion conditions and heterogeneous waste compositions. In addition, environmental conditions of fulvic acid formation in this study and those of Olsson et al. (2007) are quite different. MSWI bottom ash used in this study is a 13-year-old landfilled ash. Because fulvic acid was extracted immediately from ash sampling, all amounts of fulvic acid were generated in a landfill body. On the other hand, samples used by Olsson et al. (2007) were 4-month-old MSWI bottom ash collected from outdoor piles and were further stored for 4 months at room temperature (around 20°C) with open to the atmosphere. Therefore, the fulvic acid of Olsson et al. (2007) was produced in outdoor storage and incubation period. However, the fulvic acid tested in this study and that tested by Olsson et al. (2007) have comparable abilities for copper complexation. Although additional tests using fulvic acid extracted from other MSWI residues are necessary for verification, the obtained results imply that environmental conditions might have relatively small impact on the characteristics, in particular copper complexation, of fulvic acid generated in MSWI residues.

Fig. 4 - Experimental and calculated data for fulvic acid-copper complexation (initial copper concentration of complexation experiments: (◊) $1.0 \times 10^{-6}$ mol/L, (▲) $1.0 \times 10^{-7}$ mol/L, (●) $1.0 \times 10^{-8}$ mol/L).
Copper complexation: landfill humic acid vs generic humic acid

The complexation of copper with generic humic acid was calculated by NICA-Donnan model using reported parameters of generic humic acid (see Table 1). The calculated data were compared with the experimental data and they are illustrated in Fig. 5. Free copper concentrations remarkably decreased at pH higher than 7.8 even though large uncertainty owing to limited calibration curves was taken into account. This might be caused by Cu(OH)₂ deposition. It was partially supported by a little increased turbidity of copper solution above pH 7.8. However, the same remarkable decrease of free copper concentration under weak alkali condition was not detected in Cu-fulvic acid complexation experiments (see Fig. 4). In addition, geochemical copper speciation calculated based on the solubility product of Cu(OH)₂ (2.2 × 10⁻²⁰ mol³/L³) suggested no Cu(OH)₂ deposition under the condition of this study. Although landfill humic acid might have accelerated capacity of copper complexation under weak alkali conditions, further study is necessary for the verification. Calculated free copper concentrations were 4 to 6 orders of magnitudes lower than the experimental results. This indicates that landfill humic acid has several orders of magnitude lower copper complexation capacity than that of generic humic acid. Therefore, both landfill fulvic acid and landfill humic acid have lower affinity to copper cation than generic fulvic/humic acid. However, this does not seem to mean negligible impact of fulvic/humic acid on copper mobility in a landfill body. As mentioned in the introduction section, 82 to 100% of copper was bounded to dissolved organic matter including fulvic acid in the leachate of MSWI bottom ash (Van Zomeren and Comans, 2004). In addition, this study showed that more than 59.5% and more than 99.9% of spiked copper was bound to landfill fulvic acid and landfill humic acid, respectively. Because different solubilities of landfill fulvic/humic acid should have significant effect on their complexation with heavy metals, they should be the focus of further studies. In addition, the effect of the complexation between heavy metals including copper and fulvic/humic acid on heavy metal mobility in a landfill body, particularly the adsorption of the complex to secondary minerals in MSWI residues, should also be further investigated.

![Fig. 4 - Experimental and calculated data for humic acid-copper complexation (initial copper concentration of complexation experiments: (◊) 1.0 × 10⁻⁶ mol/L, (▲) 1.0 × 10⁻⁷ mol/L, (●) 1.0 × 10⁻⁸ mol/L).](image-url)
CONCLUSION
The complexations with copper of fulvic and humic acids extracted from 13-year-old landfilled MSWI residues were investigated to evaluate their impacts on copper mobility in a landfill body. 59.5% to more than 99.9% of spiked copper was bound to landfill fulvic acid and more than 99.9% of initial copper was bound to humic acid at pH ranging from 6 to 8. Although calculated free copper concentrations had large uncertainty, it could be suggested that humic acid had several orders of magnitude larger complexation capacity for copper than that of fulvic acid. This means larger significance of humic acid on copper mobility in a landfill body than fulvic acid. Comparison of the experimental and calculated data using NICA-Donnan model indicated that landfill fulvic/humic acid has much lower complexation capacity than generic fulvic/humic acid. On the other hand, landfill fulvic acid had comparable copper complexation capacity with incubated fulvic acid. This implies that fulvic acid generated in MSWI residues might have similar characteristics, in particular copper complexation, regardless of the humification environment. The sorption of copper bound with humic substances, particularly humic acid, to secondary minerals in MSWI residues is suggested as a further study on copper mobility in a landfill body.

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REFERENCES


