

# Reactions of Refuse Compost-Derived Humic Substances with Lead, Copper, Cadmium, and Zinc

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**Abstract:** The humic substances including humic acid (HA) and fulvic acids (FAs) extracted from a refuse compost were investigated the average conditional concentration quotients of the complexes formed by the reaction of heavy metals with the humic substances. The characteristics of these humic substances were previously investigated by a related study. The concentrations of the free ions of Pb, Cu, Cd, and Zn in the reaction systems of heavy metal-HA suspensions and heavy metal-fulvic acid (FA) solutions were measured by anodic stripping voltammetry (ASV). The sequence of the average conditional concentration quotients of the complexes formed from the reaction of humic substances with heavy metals was FA (MW<1000) > FA (MW>1000) > HA (MW>1000). The sequence of reacting heavy metals with humic substances was Pb > Cu > Cd > Zn. Reactions of refuse compost-derived humic substances with heavy metals thus affect the mobility and biotoxicities of heavy metals in soil and the associated environments.

**Keywords:** humic substances; humic acid; fulvic acid; refuse compost; average conditional concentration quotients; anodic stripping voltammetry.

## 1. Introduction

Refuse compost of organic fertilizer contains a substantial amount of organic matter, with a significant amount of humic substances. In addition, analytical and spectroscopic characterizations of HA (MW>1000), FA (MW>1000) and FA (MW<1000) extracted from the refuse compost have already been studied by Chang Chien et al. [1]. Numerous laboratory studies on the reaction between metals and humic substances have been reported in the literature. Several review articles have also been devoted to this subject [2-3]. In soil and the associated environments, natu-

rally occurring humic substances exert strong binding strength with metals (including heavy metals). It is generally attributable to the interaction of metal ions with two important acidic binding sites of carboxylic and phenolic hydroxyl groups of humic substances [4-7]. Organic ligands derived from humic substances react with heavy metals to form complexes, that influence the concentrations of free and labile heavy metal ions and their subsequent mobilities and biotoxicities in soil and the associated environments [8-9]. This study was thus undertaken to investigate the reactivities of refuse compost-derived humic substances with heavy metals. According to

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the equilibrium description of metal complexation elucidated by Perdue [10], the reaction between a metal ion (M) and a single binding site ( $L_i$ ) to form a 1:1 complex can be described by a formation constant, as exemplified by the formation constant for the reaction:  $M + L_i = ML_i$ .

$$\begin{aligned} K_i &= \{ML_i\} / \{M\} \{L_i\} \\ &= [ML_i] / [M][L_i] \cdot \gamma_{ML_i} / \gamma_M \gamma_{L_i} \\ &= K_i^c \Gamma_i \end{aligned} \quad (1)$$

where M is a metal aquo ion,  $L_i$  is a fully deprotonated binding site,  $ML_i$  is the complex formed from one mole each of M and  $L_i$ , braces { } and square brackets [ ] denote activities and concentrations, respectively, and  $\gamma$ -values are activity coefficients. The formation constant  $K_i$  is a true thermodynamic constant, independent of solution composition. The concentration quotient  $K_i^c$  and the activity coefficient ratio  $\Gamma_i$  are, however, complementary functions of ionic strength.

For mathematical convenience, a conditional concentration quotient  $K_i^*$  is often defined in which the precise terms in Eq. (1) are replaced by more convenient terms:

$$K_i^* = [ML_i (\text{bound})] / [M (\text{free})][L_i (\text{free})] \quad (2)$$

In this equation, M (free) represents all forms of the metal ion that are not bound to the ligand of interest,  $L_i$  (free) represents all forms of the ligand that are not bound to the metal ion, and  $ML_i$  (bound) represents all complexes of 1:1 metal:ligand stoichiometry. Unlike  $K_i^c$ , which is only a function of ionic strength,  $K_i^*$  is a function of ionic strength, pH, concentrations of competing metal ions and ligands, and so on. If all side reactions are well understood,  $K_i^*$  is a useful parameter that can be directly related to  $K_i^c$ . The extension of this treatment to a complex mixture such as humic substances is straightforward.

Inasmuch as the individual components of such mixtures are unknown, it is impossible to rigorously describe the competing side reactions of the ligand mixture. Conditional concentration quotients or related hybrid expressions are thus used exclusively, and an "average" conditional concentration quotient is often defined by formal analogy with Eq. (2):

$$\bar{K}^* = \Sigma [ML_i (\text{bound})] / [M (\text{free}) \Sigma [L_i (\text{free})] \quad (3)$$

where  $\Sigma [ML_i (\text{bound})]$  is the sum of the concentrations of all complexes formed between M and the multiligand mixture,  $\Sigma [L_i (\text{free})]$  is the sum of the concentrations of all binding sites that are not associated with M, and M (free) is the sum of all metal species that are not associated with the multiligand mixture.

By making various assumptions about reaction stoichiometry and the presence or absence of simple inorganic complexes (hydroxy and carbonato complexes) in the system under investigation,  $\bar{K}^*$  values are often calculated directly from experimental data as

$$\bar{K}^* = \frac{C_M - [M]}{[M](C_L - C_M + [M])} \quad (4)$$

Here  $C_M$  and  $C_L$  are the total stoichiometric concentrations of metal and ligand in the system under study (it is assumed that  $C_L$  is known), and  $[M]$  is the concentration of free metal ion. In calculating  $\Sigma [ML_i (\text{bound})]$  as  $(C_M - [M])$ , the presence of inorganic complexes of the metal ion has been neglected. In calculating  $\Sigma [L_i (\text{free})]$  as  $(C_L - C_M + [M])$ , an average metal:ligand stoichiometry of 1:1 has been assumed for the mixture of binding sites.

In this study, the characteristics including carboxylic group contents of humic substances extracted from refuse compost reported by Chang Chien et al. [1], was used as

data base to design the experimental. Then, Eq. (4) was used to calculate the average conditional concentration quotients of the complexes formed by reacting heavy metals with humic substances of compost in the heavy metal-HA suspension and heavy metal-FA solution systems at initial pH values of 4.00 and 6.50.

## 2. Materials and methods

### 2.1. Materials and characterization of humic substances

Chang Chien et al. [1] reported the extractions of humic substances from a purchased refuse compost, and the subsequent fractionations as well as purifications of HA (MW>1000), FA (MW>1000) and FA (MW<1000). They further reported the analytical characterization including elemental contents and total acidity values, and spectroscopic characterization including Fourier transform infrared (FTIR) spectrometry and solid state  $^{13}\text{C}$  NMR (nuclear magnetic resonance) analysis with cross polarization and magic-angle spinning (CPMAS) of HA (MW>1000), FA (MW>1000) and FA (MW<1000).

### 2.2. Preparation of HA-heavy metal suspensions and FA-heavy metal solutions

The equivalent concentrations of binding sites of the HA (MW>1000) suspension and FA (MW>1000) and FA (MW<1000) solutions were computed by using the obtained total acidity values described by Chang Chien et al. [1]. Total binding site capacity (meq  $\text{mL}^{-1}$ ) was calculated based on 1:1 metal:ligand stoichiometry proposed by Perdue [10].

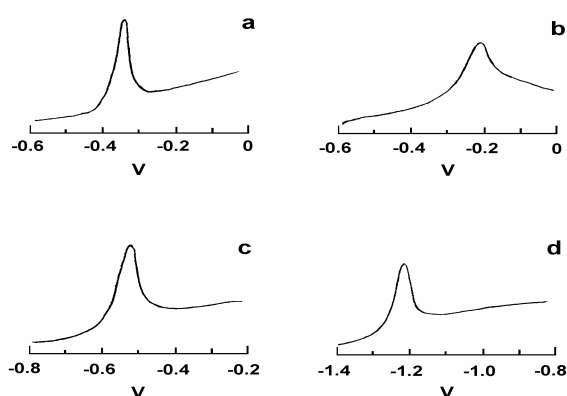
Because the HA is the fraction of organic matter that is not soluble under acidic conditions (below pH 2) but becomes soluble at greater pH [11], 1.00 mg of freeze-dried HA

(MW>1000) was weighed and suspended in about 50 mL of deionized water. In the meantime, the amount of  $\text{NaClO}_4$  equivalent to  $0.02 \text{ mol L}^{-1}$  was added to the HA suspension as the supporting electrolyte. Perchlorate salt of Pb, Cu, Cd or Zn was dissolved in about 50 mL of deionized water at the concentration equal to the binding site capacity. The HA (MW>1000) suspensions and the heavy metal solutions were adjusted to pH 4.00 and 6.50 with 0.1 M  $\text{HClO}_4$  and 0.1 M  $\text{NaOH}$ , respectively, and then made to a final volume of 50 mL with deionized water. Finally, same pH of a 50 mL of HA (MW>1000) suspension and a 50 mL of heavy metal solution were transferred to a 250-mL Erlenmeyer flask for reaction. Our preliminary kinetic study of the same reaction systems showed that humic substances reacting with heavy metals reached equilibrium in about 10 hr. Therefore, the flasks containing 100 mL of HA (MW>1000)-heavy metal suspensions were shaken in a water bath at  $25^\circ\text{C}$ , with 3 cm of shaking amplitude and 50 rpm of speed for 10 hr. For the FA, 0.90 mg of FA (MW>1000) and 0.67 mg of FA (MW<1000) were separately dissolved in about 1 L of deionized water with  $0.02 \text{ mol L}^{-1}$   $\text{NaClO}_4$  as the supporting electrolyte. The FA (MW>1000) or FA (MW<1000) solutions were adjusted to pH 4.00 and 6.50 with 0.1 M  $\text{HClO}_4$  and 0.1 M  $\text{NaOH}$ , respectively, and made to final volumes of 1 L with deionized water. Single-point titrations of heavy metals with FAs were carried out as discussed above for HA (MW>1000) samples. Reactions for HA (MW>1000), FA (MW>1000), and FA (MW<1000) were also carried out at 1:0.1, 1:0.5, 1:5, and 1:10 ligand:metal reactions. All the experiments were triplicate.

### 2.3. Determination of free heavy metal ion concentrations and computation of average conditional concentration quotients

According to the procedures described by

Zen et al. [12], a glassy carbon electrode was used to prepare the Nafion/chelating agent mercury film electrode for a BAS CV-27 Voltammograph. They reported that the preconcentrated potentials for Pb, Cu, Cd and Zn were -0.6, -0.8, -1.0 and -1.4 V, respectively, at a preconcentrated time of 5 min and a scanning rate of  $50 \text{ mV s}^{-1}$ . In addition, Zen et al. [12] reported that the Nafion/chelating agent mercury film electrodes are considerably more resistant to organic interferences than the Nafion coated mercury film electrode. In this experiment, these preconcentrated potentials were thus used as set parameters to determine the concentrations of free heavy metal ions in HA-heavy metal suspensions and FA (MW>1000)- and FA (MW<1000)-heavy metal solutions. At the end of a 10-hr reaction period, the reacting suspensions and solutions were filtered with membrane filters (cellulose nitrate) with a pore size of  $0.45 \mu\text{m}$ . The collected individual filtrates were then subjected to the determination of free ions of Pb, Cu, Cd and Zn by using a BAS CV-27 Voltammograph equipped with a Nafion/ chelating agent mercury film electrode prepared from a glassy carbon electrode and with a working and a platinum electrode. The linear anodic stripping voltammograms of Pb, Cu, Cd and Zn with concentration of  $1 \text{ mg L}^{-1}$  were shown in Figure 1.



**Figure 1.** Linear anodic stripping voltammograms of (a) lead, (b) copper, (c) cadmium, and (d) zinc. The concentration of each ion species was  $1 \text{ mg L}^{-1}$

In this experiment, the equivalent concentrations of Pb, Cu, Cd, or Zn added in the reaction systems were very low and in the ranges of  $8.28 \times 10^{-6} - 8.28 \times 10^{-4} \text{ N}$  for HA (MW>1000) reaction system and  $1.00 \times 10^{-6} - 1.00 \times 10^{-4} \text{ N}$  for FA (MW>1000) and FA (MW<1000) reaction systems. It was reported that below pH 8.0, only  $\text{Pb}^{2+}$  and  $\text{PbOH}^+$  contribute significantly to total Pb in solution [13-14]. Therefore, at pH of both 4.00 and 6.50 of the HA (MW>1000)-Pb suspension and FA (MW>1000)-Pb and FA (MW<1000)-Pb solutions,  $\text{Pb}^{2+}$  are the main species in the reaction systems. For Cu species in the reaction systems, the predominant ion below pH 6.9 is  $\text{Cu}^{2+}$  while  $\text{Cu}(\text{OH})_2^0$  is the major solution species above this pH [13-14]. At pH higher than 7.84, with 0.003 atm of  $\text{CO}_2$ ,  $\text{CdCO}_3$  (octavite) precipitates from the solution. None of the hydrolysis species are thought to contribute significantly to total Cd in solution except  $\text{CdOH}^+$  and  $\text{Cd}(\text{OH})_2^0$  above pH 7.5 [14]. In this experiment, at pH 4.00 and 6.50,  $\text{Cd}^{2+}$  is thus the main species in the reaction systems. Further, the predominant Zn species in solution below pH 7.7 is  $\text{Zn}^{2+}$ , although  $\text{Zn}(\text{OH})^+$  is more prevalent above this pH [14]. Consequently, the determined free Pb, Cu, Cd, or Zn ion at equilibrium in each reaction system by ASV technique was thus total free ion in solution except for that bound by humic ligands.

In Eq. (4) described above,  $C_M$  and  $C_L$  are the known total stoichiometric concentrations of metals and ligands, respectively, under study and  $M$  is the determined concentration of free heavy metal ions.  $\bar{K}^*$  of the reacting HA (MW>1000)-heavy metal suspensions and FA (MW>1000)- and FA (MW<1000)-heavy metal solutions can thus be computed. The obtained equivalent concentrations of free heavy metal ions at equilibrium and  $\bar{K}^*$  were subjected to statistical analysis using SAS procedures [15] and Duncan's multiple range test at  $p < 0.05$  [16].

### 3. Results and discussion

At the suspension pH of 4.00 and 6.50 (at 25 °C), the determined equivalent concentration of free heavy metal ion at equilibrium mostly significantly increased with increasing the equivalent concentration of heavy metal added in each reaction system. At the same concentration of heavy metal and total added organic matter, most of the concentrations of free heavy metal ion at equilibrium were significantly higher at pH 4.00 than at pH 6.50. Furthermore, at the suspension pH of 4.00 or 6.50, for each respective concentration of heavy metal added, the sequence of the determined equivalent concentration of free heavy metal ion at equilibrium was mostly found to be  $Zn > Cd > Cu > Pb$  (Table 1). All these characteristic trends reflected to the variation of computed  $\bar{K}^*$  in the reaction systems. At both the suspension pH of 4.00 and 6.50,  $\bar{K}^*$  by reacting  $8.28 \times 10^{-5}$  N of bonding ligand of HA (MW>1000) with  $4.14 \times 10^{-4}$  and  $8.28 \times 10^{-4}$  N of Pb in the reaction system were negative values (Table 1). On the basis of chemical equilibrium, negative values of the quotients obtained are not reasonable. A negative value of  $\bar{K}^*$  obtained from Eq. (4) by the substitution of known concentrations and the subsequent computation was due to a negative value derived from either the numerator or the denominator of the equation. In Eq. (4),  $C_M - [M]$  and  $[M]$  terms were exactly positive values (Table 1). The negative value was, therefore, derived from the term,  $(C_L - C_M + [M])$ , in the denominator of Eq. (4). The term,  $(C_L - C_M + [M])$ , can be transformed as  $\{C_L - (C_M - [M])\}$ . In the reaction conditions described above,  $C_M$  ( $4.14 \times 10^{-4}$  and  $8.28 \times 10^{-4}$  N) was 5 and 10 times, respectively, greater than  $C_L$  ( $8.28 \times 10^{-5}$  N). Under this situation, if the concentration of free Pb ion at equilibrium in the suspension was not great enough to make  $(C_M - [M]) < C_L$ ,  $\{C_L - (C_M - [M])\}$  showing the denominator term,  $(C_L - C_M + [M])$ , of Eq. (4) would be negative. This clearly indicates that

the bonding ligand of HA (MW>1000) strongly reacted with Pb, leaving lower concentrations of free Pb ion at equilibrium in the reaction systems. At the suspension pH of 4.00 and at 25 °C, values other than negative  $\bar{K}^*$  obtained, the  $\bar{K}^*$  value by reacting  $8.28 \times 10^{-5}$  N of bonding ligand of HA (MW>1000) with Pb significantly increased with decreasing the equivalent concentration of Pb added in the reaction system (Table 1). This general trend of increasing  $\bar{K}^*$  with decreasing the concentration of metal added is apparent for most of data sets, and is consistent with metal complexation with stronger binding sites at lower concentration of metal added. At the suspension pH of 6.50 and at 25 °C, the sequence of  $\bar{K}^*$  of the same reaction system followed the same trend. However, for each respective concentration of Pb added, the  $\bar{K}^*$  was significantly higher at suspension pH of 6.50 than at 4.00 (Table 1). This is attributed to higher dissociation of total functional group acidity of the HA (MW>1000) at pH 6.50 than at 4.00 [17-19], stated another way increased competition for binding sites at lower pH values.

At both the suspension pH of 4.00 and 6.50 and at 25 °C,  $\bar{K}^*$  by reacting  $8.28 \times 10^{-5}$  N of bonding ligand of HA (MW>1000) with Cu, Cd, or Zn almost showed the same trend as those with Pb. However, at the suspension pH of 4.00, at 25 °C, and for each respective concentration of the heavy metals added, the sequence of  $\bar{K}^*$  value in the reaction systems in terms of reacted heavy metals was  $Pb > Cd > Cu > Zn$  (Table 1). At the suspension pH of 6.50, the sequence of  $\bar{K}^*$  value in terms of the reacted heavy metals was  $Pb > Cu > Cd > Zn$ , but not in the case of  $8.28 \times 10^{-6}$  N of Cd and Zn added in the reaction systems (Table 1). Except for the system with the equivalent concentration of  $4.14 \times 10^{-4}$  N of Cu added at the suspension pH of 4.00, the  $\bar{K}^*$  values by reacting  $8.28 \times 10^{-5}$  N of bonding ligand of

**Table 1.** The determined equivalent concentrations of free heavy metal ions at equilibrium and the computed average conditional concentration quotients by reacting  $8.28 \times 10^{-5}$  N of binding site of HA (MW>1000) derived from the compost with each of the five equivalent concentrations of Pb, Cu, Cd or Zn at initial pH of 4.00 and 6.50

Initial pH	Equivalent concentration of heavy metal added	Equivalent concentration of free heavy metal ion at equilibrium <sup>†</sup>	Average conditional concentration quotient, $\bar{K}^{**\ddagger}$
	N		$N^{-1}$
4.00	Pb		
	$8.28 \times 10^{-6}$	$2.32 \times 10^{-6}$ dUV	$3.34 \times 10^4$ aEF
	$4.14 \times 10^{-5}$	$1.54 \times 10^{-5}$ dSTU	$2.97 \times 10^4$ bF
	$8.28 \times 10^{-5}$	$4.88 \times 10^{-5}$ cPQ	$1.43 \times 10^4$ cH
	$4.14 \times 10^{-4}$	$3.12 \times 10^{-4}$ bK	$-1.70 \times 10^4$
	$8.28 \times 10^{-4}$	$6.00 \times 10^{-4}$ aF	$-2.62 \times 10^3$
6.50			
	$8.28 \times 10^{-6}$	$1.93 \times 10^{-7}$ eV	$5.60 \times 10^5$ aA
	$4.14 \times 10^{-5}$	$9.36 \times 10^{-5}$ cM	$7.88 \times 10^4$ bB
	$8.28 \times 10^{-5}$	$3.21 \times 10^{-5}$ dR	$4.92 \times 10^4$ cD
	$4.14 \times 10^{-4}$	$2.71 \times 10^{-4}$ bL	$-7.04 \times 10^4$
	$8.28 \times 10^{-4}$	$4.58 \times 10^{-4}$ aG	$-2.81 \times 10^3$
4.00	Cu		
	$8.28 \times 10^{-6}$	$3.14 \times 10^{-6}$ dUV	$2.11 \times 10^4$ aG
	$4.14 \times 10^{-5}$	$2.45 \times 10^{-5}$ dRST	$1.05 \times 10^3$ dI
	$8.28 \times 10^{-5}$	$6.34 \times 10^{-5}$ cO	$4.83 \times 10^3$ bI
	$4.14 \times 10^{-4}$	$3.78 \times 10^{-4}$ bI	$2.04 \times 10^3$ cI
	$8.28 \times 10^{-4}$	$7.35 \times 10^{-4}$ aC	$-1.24 \times 10^4$
6.50			
	$8.28 \times 10^{-6}$	$1.51 \times 10^{-6}$ dUV	$5.90 \times 10^4$ aC
	$4.14 \times 10^{-5}$	$1.38 \times 10^{-5}$ dTUV	$3.62 \times 10^4$ bEF
	$8.28 \times 10^{-5}$	$4.49 \times 10^{-5}$ cQ	$1.88 \times 10^3$ cI
	$4.14 \times 10^{-4}$	$3.27 \times 10^{-4}$ bJ	$-6.33 \times 10^4$
	$8.28 \times 10^{-4}$	$6.08 \times 10^{-4}$ aF	$-2.64 \times 10^3$
4.00	Cd		
	$8.28 \times 10^{-6}$	$3.44 \times 10^{-6}$ dUV	$1.81 \times 10^4$ aGH
	$4.14 \times 10^{-5}$	$2.02 \times 10^{-5}$ dRST	$1.70 \times 10^4$ aGH
	$8.28 \times 10^{-5}$	$6.10 \times 10^{-5}$ cOP	$5.85 \times 10^3$ bI
	$4.14 \times 10^{-4}$	$3.26 \times 10^{-4}$ bJ	$-5.19 \times 10^4$
	$8.28 \times 10^{-4}$	$7.18 \times 10^{-4}$ aD	$-5.63 \times 10^3$
6.50			
	$8.28 \times 10^{-6}$	$2.04 \times 10^{-6}$ dUV	$3.99 \times 10^4$ aE
	$4.14 \times 10^{-5}$	$1.97 \times 10^{-5}$ dRST	$1.80 \times 10^4$ bGH
	$8.28 \times 10^{-5}$	$5.82 \times 10^{-5}$ cOP	$7.27 \times 10^3$ cI
	$4.14 \times 10^{-4}$	$3.22 \times 10^{-4}$ bJK	$-3.11 \times 10^4$
	$8.28 \times 10^{-4}$	$6.80 \times 10^{-4}$ aE	$-3.34 \times 10^3$
4.00	Zn		
	$8.28 \times 10^{-6}$	$6.21 \times 10^{-6}$ dUV	$4.12 \times 10^3$ aI
	$4.14 \times 10^{-5}$	$2.85 \times 10^{-5}$ dRS	$3.47 \times 10^3$ bI
	$8.28 \times 10^{-5}$	$7.80 \times 10^{-5}$ cN	$7.89 \times 10^2$ cI
	$4.14 \times 10^{-4}$	$3.97 \times 10^{-4}$ bH	$6.51 \times 10^2$ dI
	$8.28 \times 10^{-4}$	$8.00 \times 10^{-4}$ aA	$6.39 \times 10^2$ dI
6.50			
	$8.28 \times 10^{-6}$	$5.05 \times 10^{-6}$ dUV	$8.04 \times 10^4$ aB
	$4.14 \times 10^{-5}$	$2.32 \times 10^{-5}$ dRST	$1.21 \times 10^3$ dI
	$8.28 \times 10^{-5}$	$6.77 \times 10^{-5}$ cNO	$3.29 \times 10^3$ bI
	$4.14 \times 10^{-4}$	$3.75 \times 10^{-4}$ bI	$2.37 \times 10^3$ cI
	$8.28 \times 10^{-4}$	$7.87 \times 10^{-4}$ aB	$1.24 \times 10^3$ dI

<sup>†</sup> Concentration ( $\text{mg L}^{-1}$ ) determined by using ASV, then converted to equivalent concentration (N)

<sup>‡</sup> Computed from Eq. (4)

<sup>§</sup> Different lower case letters in columns within each metal and each pH value, and different upper case letters in columns including all metals and pH values indicate significant differences in means at  $p < 0.05$  using Duncan's multiple range test

HA (MW>1000) with  $4.14 \times 10^{-4}$  and  $8.28 \times 10^{-4}$  N of Cu or Cd added were negative at both the suspension pH of 4.00 and 6.50. On the contrary, the  $\bar{K}^*$  values by reacting HA (MW>1000) with the same concentrations of Zn were positive (Table 1). Because the strength of reacting ligand of HA (MW>1000) with Zn was the least in this experiment, large concentrations of free Zn ion still existed in the systems at equilibrium. These make ( $C_M - [M]$ ) much less than  $C_L$  in the denominator of Eq. (4) even at  $4.14 \times 10^{-4}$  and  $8.28 \times 10^{-4}$  N of  $C_M$ , which were 5 and 10 times, respectively, higher than  $C_L$  ( $8.28 \times 10^{-5}$  N). In general, the  $\bar{K}^*$  value (other than negative values) decreased with increasing equivalent concentration of heavy metal added in each reaction system at both the pH of 4.00 and 6.50, and their differences were significant (Table 1). This indicates that lower ratio of equivalent concentration of added heavy metal to that of binding site of humic substances promotes the formation of heavy metal-humic substances complex.

Rashid [20] reported that the adsorption of  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  by HA derived from sediment and peat were 98-150 mg  $g^{-1}$  HA. The sequence of the adsorption was  $Cu^{2+} \gg Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$ . Beveridge and Pickering [21] pointed out that the sequence of the affinity of soil HA to react with selected heavy metals was  $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ca^{2+} > Mg^{2+}$ . Our study revealed that the sequence of the  $\bar{K}^*$  value of reacting HA (MW>1000) extracted from the refuse compost with Pb, Cu, Cd and Zn met the reported sequence of adsorption and affinity studies. At both the solution pH of 4.00 and 6.50, and at 25 °C, the characteristic trend of the determined equivalent concentration of free heavy metal ion at equilibrium in FA (MW>1000) reaction system was almost the same as that in HA (MW>1000) reaction system (Tables 1 and 2). This trend thus reflected to the variation of  $\bar{K}^*$  in the reaction systems. At solution pH of both 4.00 and 6.50 (at 25

°C), values other than the negative  $\bar{K}^*$  obtained, the  $\bar{K}^*$  value by reacting  $1.00 \times 10^{-5}$  N of bonding ligand of FA (MW>1000) with Pb, Cu, Cd, or, Zn mostly significantly increased with decreasing the equivalent concentration of the heavy metal added in the reaction system (Table 2). However, for each respective concentration of Pb, Cu, Cd, or Zn added, the  $\bar{K}^*$  value was significantly higher at solution pH of 6.50 than at 4.00 (Table 2). This is also attributed to higher dissociation of the total functional group acidity of FA (MW>1000) at pH 6.50 than at 4.00 [17-19]. At both solution pH of 4.00 and 6.50, the  $\bar{K}^*$  by reacting  $1.00 \times 10^{-5}$  N of bonding ligand of FA (MW>1000) with  $5.00 \times 10^{-5}$  and  $1.00 \times 10^{-4}$  N of Pb, Cu, Cd, or Zn in the reaction system were negative values (Table 2). However, this is not the case by reacting  $8.28 \times 10^{-5}$  N of bonding ligand of HA (MW>1000) with  $4.14 \times 10^{-4}$  N of Cu at pH 4.00 or with  $4.14 \times 10^{-4}$  and  $8.28 \times 10^{-4}$  N of Zn at pH 4.00 and 6.50 in the reaction systems (Table 1). Stronger reacting ligand with heavy metal results in lower concentration of free heavy metal ion leaving in the reaction system, which in turn leads to negative  $\bar{K}^*$  value obtained from Eq. (4). Moreover, except for the system at pH 6.50 and at the concentration of  $1.00 \times 10^{-5}$  N of reacting ligand of FA (MW>1000) with  $1.00 \times 10^{-6}$  N of Zn, the  $\bar{K}^*$  values obtained in FA (MW>1000) systems were much greater than that in HA (MW>1000) systems for each respective ratio of the equivalent concentration of reacting ligand to that of each heavy metal added (Tables 1 and 2). Therefore, at the same ratio of equivalent concentration of bonding ligand of HA (MW>1000) or FA (MW>1000) to that of heavy metal added, FA (MW>1000) has stronger bonding strength than that of HA (MW>1000) with heavy metals. This stronger reacting strength of FA (MW>1000) is probably because of its higher contents of total acidity and carboxylic C reported by Chang-Chien et al. [1]. Except at pH 4.00 and 6.50,

1.00×10<sup>-5</sup> N of Cu or Cd added, and 1.00×10<sup>-6</sup> N of Cd or Zn added, for each respective equivalent concentration of the heavy metal- s added, the sequence of  $\bar{K}^*$  value in FA (MW > 1000) reaction systems

**Table 2.** The average conditional concentration quotients obtained from the reaction of 1.00×10<sup>-5</sup> N of binding site of FA (MW>1000) derived from the compost with each of five equivalent concentrations of Pb, Cu, Cd, or Zn at initial pH of 4.00 and 6.50

Initial pH	Equivalent concentration of heavy metal added	Equivalent concentration of free heavy metal ion at equilibrium <sup>†</sup>	Average conditional concentration quotient, $\bar{K}^*$ <sup>‡</sup>
	N		N <sup>-1</sup>
4.00	Pb		
	1.00×10 <sup>-6</sup>	1.74×10 <sup>-7</sup> eR	5.17×10 <sup>5</sup> aB
	5.00×10 <sup>-6</sup>	2.91×10 <sup>-6</sup> dQ	9.07×10 <sup>4</sup> bE
	1.00×10 <sup>-5</sup>	6.60×10 <sup>-6</sup> cO	7.80×10 <sup>4</sup> bEF
	5.00×10 <sup>-5</sup>	6.11×10 <sup>-5</sup> aE	-8.61×10 <sup>4</sup>
6.50	1.00×10 <sup>-6</sup>	5.84×10 <sup>-5</sup> bF	-2.25×10 <sup>4</sup>
	Pb		
	1.00×10 <sup>-6</sup>	7.72×10 <sup>-8</sup> eR	1.32×10 <sup>6</sup> aA
	5.00×10 <sup>-6</sup>	2.81×10 <sup>-6</sup> dQ	1.00×10 <sup>5</sup> bE
	1.00×10 <sup>-5</sup>	6.40×10 <sup>-6</sup> cO	8.79×10 <sup>4</sup> bE
4.00	5.00×10 <sup>-5</sup>	2.94×10 <sup>-5</sup> bL	-6.61×10 <sup>4</sup>
	1.00×10 <sup>-4</sup>	5.72×10 <sup>-5</sup> aG	-2.28×10 <sup>4</sup>
	Cu		
	1.00×10 <sup>-6</sup>	3.45×10 <sup>-7</sup> eR	2.03×10 <sup>5</sup> aD
	5.00×10 <sup>-6</sup>	3.55×10 <sup>-6</sup> dPQ	4.78×10 <sup>4</sup> bH
6.50	1.00×10 <sup>-5</sup>	8.07×10 <sup>-6</sup> cN	2.96×10 <sup>4</sup> cHIJ
	5.00×10 <sup>-5</sup>	3.17×10 <sup>-5</sup> bK	-6.96×10 <sup>4</sup>
	1.00×10 <sup>-4</sup>	7.75×10 <sup>-5</sup> aB	-2.32×10 <sup>4</sup>
	Cu		
	1.00×10 <sup>-6</sup>	3.14×10 <sup>-7</sup> eR	2.35×10 <sup>5</sup> aC
4.00	5.00×10 <sup>-6</sup>	3.45×10 <sup>-6</sup> dPQ	5.31×10 <sup>4</sup> bFGH
	1.00×10 <sup>-5</sup>	7.94×10 <sup>-6</sup> cN	3.26×10 <sup>4</sup> cHI
	5.00×10 <sup>-5</sup>	3.11×10 <sup>-5</sup> bK	-6.83×10 <sup>4</sup>
	1.00×10 <sup>-4</sup>	7.47×10 <sup>-5</sup> aC	-2.21×10 <sup>4</sup>
	Cd		
6.50	1.00×10 <sup>-6</sup>	7.05×10 <sup>-7</sup> dR	4.31×10 <sup>4</sup> aHI
	5.00×10 <sup>-6</sup>	6.75×10 <sup>-6</sup> cO	3.85×10 <sup>4</sup> bHI
	1.00×10 <sup>-5</sup>	7.92×10 <sup>-6</sup> cN	3.31×10 <sup>4</sup> cHI
	5.00×10 <sup>-5</sup>	3.71×10 <sup>-5</sup> bJ	-1.19×10 <sup>5</sup>
	1.00×10 <sup>-4</sup>	7.43×10 <sup>-5</sup> aC	-2.20×10 <sup>4</sup>
4.00	Cd		
	1.00×10 <sup>-6</sup>	6.71×10 <sup>-7</sup> eR	5.07×10 <sup>4</sup> aGH
	5.00×10 <sup>-6</sup>	3.60×10 <sup>-6</sup> dPR	4.52×10 <sup>4</sup> bHI
	1.00×10 <sup>-5</sup>	7.79×10 <sup>-6</sup> cN	3.65×10 <sup>4</sup> cHI
	5.00×10 <sup>-5</sup>	3.64×10 <sup>-5</sup> bJ	-1.04×10 <sup>4</sup>
6.50	1.00×10 <sup>-4</sup>	7.17×10 <sup>-5</sup> aD	-2.16×10 <sup>4</sup>
	Zn		
	1.00×10 <sup>-6</sup>	7.04×10 <sup>-7</sup> eR	4.33×10 <sup>4</sup> aHI
	5.00×10 <sup>-6</sup>	4.19×10 <sup>-6</sup> dP	2.10×10 <sup>4</sup> bIJ
	1.00×10 <sup>-5</sup>	9.42×10 <sup>-6</sup> cM	6.53×10 <sup>3</sup> cJ
4.00	5.00×10 <sup>-5</sup>	3.98×10 <sup>-5</sup> bH	-1.28×10 <sup>6</sup>
	1.00×10 <sup>-4</sup>	8.81×10 <sup>-5</sup> aA	-7.11×10 <sup>5</sup>
	Zn		
	1.00×10 <sup>-6</sup>	5.81×10 <sup>-7</sup> eR	7.52×10 <sup>4</sup> aEFG
	5.00×10 <sup>-6</sup>	3.73×10 <sup>-6</sup> dPQ	3.90×10 <sup>4</sup> bHI
6.50	1.00×10 <sup>-5</sup>	8.54×10 <sup>-6</sup> cMN	2.00×10 <sup>4</sup> cIJ
	5.00×10 <sup>-5</sup>	3.86×10 <sup>-5</sup> bI	-2.10×10 <sup>5</sup>
	1.00×10 <sup>-4</sup>	8.83×10 <sup>-5</sup> aA	-7.79×10 <sup>4</sup>

†, ‡ and § Explained in Table 1



**Table 3.** The average conditional concentration quotients obtained from the reaction of  $1.00 \times 10^{-5}$  N of binding site of FA (MW<1000) derived from compost with each of five equivalent concentrations of Pb, Cu, Cd or Zn at initial pH of 4.00 and 6.50

Initial pH	Equivalent concentration of heavy metal added	Equivalent concentration of free heavy metal ion at equilibrium <sup>†</sup>	Average conditional concentration quotient, $\bar{K}^* \ddagger$
	N		$N^{-1}$
4.00	Pb		
	$1.00 \times 10^{-6}$	$1.16 \times 10^{-7}$ eQ	$8.38 \times 10^5$ aB
	$5.00 \times 10^{-6}$	$2.26 \times 10^{-6}$ dP	$1.67 \times 10^5$ bDE
	$1.00 \times 10^{-5}$	$5.44 \times 10^{-6}$ cM	$1.54 \times 10^5$ bDE
	$5.00 \times 10^{-5}$	$2.90 \times 10^{-5}$ bJ	$-6.58 \times 10^4$
	$1.00 \times 10^{-4}$	$5.10 \times 10^{-5}$ aF	$-2.46 \times 10^4$
6.50	$1.00 \times 10^{-6}$	$4.15 \times 10^{-8}$ eQ	$2.55 \times 10^6$ aA
	$5.00 \times 10^{-6}$	$1.93 \times 10^{-6}$ dP	$2.30 \times 10^5$ bD
	$1.00 \times 10^{-5}$	$4.78 \times 10^{-6}$ cMN	$2.29 \times 10^5$ bD
	$5.00 \times 10^{-5}$	$2.90 \times 10^{-5}$ bJ	$-6.58 \times 10^4$
	$1.00 \times 10^{-4}$	$5.11 \times 10^{-5}$ aF	$-2.46 \times 10^4$
4.00	Cu		
	$1.00 \times 10^{-6}$	$3.08 \times 10^{-7}$ eQ	$2.41 \times 10^5$ aD
	$5.00 \times 10^{-6}$	$3.52 \times 10^{-6}$ dNO	$4.93 \times 10^4$ bF
	$1.00 \times 10^{-5}$	$7.88 \times 10^{-6}$ cL	$3.41 \times 10^4$ bF
	$5.00 \times 10^{-5}$	$3.13 \times 10^{-5}$ bI	$-6.87 \times 10^4$
	$1.00 \times 10^{-4}$	$7.44 \times 10^{-5}$ aC	$-2.46 \times 10^4$
6.50	$1.00 \times 10^{-6}$	$1.66 \times 10^{-7}$ eQ	$5.48 \times 10^5$ bC
	$5.00 \times 10^{-6}$	$3.11 \times 10^{-6}$ dOP	$7.49 \times 10^5$ aB
	$1.00 \times 10^{-5}$	$7.69 \times 10^{-6}$ cL	$3.90 \times 10^4$ cF
	$5.00 \times 10^{-5}$	$3.10 \times 10^{-5}$ bI	$-6.81 \times 10^4$
	$1.00 \times 10^{-4}$	$7.38 \times 10^{-5}$ aC	$-2.19 \times 10^4$
4.00	Cd		
	$1.00 \times 10^{-6}$	$6.82 \times 10^{-7}$ eQ	$4.82 \times 10^4$ aF
	$5.00 \times 10^{-6}$	$3.63 \times 10^{-6}$ dNO	$4.37 \times 10^4$ bF
	$1.00 \times 10^{-5}$	$7.80 \times 10^{-6}$ cL	$3.61 \times 10^4$ cF
	$5.00 \times 10^{-5}$	$3.68 \times 10^{-5}$ bG	$-1.12 \times 10^4$
	$1.00 \times 10^{-4}$	$7.14 \times 10^{-5}$ aD	$-2.15 \times 10^4$
6.50	$1.00 \times 10^{-6}$	$5.58 \times 10^{-7}$ eQ	$8.28 \times 10^4$ aEF
	$5.00 \times 10^{-6}$	$3.54 \times 10^{-6}$ dNO	$4.83 \times 10^4$ bF
	$1.00 \times 10^{-5}$	$7.61 \times 10^{-6}$ cL	$4.13 \times 10^4$ cF
	$5.00 \times 10^{-5}$	$3.60 \times 10^{-5}$ bGH	$-9.72 \times 10^4$
	$1.00 \times 10^{-4}$	$6.89 \times 10^{-5}$ aE	$-2.14 \times 10^4$
4.00	Zn		
	$1.00 \times 10^{-6}$	$7.04 \times 10^{-7}$ eQ	$4.33 \times 10^4$ aF
	$5.00 \times 10^{-6}$	$3.92 \times 10^{-6}$ dNO	$3.09 \times 10^4$ bF
	$1.00 \times 10^{-5}$	$9.21 \times 10^{-6}$ cK	$9.31 \times 10^3$ cF
	$5.00 \times 10^{-5}$	$3.49 \times 10^{-5}$ bH	$-8.48 \times 10^4$
	$1.00 \times 10^{-4}$	$8.69 \times 10^{-5}$ aA	$-4.86 \times 10^4$
6.50	$1.00 \times 10^{-6}$	$5.20 \times 10^{-7}$ dQ	$9.69 \times 10^4$ aEF
	$5.00 \times 10^{-6}$	$3.73 \times 10^{-6}$ cdNO	$3.90 \times 10^4$ bF
	$1.00 \times 10^{-5}$	$8.84 \times 10^{-6}$ cL	$1.48 \times 10^4$ cF
	$5.00 \times 10^{-5}$	$3.09 \times 10^{-5}$ bI	$-6.79 \times 10^4$
	$1.00 \times 10^{-4}$	$8.14 \times 10^{-5}$ aB	$-2.66 \times 10^4$

<sup>†</sup>, <sup>‡</sup> and <sup>§</sup> Explained in Table 1

in terms of reacted heavy metals was  $Pb > Cu > Cd > Zn$  (Table 2) at 25 °C. On the basis of the same ratios of the equivalent concentration of bonding ligand of humic substances to that of heavy metal added, there was no great difference in the sequence of  $\bar{K}^*$  value between HA (MW>1000) and FA (MW>1000) reaction systems (Tables 1 and 2). This indicates that the chemical behaviors of heavy metals added in the reaction systems control the metal speciation more than the nature of organic matter.

The characteristic trends of both the equivalent concentration of free heavy metal ion at equilibrium and the  $\bar{K}^*$  values in FA (MW<1000) were very similar to those in FA (MW>1000), reacting with Pb, Cu, Cd, or Zn (Tables 2 and 3). However, except for the pH at 4.00 and at  $1.00 \times 10^{-6}$  N and the pH at 6.50 and at  $5.00 \times 10^{-6}$  and  $1.00 \times 10^{-5}$  N of Zn added in the reaction systems, for each respective concentration of heavy metal added, the equivalent concentration of free heavy metal ion at equilibrium was much lower, and the  $\bar{K}^*$  value was much greater in FA (MW<1000) than in FA (MW>1000) system (Tables 2 and 3). This higher reactivity of FA (MW<1000) than that of FA (MW>1000) with Pb, Cu, Cd, and Zn is probably because of higher total acidity as well as carboxylic C content of FA (MW < 1000) reported by Chang Chien et al. [1]. As that in methods section described above, the determined free Pb, Cu, Cd, or Zn ion at equilibrium in each reaction system by ASV technique was total free ion in the solution except for that bound by humic ligand (Tables 1, 2, and 3). Further, at suspension and solution of pH 4.00 and 6.50, no precipitation species of Pb, Cu, Cd, and Zn are thought to occur in the reaction systems of the experiment. The greater  $\bar{K}^*$  values of the reaction systems at pH 6.50 than at 4.00 were thus solely because of various degree of dissociation of the HA and FAs (Tables 1, 2, and 3).

#### 4. Conclusions

At both pH of 4.00 and 6.50, the sequence of the average conditional concentration quotients,  $\bar{K}^*$  of reacting HA (MW>1000), FA (MW>1000), and FA (MW<1000) with Pb, Cu, Cd, and Zn in terms of humic/fulvic ligands was  $FA (MW<1000) > FA (MW>1000) > HA (MW>1000)$ .

The sequence of  $\bar{K}^*$  value in terms of heavy metals was  $Pb > Cu > Cd > Zn$ , which is in good agreement with the reported adsorption and affinity study of humic substance-heavy metal reaction systems. However, the chemical behaviors of heavy metals added in the reaction systems control the metal speciation more than the nature of organic matter. The reactivity of humic/fulvic ligands, chemical behaviors of heavy metals, and  $[H^+]/C_M$  all play role in governing the reaction of humic substances with heavy metals. Consequently, the effect of compost-derived humic substances in agriculture practice on the mobility and subsequent biotoxicity of heavy metals in soil and associated environments merits further attention.

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