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Reactions of compost-derived humic substances with lead, copper, cadmium, and zinc

S.W. Chang Chien [a], M.C. Wang [a,*], C.C. Huang [b]

[a] *Department of Environmental Engineering and Management, Chaoyang University of Technology, 168 Jifong E. Rd.,*
Wufong Township, Taichung County 41349, Taiwan, ROC
[b] *Department of Soil and Environmental Sciences, National Chung Hsing University,*
250 Kuo-Kuang Road, Taichung 40227, Taiwan, ROC

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Abstract

Thermodynamic stability constants of the formation of complexes from the reactions of humic substances with various metals are usually used as parameters to judge the reactivities of both humic substances and metals. However, in calculating the thermodynamic stability constants, complicated processes for the acquisition of activities of components in reactions are absolutely inevitable. In this study, we investigated the average conditional concentration quotients of the complexes formed from the reaction of metals with humic substances and the relations of these quotients to thermodynamic stability constants. The characterized humic substances including HA ($MW > 1000$), FA ($MW > 1000$), and FA ($MW < 1000$) extracted from a swine compost were prepared to react with Pb, Cu, Cd, and Zn at 25 °C and at pH 4.00 and 6.50. Reactions of HA ($MW > 1000$), FA ($MW > 1000$), and FA ($MW < 1000$) with the four metals were carried out at 1:0.1, 1:0.5, 1:1, 1:5, and 1:10 ligand:metal stoichiometry. The concentrations of the free ions of Pb, Cu, Cd, and Zn in the reaction systems of metal-HA suspensions and metal-FA solutions were measured by anodic stripping voltammetry (ASV). The sequence of the average conditional concentration quotients of the formed complexes from the reaction of humic substances with metals was FA ($MW < 1000$) > FA ($MW > 1000$) > HA ($MW > 1000$), showing the relative reactivities of the fractions of swine compost-derived humic substances. The sequence of reacting metals with humic substances was $Pb > Cu > Cd > Zn$, which is in good agreement with the sequence reported by judging the thermodynamic stability constants. The average conditional concentration quotients of the formed complexes from the reaction of humic substances with metals were thus useful parameters that can be directly related to thermodynamic stability constants and other parameters.

Keywords: Compost; Humic substances; Average conditional concentration quotient; Metals; Anodic stripping voltammetry

1. Introduction

Application of various composts, either for plant nutrition or for the purpose of utilization of wastes, increases the soil organic carbon (SOC) concentration. Composts of organic fertilizers contain a substantial amount of organic matter, with a significant amount of humic substances (Deiana et al., 1990; Chang Chien et al., 2003). Naturally occurring organic components of soil and sediment may be classified as either humic or nonhumic substances. Humic substances are believed by most geochemists to be degradation-resistant materials formed during the decomposition of vegetative matter (Hatcher et al., 1983). Humic substances contain a variety of functional groups, including COOH, phenolic OH, enolic OH, alcoholic OH, quinone, hydroxyquinone, lactone, and ether (Stevenson, 1994). 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 (Sposito, 1986; Stevenson, 1994). On the study of the rate of sorption–desorption of

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[*] Corresponding author. Tel.: +886 4 2332 3000; fax: +886 4 2374 2365.
E-mail address: mcwang@mail.cyut.edu.tw (M.C. Wang).

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volatile organic compounds (VOCs) by humic substances, Chang et al. (1997) reported that the sorption of toluene to humic acid (HA), an integral member of a soil humic substance, is found to be reversible and diffusion controlled. In addition, Shih and Wu (2002) concluded that partitioning is believed to be the major mechanism of the sorption of toluene to humin. In soil and the associated environments, naturally occurring humic substances exert strong binding strength with metals, which may be attributable to the interaction of metal ions with two important acidic binding sites of carboxylic and phenolic hydroxyl groups of humic substances (Schnitzer, 1969; Gamble et al., 1970; Vinkler et al., 1976; Piccolo and Stevenson, 1981; Cameron and Sohn, 1992; Ashley, 1996). Humic acids (HAs) may exist in either dissolved or suspended form in natural aqueous systems. In the dissolved form, HAs have the ability to form complexes with metals. When present as an organic solid phase, HAs provide a surface for metal adsorption from the aqueous system. Organic ligands derived from humic substances react with metals to form complexes, those influence the concentrations of free and labile metal ions and their subsequent mobilities and biotoxicities in soil and the associated environments (Chubin and Street, 1981; Gregor and Powell, 1988; Madrid and Díaz-Barrientos, 1998).

According to the equilibrium description of metal complexation elucidated by Perdue (1988), 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: $M + L_i = ML_i$.

$$K_i = \frac{\{ML_i\}}{\{M\}\{L_i\}} = \frac{[ML_i]\gamma_{ML_i}}{[M][L_i]\gamma_M\gamma_{L_i}} = K_i^c\Gamma_i \qquad (1)$$

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 γ-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 Γ_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:

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

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):

$$\overline{K}^* = \frac{\sum[ML_i(\text{bound})]}{[M(\text{free})]\sum[L_i(\text{free})]} \qquad (3)$$

where $\sum[ML_i(\text{bound})]$ is the sum of the concentrations of all complexes formed between M and the multiligand mixture, $\sum[L_i(\text{free})]$ 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 (hydroxyl and carbonato complexes) in the system under investigation, $\overline{K}^*$ values are often calculated directly from experimental data as

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

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 $\sum[ML_i(\text{bound})]$ as $(C_M - [M])$, the presence of inorganic complexes of the metal ion has been neglected. In calculating $\sum[L_i(\text{free})]$ 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, we used well characterized humic substances HA (MW > 1000), fulvic acid (FA) (MW > 1000), and FA (MW < 1000) extracted from swine compost to investigate the reaction with Pb, Cu, Cd, and Zn. Eq. (4) was used to calculate the average conditional concentration quotients of the complexes formed by the reaction of metals with humic substances of compost in the metal-HA suspension and metal-FA solution systems at initial pH of 4.00 and 6.50. The aim of this study was thus to investigate the average conditional concentration quotients of the complexes formed by the reaction of metals with compost-derived humic substances and the relations of the obtained average conditional concentration quotients to the reported thermodynamic stability constants as well as other parameters.

2. Materials and methods

2.1. Characterization of compost and its derived humic substances

The swine compost was purchased from Talin Sugarcane Mill, Taiwan Sugar Company (Talin Township, Chia-I County, Taiwan) to perform the experiment. HA