



Specific chemical interactions between metal ions and biological solids exemplified by sludge particulates



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HIGHLIGHTS

- pH plays an universal role on metal uptake by sludge particulates.
- Dissolved organic matter can compete with sludge particulates for metal ions at specific pH value.
- The surface acidity of sludge particulates is defined in acidity strength and acidity capacity.
- Surface complex formation can describe metal ions and sludge particulates well.

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ABSTRACT

The adsorption of metals onto biological surfaces was studied exemplified by municipal sludge particulates of the primary, the secondary, and the tertiary sludge types from four regional wastewater treatment plants. Major factors affecting the extent of metal adsorption including pH, DOM, total biomass, and total metal loading were studied. The acidity–basicity characteristics of the DOM, the metal ions (Lewis acids), and the surface of the sludge particulates make pH the most important parameter in metal adsorption. Change in pH can modify the speciation of the metal ions, the DOM, and the surface acidity of the sludge particulates and subsequently determines the degree of metal distribution between the aqueous phase and the sludge solids. Information on the acidity–basicity characteristics of the DOM and the sludge particulates are used to calculate the stability constant of metal ion–sludge complexes.

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1. Introduction

The presence of metals in the aquatic environment is a potential hazard to human and the ecosystem. In order to protect human and ecological health, it is necessary to control the flux of metals into the environment. A major approach for controlling metals in the environment is to remove metals from wastewater streams before discharge to the receiving water bodies. Another strategy is achievable by better understanding the fate and transport of metals in the water environment. There have been many studies on the removal of metals from dilute water solutions using various adsorbents. Unconventionally solid materials such as waste residues, natural minerals, and biomass materials can be potential metal adsorbents. Metal adsorbents derived from waste residues such as concrete residues (Weng and Huang, 2001), activated carbon (Corapcioglu and Huang, 1987; Huang and Blankenship, 1984), soil minerals (Elliott et al., 1986a,b), and sludge particulates (Tien and Huang, 1987, 1991; Wang et al., 1999, 2000, 2003a,b, 2006, 2007)

have been studied. These materials can be simply or minimally processed from a host of solid waste products and converted to metal adsorbents. Metal adsorbents based on well-cultured biomass materials such as bacteria, algae and fungi have been studied also. Several researchers have studied the adsorption of metals onto fungal biomass (Huang et al., 1990, 1991, 1998; Huang and Huang, 1996; Filipovic-Kovacevic et al., 2000; Al-Hakawati and Banks, 2000; Sag et al., 2001; Sag, 2013; Haytuglu et al., 2001; Akar et al., 2005; Akar and Tunali, 2006; Shroff and Vaidya, 2011; Faghihian and Peyvandi, 2012; Lin et al., 2012; Wang et al., 2012). Davis et al. (2003) reviewed the biochemistry of metal biosorption by brown algae and evaluated the role of cellular structure, storage polysaccharide, cell wall and extracellular polysaccharides on biosorption of metals. Wang and Chen (2009) report that biological materials, especially, bacteria, algae, yeast, and fungi are better metal adsorbents than ion exchange resin due to the presence of a wide variety of functional groups, such as carboxyl, imidazole, sulphhydryl, phosphate, sulfate, thioether, phenol, carbonyl, amide, and hydroxyl moieties on the cell surface. Rodriguez-Triado et al. (2012) studied the adsorption of Cu(II) and Pb(II) onto *Bacillus thioeparans* at different salinity and pH values.

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Chakravarty and Banerjee (2012) attributed the removal of Cd(II) by acidophilic bacteria to the surface functional groups of amino, carboxyl, hydroxyl, and phosphate. Most recently, Liu et al. (2013) studied the adsorption of Cu(II) and Pb(II) onto *Pseudomonas pseudoalcaligenes* biomass. Chojnacka et al. (2005) reported that surface functional groups, namely, carboxyl, phosphate, and hydroxyl or amine was responsible for the removal of heavy metals ions, Cr(III), Cd(II), Cu(II) by blue-green algae, *Spirulina* sp. Al-Rub et al. (2006) reported the suppression of Cu(II) adsorption by Pb(II) and Zn(II) on green algae, *Chlorella vulgaris*. Chen et al. (2012) reported that Ca²⁺ ions can regenerate Cd(II)-laden microalga *Scenedesmus obliquus* indicating the electrostatic nature of the metal binding reaction.

Due to unique physical and biological characteristics, sludge particulates can be ideal metal adsorbents. Stones (1955) were probably among the first to study the uptake of heavy metals by sludge particulates. Barth et al. (1965a,b) reported percentage removal of 27%, 55%, 15%, and 63% versus 2.4%, 9.0%, 2.5%, and 14% for Cr(VI), Cu(II), Ni(II), and Zn(II) by the secondary and the primary sludge particulates, respectively. Several researchers reported a two-phase metal removal process, a rapid initial phase of great magnitude followed by a slow and less important secondary phase by secondary sludge particulates (Cheng et al., 1975; Neufeld and Hermann, 1975; Kelly et al., 1979; Nelson et al., 1981; Elenbogen et al., 1987). Some researchers investigated the role of extracellular polymers on metal uptake by sludge particulates (Brown and Lester, 1979, 1982a,b; Hunter et al., 1983; Rudd et al., 1982, 1984; Kelly et al., 1979; Corpe, 1974; Saunders and Fick, 1981; Higham et al., 1984; Trevors et al., 1986; Ghosh and Bupp, 1992; Chang et al., 1995; Fukushi et al., 1996). Studies have shown that Hg(II), Pb(II), and Cd(II) are among the most removable metals, whilst Ni(II) is the least removable by sludge particulates (Cheng et al., 1975; Neufeld and Hermann, 1975; Sherrard, 1983; Tien and Huang, 1987, 1991; Barth et al., 1965a,b; Stones, 1955, 1960). Wang et al. (1998a, 1999, 2003a,b, 2006, 2007) reported that pH, dissolved organic matter (DOM), concentration of sludge particulates and type and concentration of metal ions play important role on metal uptake by sludge particulates. Davis et al. (2003) and Sag (2013) even suggested that it is feasible to use sludge particulates as metal adsorbents for the removal of metals from waste streams.

Most of these studies only provide qualitative or semi-quantitative account of the adsorption of a limited number of metal ions on sludge particulates in particular and other biomass materials in general under limited experimental conditions. Little quantitative information on how to characterize the physical-chemical properties of sludge particulates and the dissolved chemical matrixes in the wastewater environments and the specific chemical interactions among them is available. Langmuir and/or the Freundlich adsorption isotherms are the most commonly used equation to describe the equilibrium adsorption of metals by biomass adsorbents. As far as quantitative description of the uptake of metals by sludge particulates is concerned, there is a lack of unified methodology. The acidity of dissolved organic matter, derived from the biomass, and the surface acidity and surface properties of biological particulates relevant to metal ion adsorption are important information. This study aimed at developing a methodology for quantifying the DOM, the biological surface, and the interactions between metal ions and sludge particulates from municipal wastewater treatment plants using pH as a master variable. It is expected that results will be useful to the design of strategy for the control of metals in wastewater treatment plants and the possible use of sludge particulates as adsorbents for the removal of metals from industrial waste streams. Furthermore, it is possible that the results of metal adsorption onto sludge particulates can be applied to other bio-adsorption systems as well.

2. Characterization of DOM and sludge particulates

2.1. Characterization of DOM

The chemical nature of DOM in wastewater systems is complex. It is a mixture of degraded biomass detritus and organic compounds intrinsic to the wastewater stream. Quantification of the chemical functionalities of DOM is useful to estimate the degree of metal ion association with DOM and subsequent metal adsorption on sludge particulates. Acidimetric–alkalimetric titration can be employed to characterize the acidity characteristics of DOM in the sludge samples collected from any wastewater treatment plants. This method is based on the assumption that DOM contains two discrete monoprotic weak acids (two-site model), i.e., HL_A and HL_B:



where, L_A⁻, L_B⁻ = negatively charged soluble organic ligands; K_{aA}, K_{aB} = acidity constants for HL_A and HL_B, respectively. From law of mass balance, K_{aA} and K_{aB} can be expressed as:

$$\begin{aligned} K_{aA} &= \frac{[\text{H}^+][\text{L}_A^-]}{[\text{HL}_A]} \\ K_{aB} &= \frac{[\text{H}^+][\text{L}_B^-]}{[\text{HL}_B]} \end{aligned} \quad (2)$$

Since the carbonate species present in the wastewater also consume strong acid and base during titration when titration starts from neutral (generally pH is in the range from 6.0 to 8.0), correction for carbonate neutralization capacity is necessary. The cumulative volume of strong acid–base consumed, ΔV, is shown in the following mass balance equation, i.e.,

$$\Delta V = \frac{V_0}{C} \left[C_A \left(\frac{K_{aA}}{[\text{H}^+] + K_{aA}} - \frac{K_{aA}}{[\text{H}^+]_0 + K_{aA}} \right) + C_B \left(\frac{K_{aB}}{[\text{H}^+] + K_{aB}} - \frac{K_{aB}}{[\text{H}^+]_0 + K_{aB}} \right) + C_T \left(\frac{10^{-16.6} - [\text{H}^+]^2}{[\text{H}^+]^2 + 10^{-6.3}[\text{H}^+] + 10^{-16.6}} - \frac{10^{-16.6} - [\text{H}^+]_0^2}{[\text{H}^+]_0^2 + 10^{-6.3}[\text{H}^+]_0 + 10^{-16.6}} \right) + ([\text{OH}^-] - [\text{OH}^-]_0) - ([\text{H}^+] - [\text{H}^+]_0) \right] \quad (3)$$

where, V₀ = volume of DOM solution (mL); C = concentration of strong acid/base solution (M); C_A, C_B = concentration of acidic sites and basic sites, respectively (M); C_A = [HL_A] + [L_A⁻]; C_B = [HL_B] + [L_B⁻]; C_T = total concentration of carbonate (M); K_{aA}, K_{aB} = acidity constants of HL_A and HL_B, respectively; [OH⁻]₀, [H⁺]₀ = initial hydroxyl and hydrogen ion concentration (M). Using the alkalimetric–acidimetric titration data, a plot of pH versus ΔV can be made. From the titration curve, C_A, C_B, K_{aA}, and K_{aB} can be calculated using nonlinear regression by curve fitting of Eq. (3). The total carbonate concentration C_T can be determined separately by inorganic carbon measurement (IC) or by nonlinear regression technique. The DOM solution is prepared/preserved by keeping the collected samples in a refrigerator at 4 °C for 3–5 days then the mixed liquor is centrifuged at 20,000g for 10 min to obtain DOM. The COD, inorganic carbon (IC), and total dissolved solid (TDS) in the DOM samples are measured separately before titration. It is important that both sample and carbonate titrations start at the same initial pH value, which usually is in the range of 6–8. In addition, it is recommended that the pH change after each acid/base addition must not exceed 0.3 units in order to obtain reproducible titration data.

Table 1 lists the characteristics of DOM together with COD and total dissolved solids concentration from sludge sample collected from four regional municipal wastewater treatment plants, i.e., WI, PH, BA, and DC, respectively. Results indicate that the pK_a values of all samples were independent of sample source, type, and date. The average pK_{aA} and pK_{aB} values were 5.3 and 9.5, respectively.

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