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Copper and nickel speciation in mine effluents by combination of two independent techniques

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ABSTRACT

To control potentially toxic metals in water resources it is necessary to know metal speciation and changes in the metal speciation that occur after aqueous effluents containing metals are discharged into freshwaters. This work explores the speciation of nickel and copper in metal-mining aqueous effluents. Diffusive gradients in thin films (DGT) technique and competing ligand exchange (CLE) method have been applied to determine the speciation of nickel and copper. The results of this investigation demonstrate that combination of two analytical techniques having complementary analytical capabilities can provide a better physicochemical picture of metal speciation than either one of the analytical technique can do alone. The combined use of these techniques revealed that copper formed labile complexes having slow diffusion coefficient along with the presence of small labile copper complexes. Nickel-dissolved organic complexes (DOC) complexes in the aqueous effluent have been found to have fast diffusion coefficient. The results are likely to have environmental significance for providing a link between the metal species in mine aqueous effluent and their bioavailability by determining the characteristics of copper and nickel complexes in metal-mine aqueous effluents. This knowledge is expected to promote a better understanding of the lability of DOC complexes of copper and nickel in mining effluents.

1. Introduction

Metal speciation analysis in aquatic environments is promising as a powerful tool for development of predictions of bioavailability and reliable risk assessment approach. However, the presence of very complex humic substances in aquatic environment makes metal speciation very complicated and challenging. Humic substances, which are predominant components of dissolved organic complexes (DOC) in freshwaters, are usually considered to be supramolecular association of large and small organic molecules [1]. However, according to a new view of humic substances recently proposed by Sutton and Sposito [1], humic substances are collections of diverse, relatively low molecular mass components forming dynamic associations stabilized by hydrophobic interactions and hydrogen bonds. Humic substances contain a continuous distribution of metal binding sites with different binding energies. Progress in determination of reliable physicochemical parameters to describe metal complexation by DOC is hindered partially by the inherent physicochemical complexity of DOC outlined above. Additionally, natural aquatic systems generally are subject to changing conditions and are practically never at chemical equilibrium. Thus, it is very challenging and difficult to determine the speciation of metals in natural aquatic environment. Use of a certain analytical technique for metal speciation detects species with physicochemical properties within a certain range, e.g., of size, mobility, stability/lability, etc [2,3]. The determination of speciation parameters and its range depends on the analytical thermodynamic/kinetic detection windows of the technique. It is well known that the ability of an analytical technique to detect compounds depends on the sensitivity of the given detection system to one of the properties of the compounds. Every technique has a “detection window” that defines the range of values of a given property that can be sensed by the detector.

In addition to the detection window for thermodynamic stability, each analytical technique has a kinetic detection window (determined by the measurement timescale). Only complexes which can dissociate and be detected by the technique within this timescale will be “seen”. The degree to which a complex is detected by a given technique is quantified by the operational concept of lability. If a metal complex is labile under given conditions, then all of the complexed metal will be detected.

Because of the presence of heterogeneous humic substances in aquatic system, employment of only one technique for metal speciation may not be sufficient to represent a complicated aquatic system. Combination of two or more appropriate techniques, with

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their associated measurement timescale and detection window, may provide more information of metal speciation in aquatic system. It is of clear interest in this article to extract more physicochemical information of metal species in natural aquatic system by comparing the data obtained by different independent techniques.

This work has focused on the speciation of copper and nickel because of their increasing concentration in the aquatic environment as a result of industrial and agricultural activities [4,5]. Copper and nickel which may be present at relatively high concentrations in aqueous effluents from copper and nickel mines are potential toxic hazards in the freshwater environment. This work presents the investigation of chemical speciation of nickel and copper in Copper Cliff mine aqueous effluents from Sudbury, Ontario, Canada. However, these two metals show very complex chemistry in presence of humics in natural water. Osterberg et al. [6] reported that copper interacts with humic acid in a very complex way. They reported that copper may bind to the intra-particle binding sites of humics [7] and it may involve diffusion of metal ion into the particles. Similarly nickel has also been reported as another typical metal which has a slow kinetics. The difficulties involved during the determination of the speciation parameters of these metals and high concentrations of copper and nickel in Sudbury mine aqueous effluent challenged us to do further speciation studies of these metals.

In order to obtain a complete and comprehensive picture, the results obtained by DGT technique are combined with those obtained by competing ligand exchange (CLE) method in conjunction with adsorptive stripping voltammetry (AdSV) [7] in the same mine aqueous effluent samples. Identical results cannot be expected for these techniques because of the fact that they are based on different principles. However, in the same detection window (sensing the similar complexes), comparison of the data obtained by these two techniques can provide a better understanding of metal speciation. The main thrust of this work is to develop a better understanding of metal speciation by combing these two independent analytical techniques.

2. Theory

2.1. Diffusive gradients in thin films technique (DGT)

DGT measures an operationally-defined species. Only those species are measured by DGT (called DGT-labile) which are dissociated during their transport through the total thickness of the DGT diffusion layer plus the protective top layer of cellulose membrane [8,9]. The measurement timescale uniquely defines the measured species. In DGT, the quantification of the measured metal complex is done by binding the dissociated metal species by the DGT's resin binding phase; the bound metal is accumulated, and quantified.

If the m is the accumulated mass of a metal in the binding resin, and A is the area of exposed window and t is the deployment time, then the flux of metal under the steady-state (J_{ss}) can be represented by Eq. (1) [8].

$$\frac{dm}{dt} = J_{\mathrm{ss}}A \tag{1}$$

During the deployment, the flux (J_{ss}) of metal can be described by Fick's law [8]

$$J_{\mathrm{ss}} = \frac{CD}{d_{\mathrm{g}}} \tag{2}$$

where, C and D are the bulk concentration and diffusion coefficient of metal species. d_{g} is the thickness of the diffusive gel.

Combining these two equations, we can write,

$$m = \frac{CDAt}{d_{\mathrm{g}}} \tag{3}$$

In natural waters, there are free metal ions and metal ligand complexes, ML, in the solution; These metal complexes will contribute to the measured flux if the metal complexes dissociate during the transport through the diffusive gel layer. Considering the contribution of ML to the flux, Eq. (3) can be expressed as Eq. (4) [2]

$$m = \frac{(C_{\mathrm{M}}D_{\mathrm{M}} + C_{\mathrm{ML}}D_{\mathrm{ML}})At}{d_{\mathrm{g}}} \tag{4}$$

where, C_{M} is the concentration free metal ion, D_{M} is the diffusion coefficient of free metal ion, C_{ML}, is the concentration of dynamic metal complexes which can produce metal ion by dissociation within the timescale of the measurement.

The above equations are applicable only if the thickness of diffusive boundary layer (δ) in solution is insignificant, i.e., d_{g} is sufficiently larger than δ. However, recent laboratory experiments and field investigations involving diffusive gradients in thin films (DGT) have shown that the thickness (δ) of the diffusive boundary layer, which can affect the accuracy of the technique, is generally not negligible. Accordingly, the determination of δ has become a matter of considerable practical importance.

The thickness of diffusion boundary layer (δ) can be calculated by following way.

If J^i is the flux of metal at the solution on the interface of diffusive gel layer (d_{g}) and the diffusive boundary layer (δ) then, $J^i{}_{\mathrm{sol}}$ can be expressed as follows

$$J^i{}_{\mathrm{sol}} = \frac{D_{\mathrm{sol}}(C^* - C_i)}{\delta} \tag{5}$$

where, D_{sol} = diffusion coefficient of metal in the aqueous solution; C_i = concentration of metal complexes at the interface; C^* = bulk concentration of metal complexes and when, J^i is the flux of metal inside the gel layer at the interface of diffusive gel layer(d_{g}) and diffusive boundary layer (δ) then, $J^i{}_{\mathrm{gel}}$ can be expressed by

$$J^i{}_{\mathrm{gel}} = \frac{D_{\mathrm{gel}}(C_i)}{d_{\mathrm{g}}} \tag{6}$$

where, D_{gel} = diffusion coefficient of metal species in the gel.

Maintaining the continuity of metal flux at steady-state, i.e., $J^i{}_{sol} = J^i{}_{gel}$, we can write

$$\frac{D_{\mathrm{sol}}(C^* - C_i)}{\delta} = \frac{D_{\mathrm{gel}}(C_i)}{d_{\mathrm{g}}} \tag{7}$$

If the average diffusion coefficient of metal in the solution and inside the diffusive gel layers are different, i.e., $D_{\mathrm{sol}} \neq D_{\mathrm{gel}}$, then the above equation reduces to

$$\frac{D_{\mathrm{sol}}}{D_{\mathrm{gel}}} = \left(\frac{C_i}{C^* - C_i}\right)\frac{\delta}{d_{\mathrm{g}}} \tag{8}$$

Equating C_i from the above equation, we can write

$$C_i = C^*\left(\frac{D_{\mathrm{sol}}d_{\mathrm{g}}}{D_{\mathrm{gel}}\delta + D_{\mathrm{sol}}d_{\mathrm{g}}}\right) \tag{9}$$

Incorporating the value of C_i in Eq. (2)

$$J_{\mathrm{flux}} = \frac{D_{\mathrm{gel}}C^*D_{\mathrm{sol}}}{\left(D_{\mathrm{gel}}\delta + D_{\mathrm{sol}}d_{\mathrm{g}}\right)} \tag{10}$$

This is the general equation for metal flux towards the binding gel under the steady-state conditions.