CHARACTERIZATION OF SORPTION AND QUANTITATIVE ANALYSIS OF HYDROXYL COMPLEXES OF Cu AND Zn IN AQUEOUS SOLUTION: THE INTERACTIVE EFFECTS OF MINE WASTEWATER-MIXED MINERAL SYSTEMS

*1Egirani, D.E and 2Andrews, J and 2Baker, A

1Faculty of Science, Niger Delta University, Wilberforce Island, Nigeria
2Schools of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK

INTRODUCTION

Cu and Zn metal pollutants discharged by acid mine drainage and weathering of mineralized bedrock remain major sources of degraded water chemistry, potentially causing toxicity to aquatic life [Ridge and Sedlak 2004]. Although, copper and zinc metals are very important in maintaining the metabolism of the human body and inorganic fractions in these minerals. However, bioavailable studies are mostly based on interaction between aqueous solution and single mineral sorbents [Querol et al 1999]. More recently, there have been attempts at characterizing sorption behavior of Cu and Zn using interaction of wastewater with mixed mineral systems [Egirani et al 2005a, Egirani et al 2005b]. This paper explores Cu and Zn removal from natural mine wastewater using mixed mineral systems and attempts to validate the role of Cu and Zn hydroxylation in the sorption process.

Theoreric Considerations

Contaminants such as Cu and Zn metals are not fixed irreversibly by the sediments, and under changing environmental conditions they can be released by various processes into water courses [Medici et al 2011]. It is well known that these two metals when released into receiving water courses can be removed as free aqueous species and as bound forms [Sposito 1984]. The effect of complex formation on the overall adsorption of a metal ion depends on the stability of the complex formed and the relative affinity of the metal surface for the free and complex forms [Kinniburgh and Jackson 1981].

In addition, ligands (i.e. functional group that binds to a central metal to form a coordination complex) promote adsorption when they have high affinity for a metal, forming a soluble complex [Sposito 1984]. The ligands can have a direct high affinity for the mineral thus forming a mineral-ligand complex [Davis and Leckie 1978]. Also, the reactivity of mineral surfaces depends on the behavior of other functional groups in the vicinity of the reaction. These surface functional groups generate reactive sites when in contact with water and adsorption is concentrated on the higher energy sites [Schindler 1981].

Metals, including Cu and Zn, have high affinity for the aluminol and hydroxyl surface functional groups on the surfaces of clay and hydrous oxides and metals can complex with organic matter and inorganic fractions in these minerals.

ARTICLE INFO

Article History:
Received 1 1th, February, 2013
Received in revised form 13th, March, 2013
Accepted 25th, March, 2013
Published online 30th April, 2013

Key words:
Wales, mixed mineral systems, hydroxyl complexes, Cu and Zn

ABSTRACT

This study investigates sorption of Cu and Zn using mixed mineral systems to treat natural mine wastewater obtained from disused mine workings at Parys Mountain and Cwmhrheidol in Wales, United Kingdom. Mixed mineral systems of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite were tested with the mine waste water for sorption of Cu and Zn at variable pH. In addition, levels of saturation of hydroxyl complexes were analyzed. Batch reactions conducted at room temperature (23±2°C) revealed significant behavioral differences in Cu and Zn sorption by mixed mineral systems compared to each other and compared to single mineral systems. All mixed mineral systems sorbed more Cu than Zn when tested with Parys Mountain mine wastewater. On the other hand, all mixed mineral systems sorbed more Zn than Cu when tested with Cwmhrheidol mine wastewater. This study conducted using single mineral suspensions and 1:1 mixed mineral suspensions indicated progressive increase in saturation indices with increase in pH. There was no evidence of stable hydroxylation of Cu and Zn species that could significantly contribute to the sorption of these metals by mixed mineral systems.

* Corresponding author: Tel: +2348104826459
E-mail address: eenonidavidson@yahoo.com,
Surfaces of clay and oxide minerals possess silanol (SiOH) and aluminol (AlOH) reactive sites [Benjamin and Lecky 1981]. The reactivity of the silanol sites depends on the nature of the charge distribution within the crystal structure. In addition, the reactivity of the aluminol (AlOH) functional group depends on the metal involved and the structural orientation of the reactive sites [Kinniburgh and Jackson 1981]. The silanol reactive sites possess high energy sites in both mildly acidic and moderately alkaline solutions with the number of reactive sites increasing with increasing pH. At higher pH, aluminol reactive sites possess lower interaction energy sites. Therefore, the mixing of clay and hydrous oxides probably results in surface masking of these reactive sites by precipitation and surface area alteration (Soma and Soma 1989).

Furthermore, metals can be removed as hydroxyl complexes in oxic environments and as sulphides in anoxic environments. These metals are partitioned and co-precipitated with iron oxides [Sobolewski 1999]. Stability sequences for complexes are in the order Zn>Cu, thus Cu complex is easily precipitated. However, complexes impart ionic interferences to other ionic species in solution. The quantities of ionic and non-ionic species in solution are determined by the parameters of total dissolved solids, conductivity and salinity. Therefore, in the presence of dissolved species, the effective concentration of metals is lowered by precipitation on colloids and suspended particulates [Matagi et al. 1998].

Complexes formed by Cu and Zn ions are either by ligand exchange or by the hydrated ions on the mineral surfaces. In addition, Cu and Zn ions are amphoteric and at high pH form unstable complex ions that are negatively charged. The formation of surface complexes impedes sorption when they have similar charges to the sorbing cations. The formation of cationic Zn complexes attenuates the sorption of Zn ions in solution [Hu and Sulzberger 1994]. Where there is an anionic bridging effect between a surface complex and mineral surface, unit sorption of metals is enhanced [Schlautman and Johnson 1992]. The most important ligand that affects Cu and Zn adsorption is the hydroxyl ion (OH-). A sharp increase in the adsorption of Cu on kaolinite, at pH 5.5 to 6.0 range has been observed (Sposito 1984), and is attributed to sorption of Cu-hydroxyl complexes by the clay mineral. However, surface complexes formed by Cu and Zn ions on mineral surfaces are unstable and are hydrolysis dependent [Sparks 2003, Fahnni 2001].

Important questions regarding possible role of hydroxylation in the sorption of metals by mixed mineral systems remain elusive. In this paper, the effects of mixed mineral systems of kaolinite, montmorillonite and goethite on the sorption of Cu and Zn have been characterized in the laboratory and results validated using Freundlich model isotherm. Also, validation of the role of hydroxylation of these two metals during the sorption process has been quantitatively determined.
Details of characterization of minerals used and experimental methods are provided in previous papers [Egirani et al 2005a, Egirani et al 2005b]. The methodology is summarized (Figure 1) and the characteristics of the mine wastewater provided for batch mode investigation, single mineral suspensions of kaolinite, montmorillonite, goethite and 1:1 mixed mineral suspensions of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite made up to 50 ml containing 1% (by mass) were added to the mine wastewater containing 4.76±0.74 ppm Cu, 156±0.55 ppm Zn for the Cwmreihdol mine wastewater and 76.07±0.50 ppm Cu, 165±0.78 ppm Zn for the Parys Mountain mine wastewater. These solutions containing zero added electrolyte background were adjusted to the required pH (ranging from pH 4 to 8) using 0.1 M HNO₃ and 0.1 M NaOH. The mineral suspensions were equilibrated for 24 h and pH measured using a Model 3340 Jenway ion meter.

Three replicates were used for each test, and metal concentration sorbed (S) in mgkg⁻¹ was calculated from the difference between the initial metal concentration (Ci) (metal concentration before sorption) and the equilibrium concentration (Ce) (the metal concentration in solution after sorption equilibrium as follows:

\[ S = (C_i - C_e) \frac{W}{V} \]

where \( V \) is the suspension volume and \( W \) is the mass of mineral solid. The amount of metal remaining in the filtrate was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in this paper are provided in previous paper [Egirani et al 2005b]. Kd (L/Kg) was calculated from the Freundlich model equation,

\[ S = KdC_N \]

where S is the sorbed concentration (mg/kg), Kd (L/Kg) is the distribution coefficient, C is the equilibrium concentration (mg/L), and N = 1 is a chemical-specific coefficient derived from the slope of the plot.

The empirical model as provided by Egirani et al 2005a to address the mineral-metal interactions is given:

\[ Kd_{total} = Kd_1 + Kd_2 + \ldots + Kd_n \]

where Kd_{total} is the theoretical distribution coefficient for a 1:1 mixed suspension, Kd_1 is the distribution coefficient for first single mineral suspension, and Kd_2 is the distribution coefficient for second single mineral suspension, Kd_n is the distribution coefficient for n number of mineral suspensions and n is the number of mineral suspensions. The simple empirical model used for the partitioning of a sorbed metal between mineral phases in mixed suspension is based on the following conditions:

1. No significant secondary mineral phase is developed by the mixed mineral suspension except at alkaline pH.
2. Components of minerals in the mixed mineral suspension act as individual networks and not as chemisorbed species.
3. Mass of mixed sorbent must be equal to the mass of the single mineral phases

**Quantitative study of Cu and Zn hydroxyl complexes**

The degree of saturation (D_s) for the presumed complexes Cu(OH)_2 and Zn(OH)_2 was quantitatively determined by comparing the Ion Activity Product (IAP) to the conditional solubility constant (Ksp). Log D_s is the Saturation index (SI).

Where:

SI<0 the suspension is undersaturated with respect to the complex

SI = 0, suspension is saturated to the complex

SI>0, suspension is supersaturated with respect to the complex.

Where M^n⁺ is the metal molar concentration and H⁺ as suspension pH, Ksp for Cu(OH)_2 (20) and Ksp Zn(OH)_2 (17) [Younger et al 2002].

\[ IAP = [M^{2+}](OH)^{-2} \]

\[ D_s = \frac{IAP}{Ksp} \]

\[ SI = \log \frac{IAP}{Ksp} \]

\[ Cu(OH)_{2}^{+} = CuOH^{+} + OH^- \]

\[ Zn(OH)_{2}^{+} = ZnOH^{+} + OH^- \]

**RESULTS AND DISCUSSIONS**

Characterization of Cu and Zn sorption by single mineral systems Parys Mountain mine wastewaters and Cwmreihdol mine wastewaters treated with single mineral suspensions of kaolinite, montmorillonite and goethite revealed variable % of Cu and Zn sorption as shown graphically (Figures 3-8). Differences in replicate measurements for individual pH were not statistically (chi squared) different (P ≤ 0.01). Results were similar with simulated waste water of Cu and Zn treated with the same single minerals. Simulations were completed using analytical methods described in previous papers [Egirani et al 2005a, Egirani et al 2005b].

Parys Mountain mine wastewater treated with single mineral systems showed pH of at which 50% of contaminant is sorbed) Cu and Zn sorption; occurring at pH 7 for kaolinite, goethite and pH 8 for montmorillonite. A unit change in pH i.e. from pH 6 to 7 resulted in a similar change in % sorption of both Cu and Zn by montmorillonite treated Parys Mountain mine wastewater. Also, the % Cu and Zn sorbed ratio was significantly different at pH 4 but similar from pH 5 to 8 (Figures 3-5).

![Figure 3 Percentage plots for Cu and Zn removal by single and mixed mineral suspensions as a function of pH for Parys Mountain waste water](image)
At pH 7, Cu and Zn removal by kaolinite was well above the pH_50 mark whilst removal by montmorillonite was below it. Cu and Zn remaining in mine wastewaters after treatment were above the recommended EPA levels of less than 1.3mg/l Cu and less than 5mg/l Zn for drinking water (EPA 1992). Therefore, phases of settling pond reactions would be required for an acceptable reduction of Cu and Zn contaminants to support humans and aquatic life.

Characterization of Cu and Zn sorption by mixed mineral systems

The data in figure 3 show Cu and Zn sorption for all the mixed mineral systems over the range of pH studied. For the Parys mine wastewater, Cu sorption displayed a greater than pH_50 sorption at pH 7 for kaolinite/montmorillonite and kaolinite/goethite, whilst that for montmorillonite/goethite occurred at pH 6. Sorption was below the pH_50 mark for Zn sorbed by kaolinite/montmorillonite. Also, Cu/Zn % removal ratios for these mineral systems were significantly different at pH 4 but similar for the rest of the pH range. Furthermore, the Cu/Zn % ratio sorbed indicated more Cu sorption than Zn, increasing with increased pH for all mixed mineral systems (Figures 3-4).

Estimates of % of Cu and Zn sorbed calculated using the empirical model exhibited complex sorption behaviour, showing more Cu sorption than Zn. Zn sorption differences were negative (i.e. the predicted percentage of sorption was less than that obtained in laboratory tests). Cu sorption differences were positive (i.e. the predicted percentage of sorption was more than that obtained in laboratory tests) for all mixed mineral systems.
Therefore, for the Parys Mountain mine wastewater, mineral mixing over the entire range of pH depressed Zn removal. This may be due to the low solubility of Cu relative to Zn. Based on the % sorption of Cu and Zn by the mixed mineral systems at pH 7, other water treatment methods such as series of settling pond reactions would be required to meet discharge water quality as recommended by EPA.

For the Cwmrheidol mine wastewater, mineral mixing over the entire range of pH enhanced Zn removal and depressed Cu removal (Figures 6-8). Therefore, the remediation of the Cwmrheidol mine wastewater with the mixed mineral systems at pH 7 would favor Zn removal relative to Cu. Greater Zn than Cu removal suggested that the concentration of Cu in the Cwmrheidol mine wastewater could not allow Cu to compete effectively with Zn for the reactive sites at pH 7. Differences in the characteristics of Parys Mountain and Cwmrheidol mine wastewaters include total dissolved solids and sulfate concentrations, both parameters are much higher at Prays Mountain (Table 1). These two parameters might have contributed to the reverse in sorption behavior of Cu and Zn by the mixed mineral systems.

Copper and Zinc hydroxylation

In all studied cases, mixed mineral systems of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite were under-saturated with respect to the hydroxyl complexes of Cu and Zn metals (Figure 9). Differences in Cu hydroxylation for both simulated and tested Cwmrheidol natural mine wastewater were marginal. Cu hydroxylation for Parys Mountain mine wastewater and simulated mine wastewater were similar becoming different at pH > 7. In addition, differences in progressive hydroxylation of Zn for both simulated and tested Cwmrheidol natural mine wastewater were marginal. Zn hydroxylation for the Parys Mountain mine wastewater and the simulated wastewater were similar becoming different at pH>7. This means that pH does not significantly affect the formation and retention of copper complexes at lower pH. Also, hydroxylation of Cu and Zn for both the simulated and tested natural mine wastewaters are pH dependent. Neither Cu nor Zn appears to form stable hydroxyl complexes. An alternative explanation could be that Cu and Zn hydroxyl complexes were formed but became destabilized over time due to hydrolysis.

<table>
<thead>
<tr>
<th>Location</th>
<th>pH</th>
<th>Cu (mM/L)</th>
<th>Zn (mM/L)</th>
<th>Cu (mg/L)</th>
<th>Zn (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cwmrheidol</td>
<td>8.74</td>
<td>1.9e-01</td>
<td>1.2e+00</td>
<td>1.0e+01</td>
<td>1.2e+01</td>
</tr>
<tr>
<td>Parys Mountain</td>
<td>8.04</td>
<td>2.0e+00</td>
<td>1.2e+00</td>
<td>1.0e+01</td>
<td>1.2e+01</td>
</tr>
</tbody>
</table>

Table 1 Characteristics of natural mine wastewater
CONCLUSIONS

In testing analysis of both Parys Mountain and Cwmrheidol mine wastewaters, none of the mineral systems were shown to reduce the contaminants to EPA levels. Other water treatment such as a series of settling pond reactions are required for an acceptable removal of the Cu and Zn contaminants, i.e. reduction to about <1.3 mg/L Cu and <5 mg/L Zn. With Parys Mountain mine wastewater more Cu was sorbed than Zn when treated with the mixed mineral systems. This may be due to the low solubility of Cu relative to Zn. With the Cwmrheidol mine wastewater more Zn was sorbed than Cu by the mixed mineral systems. This may be attributed to the inability of Cu to compete effectively with Zn for reactive sites. The quality of mine wastewater after treatment was a function of the mineral systems. This assessment is based on the reasoning that there was disparity in the sorption behavior of the single mineral systems for Cu and Zn in Cwmrheidol and Parys Mountain mine wastewater under similar pH conditions. Differences in the characteristics of both Parys Mountain and Cwmrheidol mine wastewaters especially in total dissolved solids and sulfate concentrations might have contributed to the reverse in sorption behavior of Cu and Zn by the mixed mineral systems. In all cases, Cu and Zn metals demonstrated under-saturation of potential hydroxyl complexes. At pH > 7, saturation indices for simulated and natural mine wastewater converged, becoming similar and diverging over time. It could be that Cu and Zn hydroxyl complexes were formed but became destabilized over time due to hydrolysis.

References


Walter K, Johnson D, 1992, Microbiological and chemical characteristics of an acidic stream draining a disused copper mine. Environmental Pollution, 76: 169-175.

*******