

# Copper and zinc removal from aqueous solution by mixed mineral systems II. The role of solution composition and aging

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Received 30 December 2004; accepted 3 May 2005

Available online 11 July 2005

## Abstract

This study investigates Cu and Zn removal onto binary mixed mineral sorbents from simulated wastewater, relevant to streams impacted by acid mine drainage and effluents. Mixed suspensions of kaolinite/montmorillonite and kaolinite/goethite exhibited different sorption behavior from the single mineral components, reducing Cu and Zn removal (except Cu sorbed on montmorillonite/goethite) over the range of pH investigated. Cu and Zn removal by the electrolyzed systems showed a complex response to increased ionic strength, which increased solid concentration, leading to lower Cu and Zn sorption. Enhanced Cu sorption on the montmorillonite/goethite as age increased may be attributed to increased hydroxylation of the mineral surface resulting in the formation of new reactive sites.

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*Keywords:* Copper; Zinc; Clay minerals; (Hydr)oxides; Sorption; Mixed minerals; pH; Ionic strength; Solid concentration and aging

## 1. Introduction

Heavy metal pollutants discharged by acid mine drainage, weathering of mineralized bedrock, and wastewater treatment are the major causes of degraded stream water chemistry [1]. The need to reduce metal concentrations discharged into water bodies remains a priority in both developed and most developing countries.

The removal of dissolved metal species can be hampered by the absence of reliable sorbents and solution chemistry adequate to understanding metal sorption [2]. The removal of Cu and Zn ions from wastewater is controlled by the solution composition [3], namely, pH, ionic strength, and solid concentration, besides the residence time (aging) of the solid phase in the wastewater [4–6].

Since pH is considered a master variable in heavy metal removal in aqueous environments, its effects on Cu and Zn

removal by mixed suspensions of clays and (hydr)oxides is an area of research interest [7]. Solution pH controls (a) the solubilities of metal hydroxides; (b) hydrolysis behavior of metals; and (c) surface charge of the sorbent [8].

Ionic strength effects on heavy metal adsorption depend on the predominant sorption mechanism. Adsorption may decrease as ionic strength increases (outer sphere complexation) or not be significantly affected as ionic strength increases (inner sphere complexation) [9,10]. Increase in adsorption as ionic strength increases (promotive ionic strength effects) for organic and inorganic substances sorbed on colloidal clay and oxide particles still remains an area of research interest in conventional surface complexation theory [11]. The solid concentration effect is an anomalous adsorption phenomenon (i.e., the adsorption isotherm declines as particle concentration increases). Although the cause of this phenomenon remains unclear, the nature of metal species formed in solution is affected by changes in the mineral/solution ratio [12].

Prolonging the aging of a solid mineral phase in the absence of a sorbate results in much mineral surface reorgani-

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zation as high and new reactive sites are formed [13]. Details of the Freundlich isotherm and the associated empirical model used in validating the Cu and Zn behavior in this study are provided elsewhere in the companion paper I. In that paper the behavior of Cu and Zn in single and mixed mineral suspensions in terms of reactivity and reaction kinetics was investigated.

In this paper the sorption relationship between simulated wastewater containing Cu and Zn metals and mixed mineral suspensions of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite based on different solution composition and aging conditions was investigated. The choice to investigate Cu and Zn metals is based on the reasoning that these metals are some of the most commonly occurring base metals in wastewaters associated with effluents and mine discharge.

## 2. Experimental methods

Batch mode experiments in this study were conducted using 1:1 single mineral suspensions of kaolinite, montmorillonite and goethite. Also, 1:1 mixed mineral suspensions of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite were used to elucidate the difference in sorption between the single and mixed mineral phases. Characterization of sorbents used in this study included (a) particle size; (b) pH; (c) specific surface area (SSA); and (d) point of zero salt effect (PZSE). Details of characterization are provided elsewhere in a companion paper, I. In all batch mode experiments two components of the batch mode reactions (Cu or Zn and the electrolyte solutions) were added at the same time to the mineral suspension ( $t = 0$ ) and equilibrated for 24 h at the desired pH.

For batch mode pH investigation, single and 1:1 mixed mineral suspensions made up to 50 ml containing 1% (by mass) mineral suspension and 5 mg/l initial concentration of Cu and Zn as single sorbates at zero electrolyte background were adjusted to the required pH (ranging from pH 4 to 8) using 0.1 M HNO<sub>3</sub> and 0.1 M NaOH. The treated suspensions were equilibrated for 24 h and pH measured using a Model 3340 Jenway ion meter.

For batch mode ionic strength investigation, single and 1:1 mixed mineral suspensions made up to 50 ml containing 1% (by mass) mineral suspension of the required mineral(s) and 10, 15, 20, and 40 mg/l of Cu and Zn as single sorbates at pH 4 were adjusted to the required ionic strength, ranging from 0.0 M (i.e., no electrolyte solution was added to the mineral suspension) to 0.1 M NaNO<sub>3</sub>. Based on preliminary experiments, difference in molar concentration between Cu and Zn over the range of metal concentration (mg/l) used in this study was not sufficient to statistically ( $\chi^2$ ) significantly affect the distribution coefficient ( $P \leq 0.01$ ). The treated suspensions were equilibrated for 24 h.

For batch mode solid or particle concentration investigation, single and 1:1 mixed mineral suspensions were made

up to 50 ml containing solid concentrations (kg/l) of 0.002 to 0.01 and 10, 15, 20, and 40 mg/l of Cu and Zn metals. The treated suspensions adjusted to pH 4 and 0.01 M ionic strength was equilibrated for 24 h.

Batch mode aging investigations were carried out from 24 to 720 h using single and 1:1 aged mixed mineral suspensions containing 1% (by mass). These mineral suspensions made up to 50 ml contained 10, 15, 20, and 40 mg/l initial concentrations of Cu and Zn as single sorbates. The treated suspensions, adjusted to pH 8 with no added electrolyte, were equilibrated for 24 h. In all experimental studies samples were stored in the dark at room temperature ( $23 \pm 3$  °C) for a maximum of 24 h before analysis.

Twenty-four hours was sufficient to establish equilibrium between the solid and liquid phases because metal ion sorption reactions occur in milliseconds or minutes [14]. Kinetic experiments conducted at shorter equilibration times (i.e., beginning at 18 h) showed the same sorption behavior as at 24 h. Details of mineral suspension treatment including acidification and storage are provided in I.

Three replicates were used for each treatment, and metal concentration sorbed ( $S$ ) in mg kg<sup>-1</sup> was calculated from difference between the initial metal concentration  $C_0$  (metal concentration before sorption) and the equilibrium concentration  $C$  (the metal concentration in solution after sorption equilibrium),

$$S = \frac{(C_0 - C) \times V_{\text{total}}}{W_{\text{solid}}}, \quad (1)$$

where  $V_{\text{total}}$  is the suspension volume and  $W$  is the mass of mineral solid. The effect of polycarbonate tubes on the sorption of metal ions is so small that it can be neglected [15]. The amount of metal remaining in solution was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). Detailed system characterization and an empirical model involving the distribution coefficient ( $K_d$ ) as used in this paper are provided in I. Due to the low range of metal concentration used in this study, adsorption isotherms were of the  $C$  type, resulting in linear isotherms. Therefore,  $K_d$  was calculated from the Freundlich model equation,

$$S = K_d C^N, \quad (2)$$

where  $S$ ,  $C$ , and  $N$  are as described in I.

## 3. Results and discussion

### 3.1. Mixed mineral suspensions and pH effects on Cu and Zn removal

Cu and Zn sorption increased with increasing pH for both 1:1 single mineral suspensions of kaolinite, montmorillonite, and goethite and mixed mineral suspensions of kaolinite/montmorillonite, kaolinite/goethite, and montmorillonite/goethite (Fig. 1). The behavior of goethite in Cu and Zn removal was different from that of the rest of the single

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