

# Desorption of zinc by the kaolin from Suzhou, China

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## Abstract

This paper studied the influence of copper concentration, pH, temperature, and the ratio of solid to solution on desorption of Zn in the kaolin from Suzhou, China in a background solution of 0.01 M CaCl<sub>2</sub> by batch extraction experiments. At 0, 5, 50, 100 mg/l Cu concentration, for each 0.5 increase in pH between about 1.80 and 3.04% desorption decreases 3.80, 13.87, 9.97, and 7.65%, respectively. The pH<sub>50</sub> (pH at 50% Zn desorption) is found to follow the sequence: Cu (5 mg/l, pH<sub>50</sub>=2.60) < Cu (50 mg/l, pH<sub>50</sub>=2.70) < Cu (100 mg/l, pH<sub>50</sub>=2.95) < Cu (0 mg/l, pH<sub>50</sub>=10.65). The free energy change ( $\Delta G$ ) values, the values of enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ) have been calculated. There were no large differences in the desorption of Zn from 25 to 50 °C. The concentration of Zn in solution after desorption equilibrium increases and percent desorption decreases when the solid to liquid ratio increases from 0.025 to 0.2. The kaolin possibly cannot be used for the landfill clay liner.

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**Keywords:** Desorption; Zinc; Kaolin; Percent desorption; Thermodynamic parameters

## 1. Introduction

Zinc (Zn) is an essential micronutrient for organisms and is necessary for the functioning of various enzyme systems, deficiency of which leads to growth retardation. But it is also a toxic element when its concentration is above recommended value; toxic concentrations can cause adverse effects on animals and human body. Because of its toxicity for fish and aquatic life at relatively low concentrations, water quality criteria have been established to protect aquatic life in addition to human health. In China, Zn concentration is  $\leq 0.1$  mg/l in the water quality standard for fisheries (GB11067-89); Zn concentration is  $\leq 1.0$  mg/l in III grade water from the quality standard for ground water (GB/T14848-93).

Kaolin is mainly made of kaolinite and is a kind of fine grain clay. Its ideal chemical components are: SiO<sub>2</sub> 46.54%, Al<sub>2</sub>O<sub>3</sub> 39.50%, H<sub>2</sub>O 13.96%. Kaolin is usually used as a catalyst in some industries. In some landfills, it has been used as the engineering clay liner (a protective barrier) to impede the movement of pollutants produced from waste materials. Kaolin is also a low cost material adsorbent for removal of some pollutants from aqueous solution and remediation material for contaminated soils. Through preliminary experiment, Zn, Cu, Pb and Cd concentrations in the kaolin samples from Suzhou, China are 863.20, 20.35, 31.62 and 0.30 mg/kg, respectively. A major concern in the use of kaolin is that the concentration of Zn in soil and underground water may elevate to potentially toxic levels, which may adversely affect environmental quality. The environmental impact of heavy metal contaminants strongly depends on the metals speciation, mobility, and bioavailability; the chemical behavior of heavy metals in soils is controlled by a number of

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processes, including metal cation release from contamination source materials, cation exchange and specific adsorption onto surfaces of minerals and soil organic matter, and precipitation of secondary minerals (Voegelin et al., 2003).

Risk assessments for polluted soils are often based on batch extractions of heavy metals, assuming that the results are related to the risk of metal leaching into ground water or plant uptake. Critical data on the capacities of kaolin to desorbed Zn with being leached to contaminate ground water and food chain are required to risk assessments. In landfill leachates, pH, Cu concentration and temperature maybe fluctuate over a wide range. There is little or no report on the desorption reaction of Zn by kaolin from Suzhou, China. Because Cu concentration, pH and temperature probably are important factors influencing Zn desorption by the kaolin, the aim of this research is to study desorption of Zn by kaolin from Suzhou, China and the influence of copper concentration, pH, temperature, and the ratio of solid to solution.

## 2. Materials and methods

### 2.1. Kaolin samples

Kaolin from Suzhou, China is obtained from Chinese kaolin company, Jiangsu Province, China. A combined glass calomel electrode was used for measuring the kaolin pH in 0.01 M NaNO<sub>3</sub> solution (kaolin: solution = 1:10 mg/l). The kaolin samples were stirred by stirrer. After 1 day equilibrium was assumed and the pH was measured. Particle size distribution was measured by the MiCRO-P laser granularity instrument which was made by Malvern Instruments Ltd in United Kingdom. Mineralogy of the kaolin samples was determined via X-ray diffraction; the X-ray diffraction (XRD) patterns were recorded on a Rigaku Corporation D/max-3C X-ray diffractometer using Cu-K $\alpha$  radiation; the tube voltage was 35 mV and tube current was 15 mA; the samples were scanned at 0.2°/min in 2 $\theta$ . Chemical component was obtained by dry chemical analysis. Total Zn, Cu, Pb and Cd in kaolin was extracted from the kaolin sample using an acid digestion mixture (HF+HClO<sub>4</sub>+HNO<sub>3</sub>) in an open system (Wilkins et al., 1996) and was determined by Atomic Absorption Spectrometer (Thermo Electron; Type M6MK2). Some chemical and physical properties of kaolin studied are presented in Table 1.

### 2.2. Batch extraction experiments

#### 2.2.1. Desorption of Zn as a function of copper ions and pH

Desorption of Zn in the kaolin was conducted by the batch extraction experiments. 2.0 g of kaolin was added to 50 ml polyethylene centrifuge tube containing 20 ml 0.01 M CaCl<sub>2</sub> solution with different copper concentrations (0, 5, 50, 100 mg/l) and different pH (their initial solution pH varied between 1 and 11; pH was adjusted by few drops of HNO<sub>3</sub> or NaOH). The mixture was shaken at 25 °C in a shaker for 24 h. Previous kinetic

Table 1  
Some chemical and physical properties of kaolin studied

Chemical component/m % <sup>a</sup>	
SiO <sub>2</sub>	55.3
Al <sub>2</sub> O <sub>3</sub>	42.5
Na <sub>2</sub> O	0.07
K <sub>2</sub> O	0.42
Fe <sub>2</sub> O <sub>3</sub>	0.70
Particle size distribution/ $\mu\text{m}$ <sup>b</sup>	
<i>D</i> ( <i>v</i> ,0.1)	1.20
<i>D</i> ( <i>v</i> ,0.5)	3.70
<i>D</i> ( <i>v</i> ,0.9)	10.20
Mineralogical analysis (XRD)	
Kaolinite/m %	81
Quartz/m %	3
Total Zn (mg/kg)	863.20
pH	5.85

<sup>a</sup>Chemical components were obtained from kaolin samples, of which water has been removed.

<sup>b</sup>*D*(*v*, *x*) *y*  $\mu\text{m}$  represents that particles which have a diameter of  $\leq y$   $\mu\text{m}$  account for 100 *x* % in the volume.

studies indicated that a 24 h reaction period was sufficient to achieve equilibrium conditions when using the shaker. After shaking, the supernatant was separated by centrifugation at 3000  $\times g$  for 10 min, the supernatant was filtered through 0.45  $\mu\text{m}$  membrane filters, and the filtrate was acidified with HNO<sub>3</sub> and stored at 4 °C until Zn concentrations analysis by the Atomic Absorption Spectrometer (Thermo Electron; Type M6MK2). The detection limit is 0.0033 mg/l for Zn. There were three replicates for each treatment. The precision (RSD) was lower than 3%. The percent desorption (*D*) was calculated after 24 h reaction time as:

$$D = \frac{100CeV}{MC} \quad (1)$$

Where

<i>D</i>	The percent desorption (%),
<i>Ce</i>	The equilibrium concentration of Zn in the solution after the experiment (mg/l)
<i>V</i>	Volume of solution in the centrifuge tubes (ml),
<i>M</i>	Mass of clay in the tubes (g)
<i>C</i>	Total Zn concentration in kaolin (mg/kg).

The distribution coefficient value (*Kd*) was determined by using the formula:

$$Kd = \frac{Ce}{C(100\% - D\%)}. \quad (2)$$

#### 2.2.2. Influence of temperature on Zn Desorption

2.0 g of kaolin was added to 50 ml polyethylene centrifuge tube containing 20 ml 0.01 M CaCl<sub>2</sub> solution. The mixture was shaken at 25 °C, 30 °C, 40 °C, and 50 °C in a shaker for 24 h. The rest was the same as above experiment.

### 2.2.3. Influence of the ratio of solid to liquid on Zn desorption

20 ml 0.01 M CaCl<sub>2</sub> solution was added to 50 ml polyethylene centrifuge tube containing 0.5, 1.0, 2.0, 2.5, 4.0 g of kaolin, respectively. The mixture was shaken at 25 °C in the shaker for 24 h. The rest was the same as the above experiment.

## 3. Results and discussions

### 3.1. Effect of pH on desorption of Zn at different initial Cu concentrations

Solution pH plays a major role in the adsorption–desorption of heavy metals by soils as it directly controls the metal hydrolysis, ion-pair formation as well as surface charge of oxides, organic matter, and clay edges. Several studies have demonstrated that pH is the most influential factor controlling sorption–desorption of heavy metals in soils (Filius et al., 1998; Schwarz et al., 1999; Sukreeyapongse et al., 2002; Voegelin et al., 2003).

Desorption of Zn by the kaolin in our experiment followed the expected trend of reduced Zn desorption with increasing solution pH at every Cu concentration (Fig. 1). At every Cu concentration, Zn exhibits a desorption edge whereby desorption decreases rapidly over a relatively narrow pH range, desorption is steady between a relatively wide pH range, and then desorption decreases abruptly after some pH, which may be partly due to affinity of Zn between Zn and kaolin is more strong at high pH than that of Zn at low pH. These results supported the previous findings in another aspect that increasing pH generally caused an increase in the metal adsorption (Chantawong et al., 2003; Srivastava et al., 2005). In the desorption process, competition of protons for adsorbing sites and acid catalyzed dissolution of reactive sites may be involved.

The difference in Zn desorption behavior between different initial Cu concentrations can be interpreted in

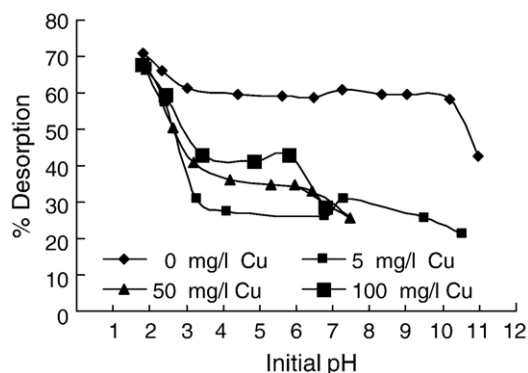


Fig. 1. Desorption of Zn at different initial pH and Cu concentrations.

terms of competition of Cu ions and protons for adsorbing sites. This difference increases with increasing solution pH, indicating that protons control Zn desorption at low pH, but with an increase in solution pH, other factors such as competition of Cu ions and precipitation, may become dominant, rendering the difference in Zn desorption increased. In Fig. 1, 0 mg/l Cu exhibits the highest desorption rate. At low pH, protons, Cu and Ca ions may adsorb onto permanent charge sites by ion exchange reactions; at higher pH, Cu may adsorb onto variable charge sites by forming inner-sphere complexes at the crystal edges and octahedral alumina face and may also form insoluble Cu(OH)<sub>2</sub> onto kaolin particle surfaces. Cu on the variable charge sites or insoluble Cu(OH)<sub>2</sub> on kaolin particle surfaces can impede Zn release, which therefore results in the highest desorption rate at 0 mg/l Cu concentration. Our finding is contrasted with the finding of Yang et al. that desorption of the adsorbed Pb<sup>2+</sup> increased greatly with increasing concentrations of added Cu<sup>2+</sup> or Zn<sup>2+</sup>.

At 0 mg/l Cu concentration, percent desorption decreases 3.80% for each 0.5 increase in pH between 1.80 and 3.04; at 5 mg/l Cu concentration, percent desorption decreases 13.87% for each 0.5 increase in pH between 1.96 and 3.28; At 50 mg/l Cu concentration, percent desorption decreases 9.97% for each 0.5 increase in pH between 1.91 and 3.19; at 100 mg/l Cu concentration, percent desorption decreases 7.65% for each 0.5 increase in pH between 1.78 and 3.4. When pH increases in the range from 1.78 to 3.4, the percent desorption shows huge decreases (desorption edge), demonstrating that protons cause desorption of Zn cation from the kaolin and the mechanism of Zn desorption is due to proton sorption at bonding sites of the kaolin. In general, Zn desorption (percent desorption and Zn concentration in solution) decreases when pH is between 1.78 and 6.43 after 24 h in the order: Cu (5 mg/l) > Cu (50 mg/l) > Cu (100 mg/l) > Cu (0 mg/l). The pH<sub>50</sub> (pH at 50% Zn desorption) is found to follow the sequence Cu (5 mg/l, pH<sub>50</sub>=2.60) < Cu (50 mg/l, pH<sub>50</sub>=2.70) < Cu (100 mg/l, pH<sub>50</sub>=2.95) < Cu (0 mg/l, pH<sub>50</sub>=10.65).

### 3.2. Influence of temperature on Zn desorption

The results are expressed as the mean value of three independent replicates. The precision was lower than 5%. It is clear from Fig. 2 that desorption of Zn was higher in the kaolin at 25 °C than at 30 °C and desorption of Zn increased with the rise in the temperature from 30 °C to 50 °C. A 5-degree temperature difference can only a little alter solution Zn concentration at equilibrium. Desorption of Zn increased from 30 °C to 50 °C, partly due to enhancement

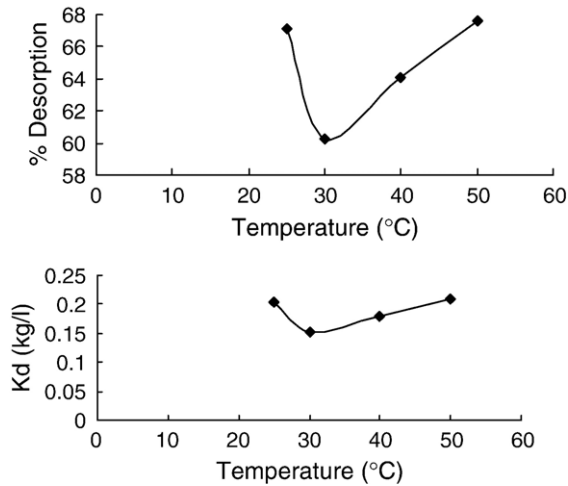


Fig. 2. Desorption of Zn at different temperatures.

of thermal energies of Zn, which makes affinity between Zn and kaolin weaker for the retention of Zn at the binding sites.  $K_d$  values of Fig. 2 also conform the process of desorption of Zn by the kaolin at different temperatures.

Thermodynamic parameters such as free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were determined using the following equations (Aziz, 2005).

$$K = \frac{C_e}{C_s} \quad (3)$$

$$\Delta G = -RT \ln K. \quad (4)$$

Integrated form of the Van't Hoff equation:

$$\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right). \quad (5)$$

Gibbs Helmholtz equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (6)$$

where  $R$  is the gas constant,  $R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ ;  $K$  is the equilibrium constant,  $C_s$  is milligrams of Zn in the kaolin after desorption equilibrium per litre of

solution in contact with the kaolin surface;  $T$  is the absolute temperature;  $K_1$  is the equilibrium constant when temperature is  $T_1$ ;  $K_2$  is the equilibrium constant when temperature is  $T_2$ ;  $\Delta G$  is the change in free energy,  $\text{kJ mol}^{-1}$ ;  $\Delta H$  is the change in enthalpy,  $\text{kJ mol}^{-1}$ ;  $\Delta S$  is the change in entropy,  $\text{kJ mol}^{-1}$ .

Evaluation of thermodynamic parameters ( $K$ ,  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ) may provide an insight into mechanism of Zn desorption in the kaolin. Thermodynamic parameters at different temperatures for Zn desorption were summarized in Table 2. These results show higher value of the equilibrium constant at 25 °C than at 30 °C for Zn desorption, indicating the higher percent desorption of Zn at lower temperature from 25 to 30 °C. For Zn desorption process, equilibrium constants increase with increasing temperature from 30 to 50 °C, indicating that an increase in temperature shifts equilibrium to the right side of Eq. (7). This is confirmed by the  $\Delta G$  values, which increase with increasing temperature from 25 to 30 °C and decrease with increasing temperature from 30 to 50 °C.  $\Delta G$  values are negative (Table 2), which means that reaction of Zn desorption is spontaneous.  $\Delta G$  of desorption of Zn is a measure of how much the concentration of Zn in solution must increase before equilibrium, so the greater the desorption, the more negative is  $\Delta G$ . In our experiment,  $\Delta G$  of Zn desorption was more negative at higher temperature from 30 to 50 °C, which suggested that the spontaneity of desorption process increased with rise in temperature from 30 to 50 °C.

$\Delta H$  values were negative from 25 to 30 °C and positive from 40 to 50 °C. But the increase in  $\Delta H$  from 12.8226 to 13.0864  $\text{kJ mol}^{-1}$  is not significant by the standard deviations (in Table 2). This provides an indication that desorption reaction is exothermic from 25 to 30 °C and endothermic from 40 to 50 °C.  $\Delta S$  values change is not significant from 25 to 30 °C and 40 to 50 °C (in Table 2).



### 3.3. Influence of the ratio of solid to liquid on Zn desorption

Variation in soil/solution ratio may influence the aqueous-phase chemistry of indigenous trace-metal ions,

Table 2  
Thermodynamic parameters for Zn desorption in the kaolin

$T$ (°C)	Mean $\pm$ S.D. values			
	$K$	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ mol $^{-1}$ )	$\Delta S$ (kJ mol $^{-1}$ )
25	2.0384 $\pm$ 0.0117	-1.7644 $\pm$ 0.0142	-44.3166 $\pm$ 0.86022 (25–30 °C)	-0.142791 $\pm$ 0.002838901
30	1.5174 $\pm$ 0.0027	-1.0504 $\pm$ 0.0046	-44.3166 $\pm$ 0.27442 (25–30 °C)	-0.142793 $\pm$ 0.000920764
40	1.7836 $\pm$ 0.0574	-1.5058 $\pm$ 0.0838	12.8226 $\pm$ 2.53998 (30–40 °C)	0.04578 $\pm$ 0.008382785
50	2.0840 $\pm$ 0.0562	-1.9718 $\pm$ 0.0724	13.0864 $\pm$ 2.26647 (40–50 °C)	0.04662 $\pm$ 0.007241087

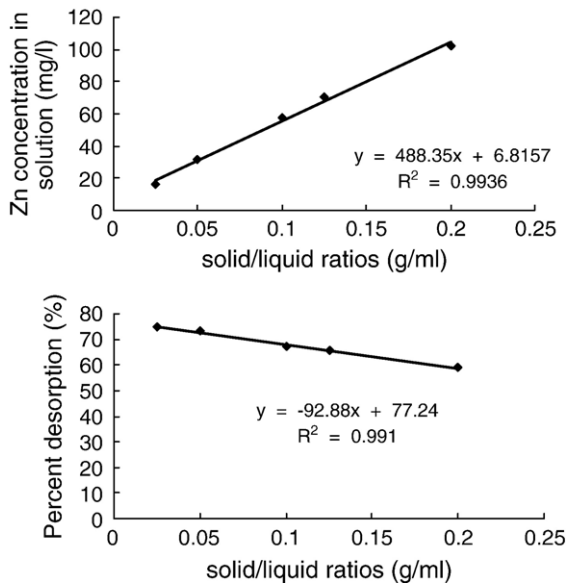


Fig. 3. Desorption of Zn at different solid/liquid ratios.

and thereby affect either or both the sorption and desorption process (Harter and Naidu, 2001). The effect of solid to liquid ratios on the Zn desorption is shown in Fig. 3. The results are expressed as the mean value of three independent replicates. The precision was lower than 5%. The maximum concentration of Zn in solution was 101.83 mg/l at a solid to liquid ratio of 0.2 while the maximum percent desorption was 74.79% at a solid to liquid ratio of 0.025. It is obvious that the concentration of Zn in solution after desorption equilibrium linearly increases and percent desorption linearly decreases when the solid to liquid ratio increases from 0.025 to 0.2 (Fig. 3). Zn desorption observed in this study was consistent with published literatures, in that the concentration of heavy metals in solution after desorption equilibrium increase and percent desorption decreases when the solid to liquid ratio increases (Fotovat et al., 1997; Papassiopi et al., 1999; Harter and Naidu, 2001). This phenomenon occurs because solution distributed to the kaolin per unit weight decreases when the solid to liquid ratio increases.

#### 4. Conclusions

When pH increases in the range from about 1.78 to 3.4, the percent desorption shows huge decreases (desorption edge). At 0, 5, 50, 100 mg/l Cu concentration, for each 0.5 increase in pH between about 1.80 and 3.04% desorption decreases 3.80, 13.87, 9.97, and 7.65%, respectively. There were no large differences in the desorption of Zn at different temperature (from 25 to 50 °C). The concentration of Zn in solution after desorption equilibrium increases and

percent desorption decreases when the solid to liquid ratio increases from 0.025 to 0.2. Cu, Pb and Cd concentrations in the kaolin are low. Under our condition studied, the Zn concentration in solution is all > 15 mg/l, which is far above Zn concentration in III grade water ( $\leq 1.0$  mg/l) from the quality standard for ground water (GB/T14848-93). The kaolin possibly cannot be used for landfill clay liner.

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