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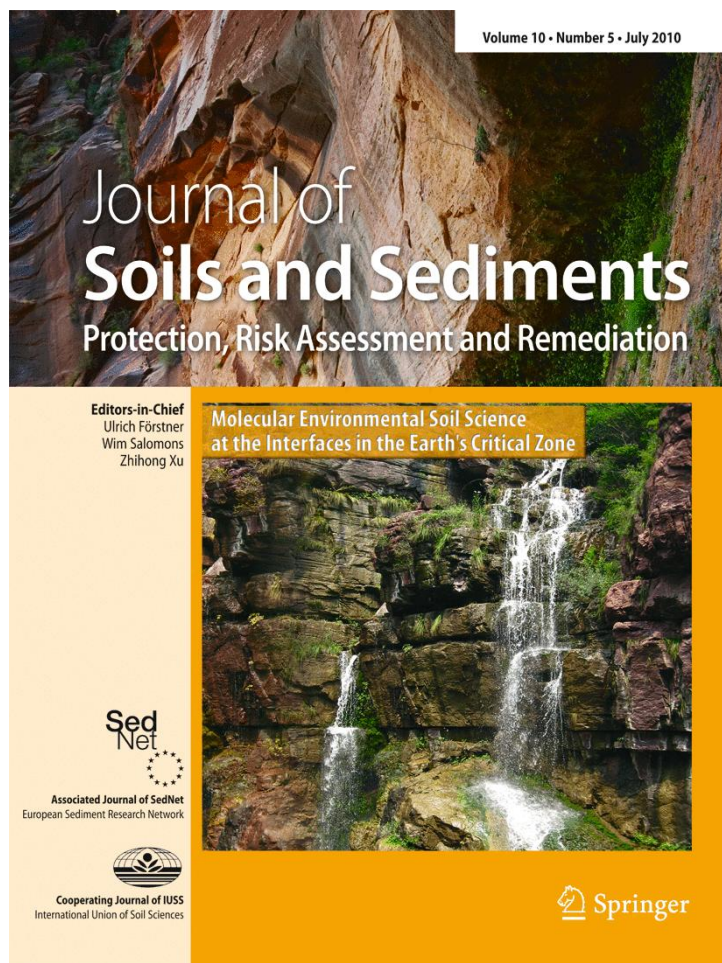
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**ISSN 1439-0108, Volume 10, Number 5**



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# Effect of 1-1 electrolyte concentration on the adsorption/desorption of copper ion on synthetic birnessite

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Received: 30 October 2009 / Accepted: 25 March 2010 / Published online: 4 May 2010  
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## Abstract

**Purpose** Oxides are ubiquitous in nature and play an important role in scavenging metal ions from soils and sediments. At the common pH range of the natural environment the well-studied Fe and Al oxides mostly carry a positive charge and adsorbed amounts of heavy metals, and their desorption percentages decrease with increasing ionic strength. The less well studied but also important Mn oxides possess negative charges in the natural environment and this will lead to a different behavior. Therefore, it is useful to further investigate how the electrolyte concentration and type affect the metal ion adsorption/desorption by Mn oxides.

**Materials and methods** The phyllo-manganate birnessite was synthesized with hydrochloric acid and potassium permanganate, and characterized by X-ray diffraction and transmission electron microscopy. The point of zero charge and specific surface area (SSA) were determined by, respectively, the rapid potentiometric titration method and

BET-N<sub>2</sub> method. The adsorption was measured after shaking the samples in contact with Cu(NO<sub>3</sub>)<sub>2</sub> solution for 2 h and further equilibration for 22 h at pH 4.5 and 25 ± 1°C. The 1-1 electrolyte concentrations were adjusted to 0, 0.001, 0.01, 0.1, 0.5, and 1 mol L<sup>-1</sup> KNO<sub>3</sub> or KCl.

**Results and discussion** The PZC and SSA of synthetic birnessite were 2.5 and 75 m<sup>2</sup> g<sup>-1</sup>, respectively. The birnessite consisted of small needle-like particles. A maximum amount of Cu<sup>2+</sup> adsorbed on birnessite of 208 ± 8 mmol kg<sup>-1</sup> and 2.77 ± 0.11 μmol m<sup>-2</sup> by using the BET area is obtained. The adsorption amount decreased gradually with increasing ionic strength. This is primarily due to screening of the electrostatic attraction. For the same reason the percentage of desorption of Cu<sup>2+</sup> previously adsorbed on birnessite increased with increasing electrolyte concentration. Furthermore, the decrease of Cu<sup>2+</sup> adsorption with increasing ionic strength was higher in KCl solution than in KNO<sub>3</sub> solution. This difference is most likely related to Cu<sup>2+</sup>-Cl<sup>-</sup> complexation.

**Conclusions** The type and concentration of 1-1 electrolyte affect the Cu<sup>2+</sup> adsorption/desorption characteristics on Mn oxide. The amounts of Cu<sup>2+</sup> adsorbed on birnessite reduced, and the desorption percentage increased with increasing 1-1 electrolyte concentration. These results are opposite to that of metal ion binding to positive Fe and Al oxides. The principal differences can be explained on the basis of generic electrostatic effects.

Responsible editor: Caixian Tang

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**Keywords** Adsorption/desorption · Aluminum oxide ·  
Birnessite · Cu ion · Electrolyte concentration · Ionic  
strength · Iron oxide · Manganese oxide

## 1 Introduction

Metal oxides are one of most active and important components in soils and sediments (Sposito 2008). Although

their content in soils cannot match that of silicates, they play an important role in the chemical, physical, and biological reactions in soils due to their fine particles and the fact that they are present as coatings on clay surfaces (McKenzie 1989; Dixon and Skinner 1992; Huang et al 2008). Well studied are the Fe and Al oxides that, in general, have a high point of zero charge (PZC) and a positive surface charge at natural solution conditions (Trivedi et al. 2004; Ponthieu et al. 2006). Consequently, the adsorption of metal cations is only moderate. In contrast, Mn oxides exhibit a low PZC, a negative surface charge under normal solution conditions and a relatively high adsorption of heavy metal ions (McKenzie 1989; Hseung and Chen 1990; Post 1999; Tripathy et al 2001; Feng et al. 2007). The characteristics of adsorption/desorption of heavy metals on manganese oxides has been studied from the point of view of environmental and geochemical aspects (Hseung and Chen 1990). Generally, the adsorption order on Mn oxides can be represented as,  $Pb > Cu > Co > Zn > Ni > Ca > Mg$ , and as adsorption mechanisms specific adsorption, electrostatic adsorption, internal layer exchange, hydrolysis adsorption, surface complexation, and isomorphic substitution have been suggested (Loganathan and Bureau 1973; McKenzie 1989; Hseung and Chen 1990; Fu et al. 1991; Kanungo et al. 2004; Tan et al. 2005). Li et al. (2004) and Pan et al. (2004) have used extended X-ray absorption fine structure spectroscopy to study the microscopic structures of metal ions adsorbed at Mn oxides and the information has been used to reveal the relationships between adsorption reversibility and microstructure of the adsorbed species. These microstructures have been used to explain the macroscopic adsorption–desorption isotherms.

The adsorption characteristics of heavy metals on metal oxides will be affected by the presence of simple 1:1 electrolytes. At pH ranges where Fe and Al oxides are positive the adsorption of heavy metals increases with increasing electrolyte concentration as long as the salt concentration is not too high ( $\leq 0.1$  M). However, the magnitude of the effect depends on the specific salt (e.g., Zhou et al. 1996a, Criscenti and Sverjensky 1999, Trivedi et al. 2004, Tao et al., 2004). When the salt concentrations increase up to 1 M specific salt effects may become very strong and a general trend is no longer observed (Criscenti and Sverjensky 1999). In addition, Zhou et al. (1996b) observed that the desorption percentage decreased with increasing electrolyte concentration. For manganese oxides the effect of electrolyte concentration on the adsorption of heavy metal ions is less well studied. For amorphous hydrous manganese dioxide Kanungo et al. (2004) found that for  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  a decrease in the adsorption occurred with increasing electrolyte concentration, but  $Zn^{2+}$  showed a complex behavior. No studies are available on the desorption behavior of heavy metal ions. Therefore, the

influence of 1:1 electrolyte concentration and type on adsorption and desorption of  $Cu^{2+}$  on birnessite, a crystalline manganese oxide, is studied to further evaluate the role of manganese oxides in metal ion binding. The phyllomanganate birnessites ( $\delta$ - $MnO_2$ ) are most common among the manganese minerals in soils and sediments. Birnessite is made up of layers of  $MnO_6$  octahedrons separated by monolayers of water (McKenzie 1989; Dixon and Skinner 1992).

## 2 Material and methods

All reagents used were of analytical grade. Double distilled water was used for the experiments.

The phyllomanganate *birnessite* was synthesized according to McKenzie (1989). With this method 200 mL of 5 mol  $L^{-1}$  HCl solution was added drop by drop to 1.25 L of a boiling solution of 0.4 mol  $L^{-1}$   $KMnO_4$  under continuous stirring. After the addition was finished, the suspension was heated for a further 10 min to age the precipitate. The precipitate was cooled and washed with water several times and then further purified by electro-dialysis at a voltage of 150–220 V until the supernatant conductivity was less than 20  $\mu S\ cm^{-1}$ . After decantation the suspension was dried in an oven at 60°C and stored in a container.

X-ray diffraction (XRD) analysis was performed using a D/Max-3B diffractometer (Rigaku, Japan) with monochromatic  $Fe\ K\alpha$  ( $\lambda = 0.19373$  nm) radiation. The diffractometer was operated at a tube voltage of 40 kV and a tube current of 20 mA. Intensities were measured at  $2\theta = 10$ – $90^\circ$  using a count time of 0.4 s/step and step intervals of  $0.02^\circ$ .

Transmission electron microscopy (TEM) analysis was carried out with Philips-CM 12 operated at 120 kV. The samples were gently crushed to powder, then dispersed in absolute alcohol and sonicated prior to deposition on a holey carbon film.

Total manganese content of birnessite was determined by dissolving 0.1 g of birnessite in 25 mL of 0.1 mol  $L^{-1}$  hydrochloric acid hydroxylamine. Subsequently, the solution was further diluted to 250 mL with water. The Mn content in the solution was determined by atomic absorption using a further 100-fold dilution.

The specific surface area of the birnessite was measured using  $N_2$  adsorption (Quantachrome Autosorb-1) and applying the BET method. The sample was outgassed at 80°C.

The point of zero charge of the birnessite sample was determined using the rapid potentiometric titration method (Tan et al. 2008). The pH values of the aqueous solutions were measured using a pH meter (Thermo Orion model 410) with a combined glass-calomel electrode (Thermo Orion model 9165BN).

The Cu adsorption isotherm in 0.01 mol L<sup>-1</sup> KNO<sub>3</sub> was determined by adding 10 mL of 0.01 mol L<sup>-1</sup> KNO<sub>3</sub> solutions containing various concentrations of Cu(NO<sub>3</sub>)<sub>2</sub> (0.01 to 6 mmol L<sup>-1</sup>) to ten centrifuge tubes with 0.05 g birnessite. The pH value was adjusted to 4.5 by pH-stat (Metrohm 836 Titrando) and the tubes were shaken for 2 h at 25±1°C and further equilibrated for 22 h. Preliminary experiments with equilibration times of 22, 34, and 46 h standing showed that 22 h was sufficient. After equilibration the suspensions were centrifuged at 22,400×g for 10 min in a J2-MC Super-speed refrigerated centrifuge (Beckman, USA). The supernatants were collected and analyzed for Cu<sup>2+</sup> and Mn<sup>2+</sup> concentrations. The amounts of adsorbed Cu<sup>2+</sup> were obtained from the difference between the initial and final amount of Cu in solutions. From the Mn concentrations the amounts of Mn<sup>2+</sup> released during the whole adsorption process were obtained by comparison with a control group without adding Cu<sup>2+</sup>. All measurements were performed twice and the results were averaged.

The effect of 1-1 electrolyte concentration on Cu<sup>2+</sup> adsorption was investigated using a series of tubes containing 0.05 g birnessite and 10 mL 1 mmol L<sup>-1</sup> Cu(NO<sub>3</sub>)<sub>2</sub> solutions with various concentrations (0, 0.001, 0.01, 0.1, 0.5, and 1 mol L<sup>-1</sup>) of KNO<sub>3</sub> or KCl at pH 4.5. The suspensions were shaken for 2 h, equilibrated for 22 h at 25±1°C, and centrifuged. The supernatants were collected and analyzed for Cu<sup>2+</sup> and Mn<sup>2+</sup> concentrations and the pH values were measured. All measurements were performed twice and the results were averaged.

Effect of 1-1 electrolyte concentration on the desorption of previously adsorbed Cu<sup>2+</sup>. In these experiments Cu<sup>2+</sup> was first adsorbed on birnessite from aqueous solutions containing no added 1-1 electrolyte. To this end 10 mL 0.5 mmol L<sup>-1</sup> Cu(NO<sub>3</sub>)<sub>2</sub> solution at pH 4.5 was added to a series of centrifuge tubes with 0.05 g birnessite. The suspensions were equilibrated in the usual way and centrifuged. The concentrations of Cu<sup>2+</sup> and Mn<sup>2+</sup> in supernatants were detected and the adsorbed amounts were

calculated. Subsequently, the supernatants were replaced by 10 mL of KNO<sub>3</sub> or KCl solutions of 0, 0.001, 0.01, 0.1, 0.5, and 1 mol L<sup>-1</sup> at pH 4.5 and the samples were re-equilibrated by shaking for 2 h and further standing for 22 h. Then the concentrations of Cu<sup>2+</sup>, Mn<sup>2+</sup> in supernatants were determined. Subsequently, the supernatants were again replaced by the corresponding salt solution, equilibrated, centrifuged, and again Cu<sup>2+</sup> and Mn<sup>2+</sup> concentrations were measured. Both results were used to calculate the total desorption of Cu<sup>2+</sup> in each tube. All measurements were performed twice and the results were averaged.

The amounts of Cu<sup>2+</sup> and Mn<sup>2+</sup> in the supernatants were measured by atomic absorption using a Varian AAS240FS spectrometer.

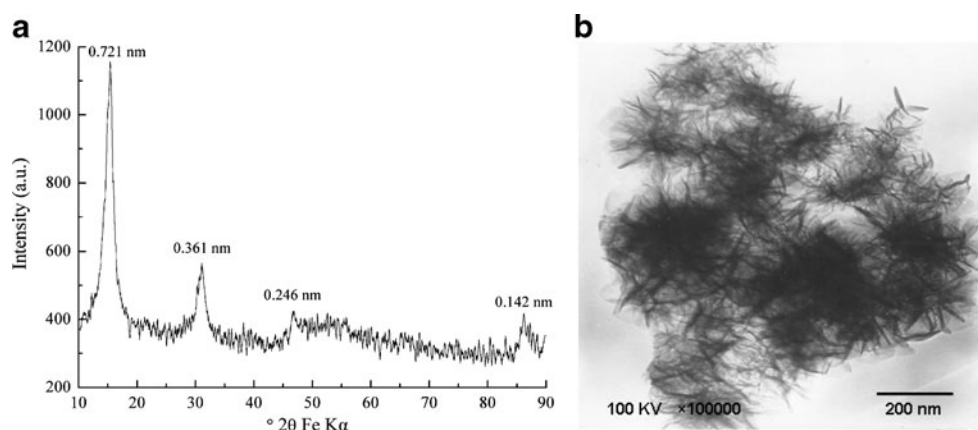
### 3 Results and discussion

#### 3.1 Characteristics of the birnessite sample

The powder XRD pattern of the birnessite sample is depicted in Fig. 1a. The spectrum shows four peaks at respectively 0.721, 0.361, 0.246, and 0.142 nm that are characteristic for birnessite. The intensity of the main peak at 0.721 nm reached 1,160 (CPS). This indicates that the sample is a single-phased birnessite of good crystallinity. The TEM image of the birnessite sample is depicted in Fig. 1b. The image reveals small needle-like particles that are on the TEM grid clustered to ball-like aggregates with a size of 50–100 nm. This result is in good agreement with the morphology of needles and balls as described by McKenzie (1971).

The total content of Mn in birnessite was 60.1%, which is close to the theoretical Mn content (63.2%) of MnO<sub>2</sub>. This indicates that the birnessite was nearly pure. The specific surface area obtained by the BET-N<sub>2</sub> method was 75 m<sup>2</sup> g<sup>-1</sup>. This value is relatively low compared to results obtained by Tonkin et al. (2004) for birnessite and δ-MnO<sub>2</sub>. This corresponds with the good crystallinity of the present

**Fig. 1** Powder XRD pattern (a) and TEM image (b) of the birnessite sample





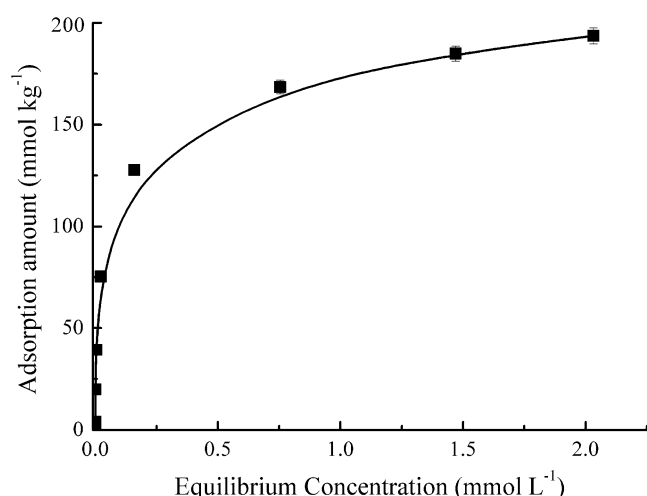
sample. The PZC of our birnessite sample was 2.5, which was similar to the value 2.2 and 2.5 reported in literatures (Kanungo and Mahapatra 1989; Tripathy et al. 2001).

### 3.2 Adsorption isotherm of $\text{Cu}^{2+}$ on birnessite at 0.01 mol $\text{L}^{-1}$ $\text{KNO}_3$ and pH 4.5

The  $\text{Cu}^{2+}$  adsorption isotherm on birnessite is depicted in Fig. 2. The isotherm can be assigned to a high affinity L type (Giles et al. 1960): a very steep increase at low concentrations and a pseudo plateau at higher concentrations. In order to assess the (pseudo) adsorption maximum, the isotherm was fitted by the Langmuir model using the following linearized form of the Langmuir equation:

$$\frac{1}{X} = \frac{1}{X_m} + \frac{1}{KX_m} \frac{1}{C} \quad (1)$$

where  $X$  is the amount adsorbed per unit weight ( $\text{mmol kg}^{-1}$ ),  $X_m$  represents the maximum amount adsorbed,  $C$  is the equilibrium metal ion concentration, and  $K$  denotes the adsorption constant (Adamson 1984). The data fit well to the straight line ( $R^2=0.994$ ); the (conditional) adsorption constant equals 28  $\text{L mmol}^{-1}$  and a maximum amount of  $\text{Cu}^{2+}$  adsorbed on birnessite of  $208 \pm 8 \text{ mmol kg}^{-1}$  is obtained. This amount can also be expressed as  $2.77 \pm 0.11 \text{ } \mu\text{mol m}^{-2}$  by using the BET area. The maximum adsorption can be compared with 385  $\text{mmol kg}^{-1}$  for  $\text{Cu}^{2+}$  adsorption on amorphous hydrous manganese dioxide at pH 4.45 and 0.5  $\text{mol L}^{-1}$   $\text{NaCl}$  (Kanungo et al. 2004). The fact that the present value is considerably lower than that for amorphous Mn oxide is associated with the good crystallinity and relatively low specific surface area of the birnessite sample.

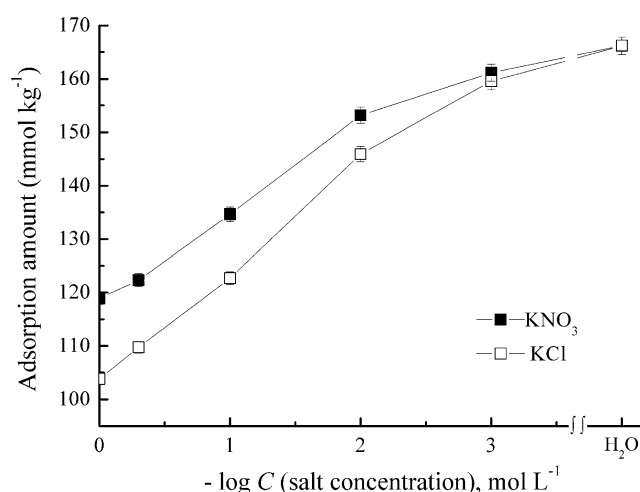


**Fig. 2** Copper adsorption isotherm expressed as adsorbed amount vs equilibrium concentration at  $25 \pm 1^\circ\text{C}$ , pH 4.5, and 0.01  $\text{mol L}^{-1}$   $\text{KNO}_3$

### 3.3 Effect of 1-1 electrolyte concentration on $\text{Cu}^{2+}$ adsorption on birnessite at pH 4.5

The effect of 1-1 background electrolyte concentration on the adsorption of  $\text{Cu}^{2+}$  on birnessite is depicted in Fig. 3, where the adsorbed amount is plotted as a function of  $-\log C$  (salt) with the salt concentration in  $\text{mol L}^{-1}$ . The general trend is that the adsorbed amount decreases with increasing 1-1 electrolyte concentration. This can be explained by the generic effect that the screening of the electrostatic attraction between the metal cation and the anionic  $\text{MnO}_2$  surface increases with increasing salt concentration. Criscenti and Sverjensky (1999) and Zhou et al. (1996a, b) have reported that the adsorption of heavy metals on positively charged Fe and Al oxides increases with increasing electrolyte concentration for salt concentrations up to about 0.1  $\text{mol L}^{-1}$  where the generic electrostatic effect dominates. However, for high salt concentrations (e.g., 1  $\text{mol L}^{-1}$ ) salt specific effects mostly overrule the generic effect and general trends are missing (Criscenti and Sverjensky 1999). The fact that the trend at moderate salt concentrations is opposite to that for birnessite is due to the fact that in this case screening of the *electrostatic repulsion* between metal cations and cationic surface sites occurs.

Alternatively, the screening of the electrostatic interaction between metal ions and a charged surface can be explained on the basis of the potential decay in the electric double layer. Mn, Fe, and Al oxide surfaces behave, in general, pseudo Nernstian, which implies that the surface potential is strongly depending on the pH but hardly on the salt concentration or metal ion concentration (Koopal 1996). However, the potentials in the Stern layer (adjacent to the surface) decrease (in absolute magnitude) with increasing salt concentration due to compression of the double layer. A lower magnitude of the absolute values of



**Fig. 3**  $\text{Cu}^{2+}$  adsorption on birnessite vs the negative logarithm of the background electrolyte concentration at pH 4.5 (initial  $\text{Cu}(\text{NO}_3)_2$  concentration 1  $\text{mmol L}^{-1}$ )

the Stern layer potentials implies that in the case of negative Mn oxide the metal ion attraction is weaker and in the case of positive Fe and Al oxides that the metal ion repulsion is weaker. Therefore, although both Fe, Al, and Mn oxides exhibit variable charged surfaces, the effect of background moderate electrolyte concentrations on the adsorption of metal ions is opposite for Mn oxides and Fe or Al oxides.

Next to the generic effect described above there is also a weak specific salt effect: KCl decreases the Cu adsorption on birnessite more strongly than KNO<sub>3</sub>. For KCl the amount of Cu<sup>2+</sup> adsorbed decreases from 166 to 104 mmol kg<sup>-1</sup> and for KNO<sub>3</sub> a reduction of 166 to 119 mmol kg<sup>-1</sup> is observed. The reason for this is most likely a difference in specific interaction of the electrolyte anions with the Cu ions in bulk solution. In solution Cl<sup>-</sup> and Cu<sup>2+</sup> ions form complexes according to the reactions



The Cu species in KCl solutions are calculated using the ECOSAT4.9 (Keizer and Van Riemsdijk 1999) for different KCl concentrations at 1 mmol L<sup>-1</sup> Cu(NO<sub>3</sub>)<sub>2</sub> and pH 4.5. The results are listed in Table 1. A significant complexation of Cu<sup>2+</sup> with Cl<sup>-</sup> as CuCl<sup>+</sup> (58.4%) and CuCl<sub>2</sub> (17.6%) occurs at 1 mol L<sup>-1</sup> KCl, while at 0.01 mol L<sup>-1</sup> or lower KCl concentration over 95% of Cu species was Cu<sup>2+</sup>. Reactions (2) and (3) replace divalent Cu<sup>2+</sup> by monovalent or uncharged Cu species and this will decrease the adsorption of Cu ion on negative charged birnessite. Similar complexation with NO<sub>3</sub><sup>-</sup> does not occur, therefore, the adsorption of Cu<sup>2+</sup> in KNO<sub>3</sub> is higher than that in KCl solution.

### 3.4 Effect of 1-1 electrolyte concentration on the solution pH and released amount of Mn<sup>2+</sup>

In order to investigate the differences between KCl and KNO<sub>3</sub> in more detail the pH and Mn dissolution upon salt addition have been measured. In Fig. 4 the effect of salt

addition on the pH in solution is depicted, both in the absence (panel a) and presence of 1 mmol L<sup>-1</sup> Cu(NO<sub>3</sub>)<sub>2</sub> (panel b). Figure 4 shows that in general the pH increases with the increasing electrolyte concentration; however, the increase is stronger in the absence of Cu ions than in its presence. Clearly, in the presence of Cu ions some H<sup>+</sup> ions are released from surface during Cu<sup>2+</sup> adsorption. This finding is in accordance with reports of Loganathan and Burau (1973) and Fu et al. (1991). The adsorbed Cu<sup>2+</sup> ions screen the birnessite surface charge better than simple monovalent counterions and this leads to proton desorption and an increase of the negative surface charge.

The general trend that the pH increases with salt addition is independent of the presence of Cu and must be a phenomenon related to the nature of birnessite. Increasing the 1-1 electrolyte concentration leads to an increasing release of OH<sup>-</sup> in solution, which is larger for Cl<sup>-</sup> than for NO<sub>3</sub><sup>-</sup>. The release of OH<sup>-</sup> is accompanied with dissolution of Mn ions in solution. In Fig. 5 the released amount of Mn<sup>2+</sup> as a function of the 1-1 electrolyte concentration in the presence of Cu<sup>2+</sup> (corresponding with Fig. 4b) is depicted. Also here an increase of dissolution with increasing 1-1 electrolyte concentration is observed. Apparently, the dissolution of birnessite in the form of Mn hydroxide complexes is promoted by salt addition. The effect that KCl leads to a higher Mn<sup>2+</sup> release than KNO<sub>3</sub> is a specific effect that can be explained by complexation reaction (4)



NO<sub>3</sub><sup>-</sup> complexation with Mn<sup>2+</sup> does not occur (Krishnamurti and Huang, 1998).

### 3.5 Effect of 1-1 electrolyte concentration on Cu<sup>2+</sup> desorption

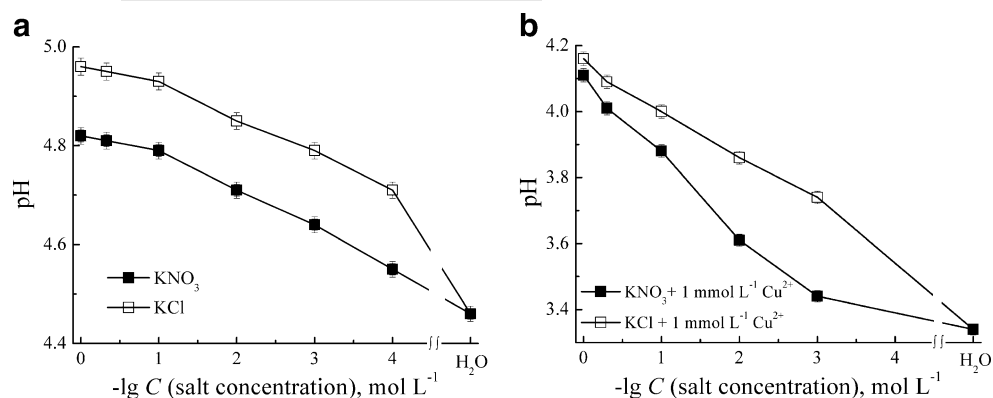
The desorption of Cu<sup>2+</sup>, initially adsorbed on 0.05 g birnessite from 10 mL aqueous solution containing 0.5 mmol L<sup>-1</sup> Cu(NO<sub>3</sub>)<sub>2</sub>, upon dilution with KCl and KNO<sub>3</sub> solutions is depicted in Fig. 6. The desorption percentage of Cu<sup>2+</sup> increases with the increasing 1-1 electrolyte concentration and the difference between the two types of salt is small. As expected on the basis of Fig. 3 the effect of KCl is slightly stronger than that of KNO<sub>3</sub>. When the concentration of KNO<sub>3</sub> or KCl solution reach 1 mol L<sup>-1</sup>, the desorption percentages are 9% and 13%, respectively. In general, the maximal percentage of Cu<sup>2+</sup> desorption is very limited. This is related to the nature of the experiment and the high affinity nature of the Cu<sup>2+</sup> adsorption isotherm. After replacing the Cu(NO<sub>3</sub>)<sub>2</sub> solution with the 1-1 electrolyte solution, a new Cu<sup>2+</sup> concentration builds up in solution and even at low Cu<sup>2+</sup> concentrations the adsorption is appreciable. Secondly, when desorption from the surface occurs, a Cu<sup>2+</sup> concentra-

**Table 1** The Cu species (%) in different concentration of KCl at pH 4.5 calculated with ECOSAT4.9

KCl concentration mol L <sup>-1</sup>	Percentage of Cu species (%)		
	Cu <sup>2+</sup>	CuCl <sup>+</sup>	CuCl <sub>2</sub>
0.001	99.1	0.3	0
0.01	96.9	2.5	0
0.1	79.1	19.9	0.6
0.5	40.7	51.2	7.7
1	23.2	58.4	17.6

The Cu(NO<sub>3</sub>)<sub>2</sub> concentration is 1 mmol L<sup>-1</sup>

**Fig. 4** pH of the birnessite suspension (0.05 g in 10 mL) vs the negative logarithm of the electrolyte concentrations. **a** Absence of Cu; **b** presence of Cu (1 mmol L<sup>-1</sup>)



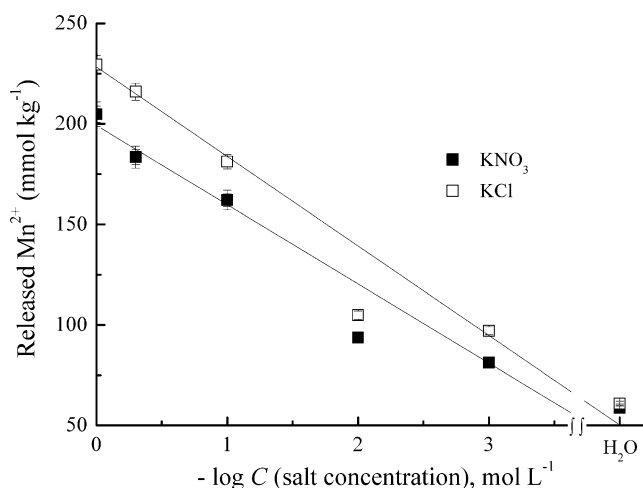
tion builds up in the sub-surface layer. As soon as the high affinity part of the isotherm is reached, this sub-surface concentration is very low; consequently the diffusion of the Cu ions from the sub-surface layer to the bulk solution is very slow because there is only a very small concentration gradient. In the explanation of poor desorbabilities the latter aspect is often neglected. The observed desorption percentages are much lower than those observed by Zhou et al. (1996b) for aluminum and iron oxides. In the latter case pure water was used for diluting and the percentages of Cu<sup>2+</sup> desorption were as high as 30–80%. The difference is primarily related to the fact that in the absence of 1-1 electrolyte the adsorption isotherm of Cu<sup>2+</sup> to Al and Fe oxides is not of the high affinity type. The much lower affinity is due to the fact that ion and surface have the same charge sign and that in pure aqueous solution the screening of the electrostatic repulsion is very weak.

#### 4 Conclusions and prospects

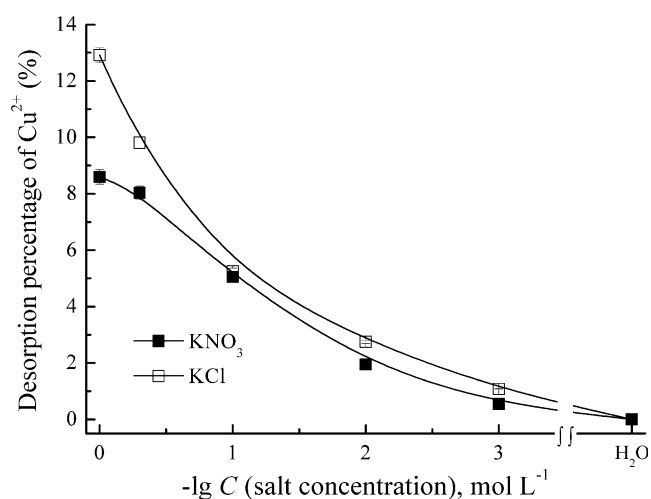
Mineral oxides are active and important components in soils and sediments. They possess a variable charged

surface of which the types and amounts of surface charges change with a variation of pH values. In the normal pH range in nature manganese oxides are negatively charged, whereas aluminum and iron oxides are positively charged. The adsorption of Cu<sup>2+</sup> on negatively charged birnessite, a manganese oxide, decreases with increasing 1-1 electrolyte concentration. This can be explained by the increased screening of the electrostatic attraction with increasing electrolyte concentration. At moderate electrolyte concentrations ( $\leq 0.1$  mol L<sup>-1</sup>) the behavior is opposite to that of positively charged aluminum and iron oxides, increasing adsorption with increasing 1-1 electrolyte concentration, because here the electrostatic repulsion is screened. The amount of Cu<sup>2+</sup> adsorption on birnessite in KNO<sub>3</sub> solution is higher than that in KCl solution. This difference is primarily related to Cu<sup>2+</sup>–Cl<sup>-</sup> complexation in bulk solution and the fact that the electrostatic attraction of CuCl<sup>+</sup> with the surface is less than that of Cu<sup>2+</sup>.

Furthermore, the desorption percentage of Cu<sup>2+</sup>, previously adsorbed on birnessite from an aqueous 1 mmol L<sup>-1</sup> Cu(NO<sub>3</sub>)<sub>2</sub> solution, increased with increasing concentration



**Fig. 5** Released Mn<sup>2+</sup> vs the negative logarithm of the electrolyte concentration in a suspension of 0.05 g birnessite in 10 mL 1 mmol L<sup>-1</sup> Cu(NO<sub>3</sub>)<sub>2</sub>. The corresponding pH values are depicted in Fig. 4



**Fig. 6** Desorption percentage of Cu<sup>2+</sup> adsorbed on birnessite vs the negative logarithm of the electrolyte concentrations. The initial adsorption conditions are a suspension of 0.05 g birnessite in 10 mL 0.5 mmol L<sup>-1</sup> Cu(NO<sub>3</sub>)<sub>2</sub>



of 1-1 electrolyte, but the total desorption is only small. The latter behavior is different from that of Al and Fe oxides where a much stronger desorption has been found. The explanation lies in the different shapes of the isotherms. The adsorption isotherm of  $\text{Cu}^{2+}$  on birnessite is of the high affinity type, this leads to a poor desorbability. The isotherms of metal ions to Al and Fe oxides are much less high affinity and allow a better desorption.

In generalizing the present findings we may say that although specific salt effects are always present, the generic electrostatic effects dominate, both for Al and Fe oxides and Mn oxides, as long as the 1-1 electrolyte concentrations are moderate ( $\leq 0.1 \text{ mol L}^{-1}$ ). In future research on metal ion binding to manganese oxides a combination of adsorption experiments, spectroscopy, and modeling is required to unravel the specific role of anions at moderate electrolyte concentrations in more detail.

**Acknowledgments** This investigation was supported by the National Natural Science Foundation of China (No. 40671088, 40830527), the Program for New Century Excellent Talents in University (NCET-08-0781), and the One Hundred Elitist Program of the Chinese Academy of Sciences. Authors also thank the State Key Laboratory of Soil Erosion and Dry Land Farming on the Loess Plateau, the Institute of Soil and Water Conservation, the Chinese Academy of Sciences for financial support (Project No.10501).

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