

Effect of Ionic Strength and Valence on Extractability of Cu and Zn from Sewage Sludge

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Received February 10, 2001

Key words: ionic strength, heavy metals, sewage sludge, valence.

The activities of dissolved ions are affected by the ionic strength of the soil solution. The significance of the ionic strength in soil solution with respect to mineral equilibria had been well documented.¹⁾ The ionic strength of an electrolytic solution is a measure of the intensity of the electrical field in the solution. One reason for its importance is the effect that ionic strength has on the variable charge of soil colloids, as the availability of cations is largely dependent on the surface charges carried by the soil colloids.²⁾ Another reason for the significance of ionic strength is its contribution to the determination of the activity of individual ions in solution. Thus, a change in ionic strength results in a change in ion activity and then, a shift in the equilibrium of the solution.³⁾ The dissolution of solids and subsequent release of ions into the soil solution may interfere with the exchange processes, displacing cations from exchange sites. Under field conditions, the ionic strength of the soil solution will vary over the growing season, due to environmental conditions especially the moisture status. Fertilizer additions, either chemical or organic, as well as mineral dissolution also affect the ionic strength of the soil solution. The aim of this study was to investigate the effects of ionic strength and valence on the extractability of Cu and Zn from the sewage sludge.

An anaerobically digested sludge was obtained from the North End Water Pollution Control Centre of the City of the Winnipeg, Canada. The sewage sludge was lyophilized at -70°C using a freeze drier. The total concentrations of Cu and Zn in the sewage sludge were determined using an acid digestion procedure with 3 : 1 ratio of nitric/perchloric acid.⁴⁾ Table 1 presents the chemical characteristics of the sewage sludge. The monovalent KCl and the divalent CaCl_2 salts were chosen and extracting solutions were prepared at ionic strengths ranging 0.001~2.0 M for KCl and 0.003~3.0 M for CaCl_2 . Twenty

milli-liter of extracting solution was added to duplicate 2 g samples of lyophilized sludge, the suspension was shaken for 6 h and centrifuged. The supernatants were analyzed for Cu and Zn by atomic absorption spectrophotometer.

The amounts of Cu and Zn extracted from the sewage sludge by CaCl_2 and KCl are shown in Table 2 and 3, respectively. For both extracting solutions, approximately 6~11% of the total Cu and 0.1~2% of the total Zn were released in all cases. Extraction with CaCl_2 and KCl showed that at comparable ionic strengths, KCl extracted more Cu than did CaCl_2 , whereas the amount of Zn extracted was not affected by the type of extracting solution used; 0.03 M CaCl_2 extracted 40.4 mg Cu kg^{-1} , 0.04 M KCl extracted 55.7 mg Cu kg^{-1} , while the amounts of Zn extracted remained fairly consistent for both KCl and CaCl_2 over the range of ionic strengths used. Increasing the ionic strength of the extracting solution did not result in higher contents of Cu and Zn except, however, when the concentration of the extracting solution was greater than 1.0 M, which normally would not be encountered under natural soil environment. The ionic strengths of soil solution are normally in the range of 0.01~0.05 M.⁵⁾

Table 2 shows that increasing the ionic strength of the CaCl_2 extracting solution up to approximately 0.2 M resulted in decreased amounts of Cu and Zn released. That is, Cu and Zn became less available as ionic strength of the extracting solution increased up to approximately 0.1 M, beyond which the amount extracted increased again. These results were contrary to what was expected considering the effect of increasing ionic strength on exchange reactions. To explain this phenomenon, one must consider the effect of solution ionic strength on the conformation of the organic polymers within the sludge. It has been well-documented that the ionic strength of the solution is inversely related to the thickness of the electrical double layer around the charged particles.⁶⁾ Therefore, the repulsive forces between organic polymers and segments of polymers are reduced, allowing the segments to come closer. The consequences, according to Silberberg⁷⁾ are: (i) within a polymer, neighbouring sections of the chain could form chemical bonds which would result in loops and coiling; and (ii) between polymers, van der Waals forces could result in further coagulation. Hayes and Swift⁶⁾ suggested that the coagulation of the organic macromolecule would also result in slowing down the ion exchange process. In this situation, tortuosity and general frictional forces within the molecule will be greatly increased, and the passage of ions through the macromolecule will be restricted. The end result in the sludge system is the organic matter containing Cu and Zn, which is less

Table 1. Chemical properties of the sewage sludge used.

pH (1 : 2)	Organic C (g kg^{-1})	CEC (cmol(+) kg^{-1})	Total Cu (mg kg^{-1})	Total Zn (mg kg^{-1})
7.0	223	55.5	610	790

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Table 2. Amount of Cu and Zn extracted from sewage sludge as affected by ionic strength of CaCl₂ solution.

Ionic strength (M)	pH	Cu		Zn	
		(mg kg ⁻¹)	% of total*	(mg kg ⁻¹)	% of total
0.001	7.2	56.0	9.2 ± 0.2	1.5	0.19 ± 0.01
0.003	7.5	55.6	9.1 ± 0.1	1.4	0.18 ± 0.01
0.015	7.4	45.6	7.5 ± 0.1	1.1	0.14 ± 0.01
0.03	7.4	40.4	6.6 ± 0.1	0.8	0.11 ± 0.01
0.15	7.2	37.1	6.1 ± 0.2	2.1	0.27 ± 0.01
0.3	7.2	38.1	6.3 ± 0.1	3.6	0.46 ± 0.03
1.0	6.8	44.5	7.3 ± 0.2	9.0	0.76 ± 0.01
1.5	6.5	44.0	7.2 ± 0.3	8.9	1.10 ± 0.01
3.0	6.3	47.9	7.9 ± 0.2	16.7	2.10 ± 0.03

*mean ± S.E.; average of two replicates.

Table 3. Amount of Cu and Zn extracted from sewage sludge as affected by ionic strength of KCl solution.

Ionic strength (M)	pH	Cu		Zn	
		(mg kg ⁻¹)	% of total*	(mg kg ⁻¹)	% of total
0.001	7.8	56.4	9.3 ± 0.1	1.5	0.19 ± 0.03
0.004	7.7	58.8	9.7 ± 0.1	1.5	0.19 ± 0.03
0.02	7.3	57.0	9.4 ± 0.1	1.4	0.18 ± 0.01
0.04	7.2	55.7	9.2 ± 0.1	1.2	0.15 ± 0.01
0.2	7.2	57.3	9.4 ± 0.2	1.2	0.15 ± 0.01
0.4	7.2	59.8	9.8 ± 0.1	1.3	0.16 ± 0.01
1.0	7.2	65.4	10.7 ± 0.1	2.0	0.25 ± 0.01
2.0	7.2	68.9	11.3 ± 0.1	2.4	0.31 ± 0.01

*mean ± S.E.; average of two replicates.

accessible and thus less extractable in a solution of intermediate ionic strength. A second theory could explain the observation of less Cu and Zn extracted with increasing ionic strengths of CaCl₂. The increasing salt concentration may result in a structural reorganization of the ligand due to the replacement of water molecules surrounding the adsorbent and the adsorbate.⁸⁾ Thus, the frequency and strength of metal-ligand interactions increase.

Extracting solutions of very high ionic strengths (higher than 0.2 M) resulted in increasing amounts of Cu and Zn released from the sludge. This is possibly due to the dissolution of inorganic forms of Cu and Zn rather than the increased exchange reactions.⁹⁾ The pH of the extracting solution decreased with increasing ionic strength, in the CaCl₂ system, lending further support to the possibility of dissolution reactions.

The effect of the KCl extracting solution differed from that of the CaCl₂ extracting solution that the decreases in the amounts of Cu and Zn released with increasing ionic strength were not as pronounced (Table 3). The difference can be attributed to the valence of the cation of the extracting solution. Divalent ions are able to form bridge complexes between organic macromolecules causing aggregation.^{10,11)} The fact that Cu-containing colloidal particles experience greater coiling and aggregation in divalent electrolytes is not a conclusive evidence that the Cu is always less extractable. In fact, given

time, the difference in the inextractability of Cu and Zn may be not existed comparable ionic strengths. If a macromolecule is strongly coiled (i.e., Ca system), the diffusion kinetics is much slower than in an uncoiled or dispersed system (i.e., K system). In our study, it was not determined whether the equilibrium was reached within the 6 hours reaction period. If the equilibrium was not reached, there would have been very little effect of coiling on the extractability of Cu in both CaCl₂ and KCl extracting systems.

A comparison of the amounts of Cu and Zn extracted by salts of different cation valence but the same ionic strength is given in Table 2 and 3. Less Cu was extracted with the high ionic strength CaCl₂ solution than the low ionic strength solution. For Zn, however, much Zn was extracted with the high ionic strength CaCl₂ solution. Comparisons across Table 2 and 3 show that relatively equal amounts of Cu were extracted by both CaCl₂ and KCl at both ionic strengths indicating dissolution reactions. The amount of Zn extracted by the 1.0 M KCl was less than that extracted by the 1.0 M CaCl₂. These data further support that Zn is specifically adsorbed by singly coordinated hydroxyls on the short-range ordered oxides, which may be purely inorganic or commonly organo-mineral in nature.¹²⁾ Thus, the doubly charged Ca cation can displace the Zn with greater ease than can the monovalent K cation. The difference in behaviour between Zn²⁺ and Cu²⁺ with short-range ordered compounds arises from the fact that Zn²⁺ does

not have partially filled d orbitals. Thus, Zn^{2+} reacts strongly with hydroxyls only, whereas Cu^{2+} can also be specifically bound by organic functional groups.¹³⁾

This study revealed the availability of Cu from this sewage sludge is greater than that of Zn. However, the extractabilities of both Cu and Zn were low even in solutions of high ionic strengths. Increasing the ionic strength of the extracting solution within the normal soil range did not result in the increased amounts of Cu and Zn released from the sewage sludge. The extracting solutions with ionic strengths higher than 1.0 M result in an increase in released Cu and Zn. These data suggest the physical effect of ionic strength on the organic polymer conformation, which resulted in the occlusion of Cu and Zn within the polymer. At high ionic strength, chemical reactions such as increase in exchange reactions and dissolution of solid phases appeared to dominate, which resulted in greater amounts of released Cu and Zn from sewage sludge.

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