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Mechanisms for biosorption of chromium(III), copper(II) and mercury(II) using water extracts of *Moringa oleifera* seed powder

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In continuation of our work on heavy metal remediation using *Moringa* seed powder, this study examines the mechanisms of metal sorption on water extracts of *Moringa oleifera* (MO) seed powder using extended X-ray absorption fine structure (EXAFS). Chromium(III) is hydrolysed to form a mixture of $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$ and $[Cr(OH_x)_2<(OH)_2>]_n^{n\cdot(2x-3)+}$ complexes, x = 1 or 2. The chromium(III) complexes are octahedral with mean Cr-O bond distance of 1.97(2) Å. Copper (II) forms complexes with ligands with oxygen and/or nitrogen donor atoms, most likely amino and carboxylate groups. Copper(II) retain the typical Jahn-Teller distortion with Cu-O/N bond distances of 1.97(2) and 2.21(4) Å. Furthermore, a Cu···C distance at 2.96 Å, and a corresponding Cu-O-C 3-leg scattering path at 3.10 Å are observed as well, strongly supporting that a large fraction of carboxylate groups are bound to the copper(II) ion on the equatorial plane. Mercury (II) forms mainly linear complexes with nitrogen donor ligands, d(Hg-N) = 2.15(2) Å, most probably from amino groups in amino acids or proteins. This shows that the softer metal ions, copper(II) and mercury(II), form complexes with oxygen and/or nitrogen donor ligands in the MO extracts, while the harder and more highly charged chromium(III) ion becomes hydrolysed. The study therefore suggests that the successful biosorption of heavy metals by *Moringa*, a potential heavy metal removing agent, is attributable to its oxygen and nitrogen donating carboxylate and amino groups.

Key words: Chromium, Copper, Mercury, *Moringa oleifera*, EXAFS.

INTRODUCTION

There is a widespread recognition that the presence of heavy metals such as chromium(III,VI), copper(II) and mercury(I,II) in water is hazardous to the environment and human health and their discharge into surface waters is a concern worldwide (Alloway, 1995). Many processes for the removal of heavy metals from water and waste-waters have been proposed. Chemical precipitation, physical treatment such as ion exchange and adsorption are some of the processes that have been reported to be the most effective ones in the removal of heavy metals.

However, these processes involve use of chemicals and synthetic polymers whose impact on the environment has not been fully investigated. This has led to an increased interest in the subject of natural coagulants for heavy metal remediation of wastewaters. Numerous biomate-rials have been investigated such as petiolar felt-sheath of palm (Iqbar et al., 2002), cotton boll (Ozsoy and Kumbur, 2006), coconut copra meal (Efojoma and Ho, 2007), coir pith (Suksabye et al., 2007) and *Moringa oleifera* (MO) seed powder (Mataka et al., 2006; Sharma et al., 2006; Sajidu et al., 2006). Our earlier work indi-cated remarkable sorption ability of crude water extracts of MO and *Moringa stenopetala* (MS) for chromium(III), copper(II), zinc(II) and cadmium(II) cations in aqueous solution (Sajidu et al., 2006). In continuation of that study

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Table 1. Mean bond lengths (or distances), R/Å, Debye-Waller factors, σ^2, numbers of distances, N, and energy shift, ΔE_o, of metals in the EXAFS studies of the metal treated *Moringa oleifera*.

Interaction	N	R/Å	σ^2/ Å	ΔE_o,
Cr-O	6	1.97	0.0021	-7.5
Cr···Cr	2	3.01	0.0059	
Cr···Cr	2	3.59	0.0080	
Cr···Cr	2	4.49	0.0128	
Cu-O	4	1.97	0.0043	-7.5
Cu-O	2	2.21	0.0121	
Cu-C	4	2.96	0.0071	
Cu-O-C	8	3.10	0.0069	
Hg-N	2	2.15	0.0067	-5.73

the current work investigated the mechanisms through which chromium(III), copper(II) and mercury(II) are sorbed onto crude water extracts of MO using extended X-ray absorption fine structure (EXAFS).

MATERIALS AND METHODS

A solution containing 20 mmol·dm^{-3} chromium(III) perchlorate was prepared by dilution of a 1.4 mol·dm^{-3} stock solution (prepared from chromium(III) perchlorate hexahydrate, $Cr(ClO_4)_3 \cdot 6H_2O$ (Aldrich) in 1.0 mol·dm^{-3} hydrochloric acid). Aqueous copper(II) solution (20 mmol·dm^{-3}) was prepared by dissolving analytical grade copper(II) nitrate, monohydrate, $Cu(NO_3)_2 \cdot H_2O$ (Aldrich) in deionized water while aqueous mercury(II) trifluoromethanesulfonate solution (20 mmol·dm^{-3}) was prepared by dissolving anhydrous $Hg(CF_3SO_3)_2$, prepared as described elsewhere (Molla-Abbassi et al., 2002) in 0.01 mol·dm^{-3} nitric acid in order to suppress hydrolysis. 15 ml of MO water extracts, prepared as described elsewhere (Sajidu et al., 2006), was added to 15 ml of 20 mmol·dm^{-3} metal solution and the pH was adjusted to about 7 by dropwise addition of 1.0 mmol·dm^{-3} NaOH. The solution mixtures were stirred for 48 h and then centrifuged at 3000 rpm for 15 min. The metal-rich residues were then dried at room temperature for EXAFS measurements. Chromium and copper K-edge and mercury L$_3$-edge X-ray absorption spectra were collected at beam-line I811, MAX-lab, Lund University, Sweden, which was operated at 1.5 GeV and a maximum current of 200 mA. Data collection was performed simultaneously in transmission mode using ion chambers with stationery gases and in fluorescence mode using a Lytle detector with flow of argon and/or krypton gas depending on energy. The EXAFS station was equipped with Si[111] double crystal monochromator. In order to remove higher order harmonics, the beam intensity was detuned to 30, 50 and 50% for chromium, copper and mercury, respectively, at the end of the scans. Internal energy calibration for the chromium, copper and mercury was made with the corresponding metal foil, and in case of mercury with a boron nitride diluted mercury(II) chloride sample (Thompson et al., 2001), assigning the first inflection point on the absorption edge to 5989.0, 8980.3 and 12284.0 eV, respectively. The treatment of the EXAFS data was carried out by means of the EXAFSPAK program package (George and Pickering, 1993) using standard procedures for pre-edge subtraction and spline removal. The k^3-weighted model functions were calculated using *ab initio* calculated phase and amplitude parameters obtained by the FEFF7 program (Ankudinov, 1996). The standard deviations given for the refined parameters in Table 1 of the results are obtained from k^3 weighted least squares refinements of the EXAFS

function $\chi(k)$, and do not include systematic errors of the measurements. These statistical error estimates provide a measure of the precision of the results and allow reasonable comparisons e.g. of the significance of relative shifts in the distances. However, the variations in the refined parameters, including the shift in the E_o value (for which $k = 0$), using different models and data ranges, indicate that the absolute accuracy of the distances given for the separate complexes is within ±0.01 to 0.02 Å for well-defined interactions.

RESULTS AND DISCUSSION

The EXAFS function for chromium in the MO extracts and the corresponding Fourier Transform (FT) (Figure 1) fit very well with structures of hydrolysed chromium, existing as a trimeric complex, $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$, the dominating species in aqueous solution in the pH range 2.8 - 4.5 and as indefinite chains $[Cr(OH)_2 <(OH)_2 >]_n^{n \cdot (2x-3)+}$, the dominating species in very alkaline aqueous solutions, pH >13 (Torapava et al., unpublished data). The FT shows light back-scatterers, certainly oxygen, at short distance, 1.97(1) Å, and a heavier back-scatterer, most probably chromium, at 3.01(2) Å, and a smaller contribution at ca. 3.9 Å, most probably multiple scattering within the expected CrO_6 core. The results from the parameter refinements of the EXAFS data are summarized in Table 1.

The copper(II) EXAFS spectrum (Figure 2) is consistent with an octahedral oxygen shell with Jahn-Teller distortion. The mean Cu-O/N bond in the equatorial plane is 1.97(2) Å whereas the two axial Cu-O bond length is 2.21(4) Å. The goodness of fit parameters improve significantly after introducing a Cu···C distance and a corresponding Cu-O-C three-leg scattering path refined to 2.96(3) and 3.10(3) Å, respectively (Table 1). This suggests that the equatorial oxygens around the Cu are part of carboxylate groups in the MO water extracts whereas the axial oxygens are probably part of water molecules. Introduction of Cu-Cu distances of possible hydrolysis products of copper(II), as previously found of copper(II) adsorbed on clay minerals (Peacock and
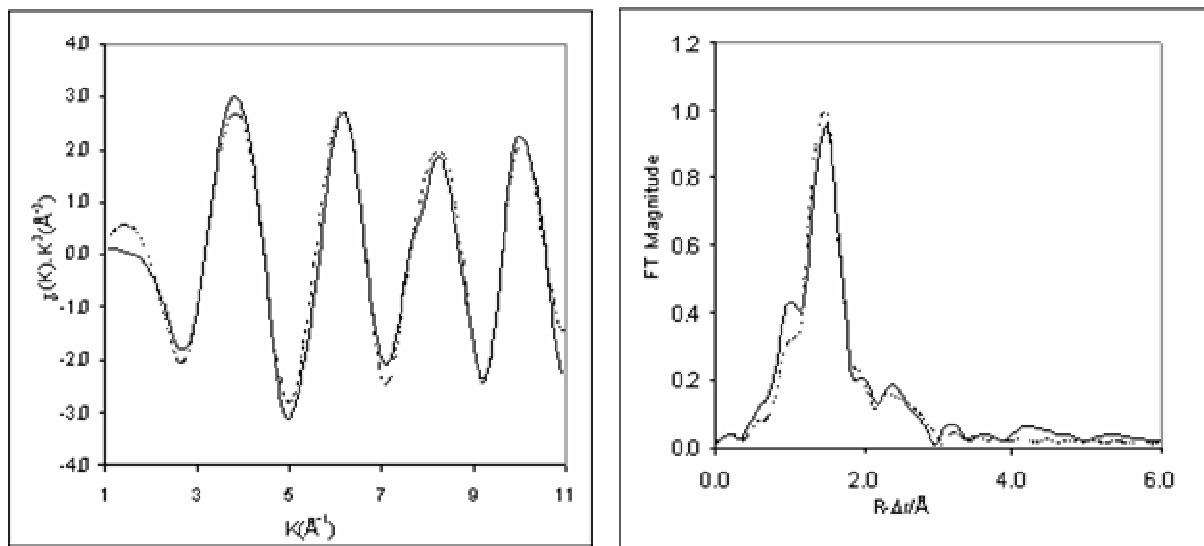
Figure 1. Left panel: k^3-weghted Cr K-edge EXAFS χ spectrum for Cr-*Moringa* samples (solid line) compared with the theoretical signal (dotted line). Right panel: Non-phase shifted Fourier transforms of the experimental data (solid line) and the theoretical signal (dotted line) calculated over the range 3.0 < k < 13.0 Å^{-1}.
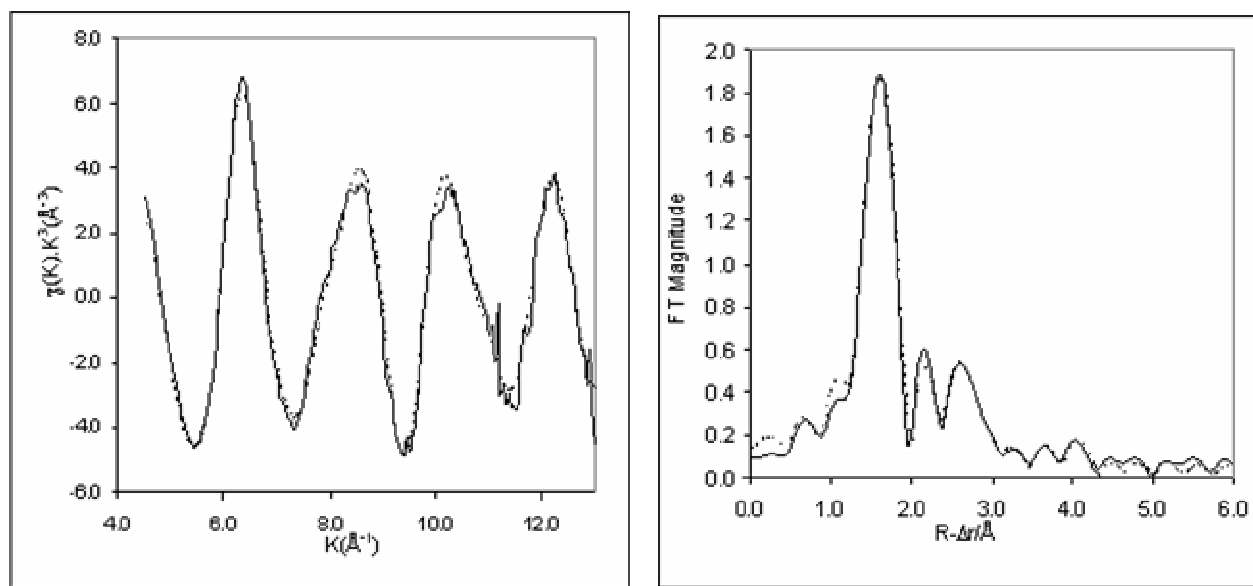

Figure 2. Left panel: k^3-weghted Cu K-edge EXAFS χ spectrum for Cu-*Moringa* samples (solid line) compared with the theoretical signal (dotted line). Right panel: Non-phase shifted Fourier transforms of the experimental data (solid line) and the theoretical signal (dotted line) calculated over the range 1.0 < k < 11.0 Å^{-1}.

Sherman, 2005) did not improve the fit. This shows that the complexation of copper(II) by the ligand groups in MO extracts are sufficiently strong to resist hydrolysis at neutral pH.

The EXAFS spectrum for the MO treated with mercury(II) is dominated by a shell of light-back-scatterers around the mercury at bond length of 2.15 Å (Figure 3). The distance at 2.15 Å is consistent with Hg-N

bond of mercury(II) in amide or amine groups. This indi-cates that the mercury(II) is sorbed on the MO water extracts through nitrogen (probably from amino acids) as the donor atom. The raw absorption spectrum (not shown) of the mercury(II) treated MO also showed presence of significant concentration of selenium in the MO water extracts. This was seen as a large absorption edge at about 12658 eV corresponding to the K-edge of selenium,
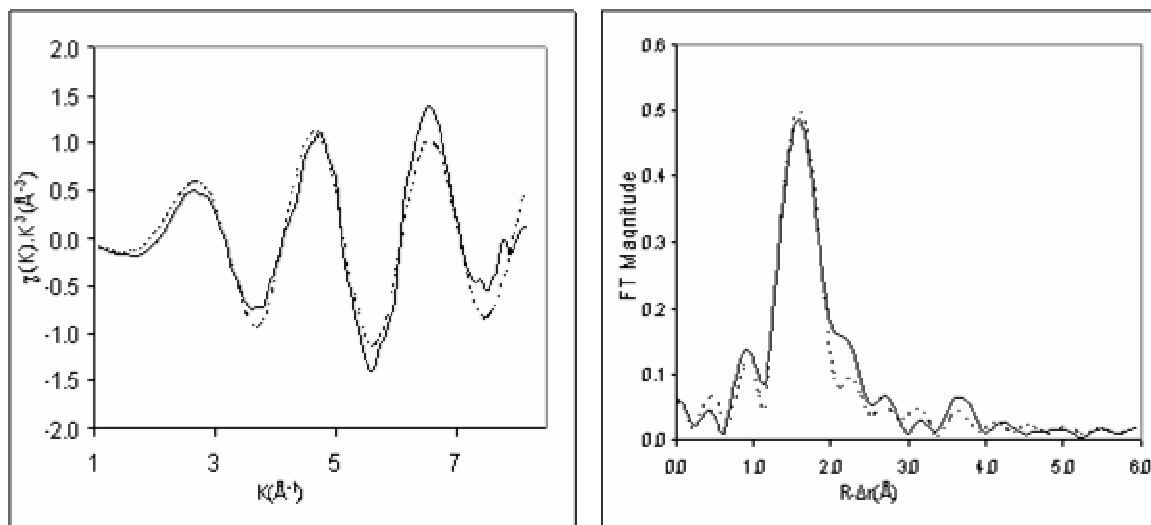
Figure 3. Upper panel: k^3-weghted Hg L_{III}-edge EXAFS χ spectra for Hg-clay samples at pH 2.2 (solid line) compared with the theoretical signal (dotted line). Lower panel: Non-phase shifted Fourier transforms of the experimental data (solid line) and the theoretical signal (dotted line) calculated over the range $1.0 < k < 8.0$ Å^{-1}.

which caused the termination of the spectrum at k=8 Å^{-1}. It should therefore be expected that mercury(II), as a soft electron-pair acceptor, forms strong complexes with selenium donor ligands; selenium compounds in fact are used as mercury scavengers (Falnoga and Tušek-Žnidarič, 2007) However, no Hg···Se distances were found to contribute to the EXAFS function observed in the data treatment. This strongly indicates that the nitrogen donor groups are much more abundant and readily available for complexation in the Moringa extracts, than the selenium compounds present in MO.

In conclusion the successful sorption of heavy metals by MO water extracts can be explained by different uptake mechanisms. Chromium(III) cations are sorbed as hydrolysed octahedral trimeric and indefinite chain complexes. Copper(II) is sorbed through complexation at neutral pH values by coordination to the carboxylate groups, whereas mercury(II) is sorbed through the nitrogen donating amide groups. The results will assist in design and the optimisation of low cost effective heavy metal remediation techniques when considering use of natural coagulants.

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