

Mechanisms of Copper and Mercury Adsorption on Bentonite Clays from EXAFS Spectroscopy

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Copper(II) and Mercury(II) cations are classified as important heavy metal pollutants in industrial wastewaters. In this study, Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy was used to provide information about the coordination environment and nearest neighbouring atoms involved in the copper(II) and mercury(II) ions adsorption on raw and calcined bentonite clays from Northeast Brazil. EXAFS experiments were carried using a channel-cut Si (111) monochromator. All the spectra were performed in transmission mode and Cu (8987 eV) K and Hg (12284 eV) L edges were collected. Each spectrum corresponded to an average of 3 independent scans. Standard compounds (copper and mercury oxides) were used in order to distinguish the bond differences between the heavy metal and coordination spheres (O atoms). Based on EXAFS investigation, it is possible to conclude that the structure of heavy metal ions on clays does not depend primarily of the calcinations of the structure. The main metal interaction observed for copper and mercury ions occurred on hydroxyl groups.

1. Introduction

In the last years, environment contamination by heavy metals has gained much attention due to the significant impact on the public health. Copper is an ion extremely toxic and used in different industrial applications. Several methods are used to remove toxic metals from aqueous solution such as ion exchange, reverse osmosis, adsorption (Gimenes et al., 2013), complexation and precipitation (Juang and Shao, 2002). Adsorption is considered an effective and economical method for removal of pollutants from industrial wastewater at low concentration (Ng et al., 2002).

The bentonite clay is composed by unit cells made up of two silica tetrahedral sheets with a central alumina octahedral sheet. This material has been described as a promising adsorbent for removal of heavy metals such as copper (Almeida Neto et al., 2013; 2012), cadmium and lead (Galindo et al., 2013) and nickel (Vieira et al., 2010 a, b). Most of the studies on heavy metal adsorption have been dedicated to the determination of the overall uptake performance; however, there is limited information available on identifying adsorption mechanism.

Analytical techniques, such as XPS (Dambies et al., 2001), Mössbauer spectrometry (Bhatia and Ravi, 2000), XANES and EXAFS (Gardea-Torresdey et al., 2002), can be used to identify surface groups that are primarily responsible for binding metallic species and the state of adsorbed metals. Extended X-ray absorption fine structure spectroscopy (EXAFS) provides information about the coordination structure, like the number of atoms in the neighbourhood of a determined coordination sphere (-OH), and the bond distance between heavy metal and site. This technique presents several important advantages in studying local structures, since is sensitive only to the short-range order and can show the structure of both crystalline and non-crystalline samples.

EXAFS is sensitive to the local structure around specific species of interest, such heavy metals ions. Because of this, it is possible to use this technique to directly measure partial pair correlation functions, around the targeted atoms in solution with a relatively small number of structural variables (Gardea-Torresdey et al., 2002). This interaction creates a wave function that can be Fourier transformed to give a pseudo-radial distribution function. In this analysis the major peak observed in the Fourier transform is the

interatomic distance between target metal and coordination sphere, in this case between heavy metal (copper or mercury) and functional groups of clays.

In this paper, Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy was used to provide information about the coordination environment and nearest neighbouring atoms involved in the heavy metal ion adsorption on bentonite (Bofe and Verde-lodo) clays. Copper and mercury ions were studied due to their toxicity, which, depends mainly of their oxidation states and concentration. This approach provides with valuable insight for explaining the adsorption mechanism exhibited by these heavy metal ions on clays.

2. Experimental

2.1 Materials

The bentonite Bofo and Verde-lodo clays, from the northeast of Brazil, were used in this study. The adsorption experiments were performed on raw and calcined clays. Bofo and Verde-lodo clay were calcined at 773 K for 24 h in order to improve metal adsorption properties.

2.2 Metal Adsorption

Equilibrium tests were performed with different concentrations of adsorbate and temperatures. For maintaining pH of the medium, solutions of $\text{NH}_4(\text{OH})$ with concentrations of 0.01 mol/L HNO_3 or 0.01 mol/L were added in order to adjust the pH value. The pH was monitored before and after adsorption. Cu(II) and Hg(II) were removed at pH 4.5 for 60 h at 25 °C. The Cu (II) and Hg (II) solutions were prepared using copper nitrate and mercuric acetate, respectively. Diagrams of copper and mercury species distribution as function of pH for Cu^{2+} and Hg^{2+} ions were simulated using Hydra (Hydrochemical Equilibrium-Constant Database) software (Puigdomenech, 2004).

2.3 EXAFS experiments

EXAFS experiments were performed with saturated samples in the highest concentrations of equilibrium tests and carried out at Brazilian National Synchrotron Light Laboratory (LNLS), using a channel-cut Si (111) monochromator. All the spectra were performed in transmission mode and were collected around Cu (8,987 eV) K and Hg (12,284 eV) L edges. Each spectrum corresponded to an average of three independent scans. Standard compounds (copper oxide and mercuric oxide) were used in order to distinguish the bond differences between the heavy metal and coordination spheres (O atoms).

2.4 Analysis of EXAFS data

The kinetic energy of the photoelectrons ejected from the clay samples and standard compound was calculated based on the edge position of the metal of interest (8,987 and 12,284 eV, for Cu and Hg) and converted to the vector (k) space. This provide an EXAFS curve, which depends on the module of the wave vector (reciprocal space), then Fourier transformed to radial coordinates and converted into interatomic distance space (real space). These data directly reflect the average local environment around the absorption atoms. Afterwards, it approaches to the distribution of neighbouring atoms around the adsorbed central atom, where each peak obtained corresponds to a coordination sphere. First, for the treatment of EXAFS data, it was necessary analyse a standard compound, whose structural parameters were already known. All EXAFS data were analyzed using ATHENA[®] software (IFEFFIT package). This computational program could perform all transformations described before.

3. Results and Discussion

3.1 Effect of pH

The distribution of copper and mercury species as a function of pH for concentration of metal adsorption was simulated using Hydra software, as shown in the Figure 1. It is observed that, for the study range of pH, the dominant specie is Cu^{2+} for values up to 5.0. The increment of pH in this range reduces Cu^{2+} concentration while increases the CuO concentration. This fact indicates that adsorption occurs for pH < 5.0 the Cu^{2+} , since there is no chemical precipitation of this metal.

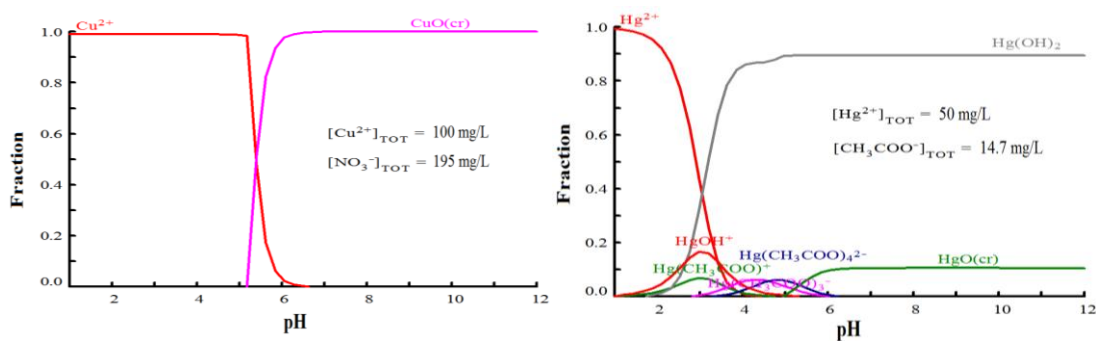


Figure 1: Metal speciation for (A) 100 mg/L Cu and (B) 50 mg/L Hg

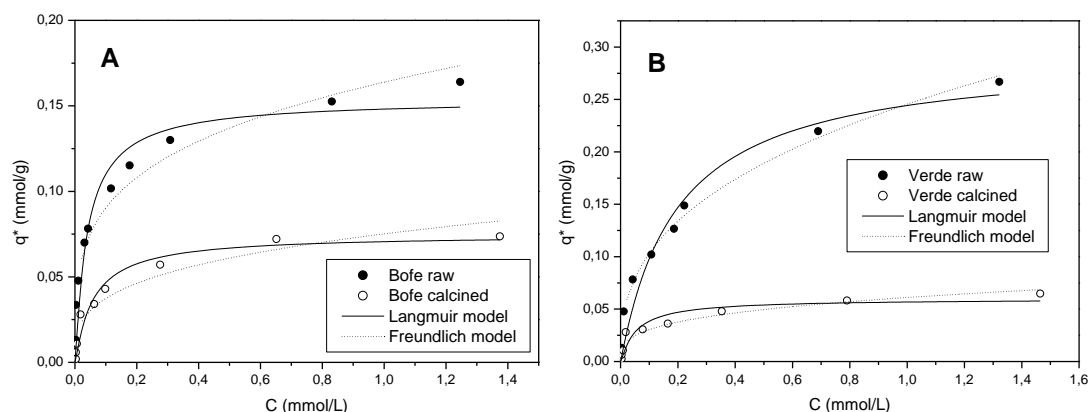


Figure 2: Plots of q^* vs. C for Cu(II) ions uptake on: (A) Bofe raw and calcined clay; (B) Verde-Iodo raw and calcined clay (Experimental conditions: clay 1 g/L, pH 5.7, time 360 min, temperature 298 K)

3.2 Copper and Mercury Adsorption

The isotherm plots of the ion's concentration on the solid phase, q^* , vs. concentration of the ion on the liquid phase, C , at 298 K were given in Figure 2. It is observed that, for any equilibrium concentration of Cu(II) ions, the Bofe and Verde-Iodo raw clays presented much higher uptake of Cu(II) ions than Bofe and Verde-Iodo calcined clays.

The Langmuir and Freundlich plots (Figure 2) were obtained from Eqs(1) and (2), respectively:

$$q^* = \frac{q_m b C}{1 + b C} \quad (1)$$

$$q^* = a(C)^n \quad (2)$$

The parameters obtained for non-linear curve fit are shown in Table 1.

The Langmuir monolayer capacity, q_m , has values of 0.06 to 0.29 mmol/g (Table 1). Calcination has negative influence on the monolayer capacity of both clays. The q_m values follow the same increment order as the Freundlich adsorption capacity, i.e. Bofe raw < Verde raw. This result is in conformity with the order of adsorption capacity of the four clay adsorbents.

The adsorption of mercury showed low values of removal amount. The EXAFS analysis for mercury adsorbed were performed by transmittance and spectrum obtained in the XANES region due to low amount of this metal

Table 1: Langmuir and Freundlich coefficients for adsorption of Cu(II) ions on clays

System	Langmuir			Freundlich		
	q_m (mmol/g)	b (L/g)	R^2	a	n	R^2
Cu/Bofe raw	0.1540	25.3234	0.9585	0.1639	0.2582	0.9553
Cu/Bofe calcined	0.0748	16.7868	0.9725	0.0752	0.3015	0.9259
Cu/Verde raw	0.2926	5.0544	0.9649	0.2455	0.3769	0.9914
Cu/Verde calcined	0.0599	18.1980	0.9288	0.0611	0.3009	0.9378

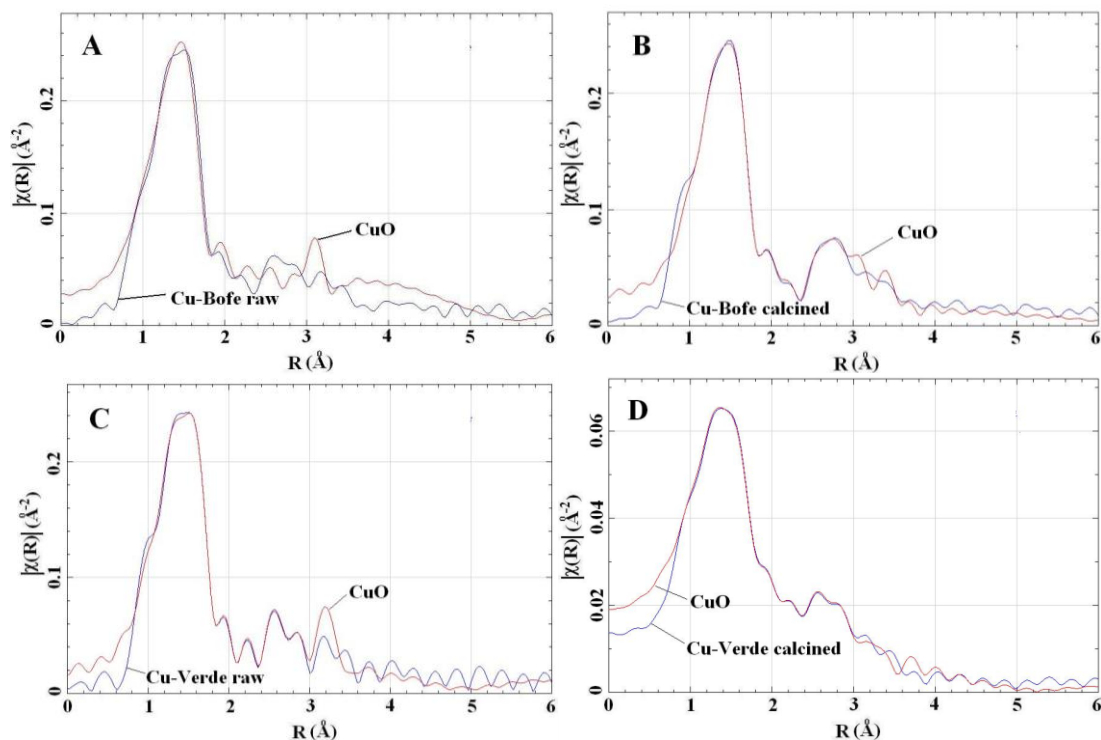


Figure 3: Radial structure function of the copper ions adsorption on (A) Bofe raw, (B) Bofe calcined, (C) Verde-Iodo raw and (D) Verde-Iodo calcined clays

3.3 Copper-Clay Complex

The EXAFS spectra of the copper adsorption are shown in Figure 3 (Fourier transforms, real space). The Cu K-edge EXAFS spectra were taken up to 8,987 eV.

Each peak in the absorption spectra represents one coordination sphere and its distance to the target atom. There are three stronger peaks located at 1.80 Å approximately in the FT curve for CuO, where the first one arises from an oxygen shell (Cu-O), while the second one comes from a Cu type shell (Cu-Cu), and the third one arising from Cu-O-Cu bond. For copper hydroxide, a stronger peak at 1.5 Å was observed, corresponding to Cu-O bond (Collins et al., 1999).

A strong peak was observed, in all the cases, at approximately 1.5 Å (first metal coordinate sphere), that corresponds to the backscattering oxygen atoms of the first shell.

The EXAFS spectrum of the copper(II) treated clays (Figure 3) consist in an octahedral oxygen shell with Jahn-Teller distortion. The equatorial Cu-O bond is 1.93 Å whereas the two axial Cu-O bond lengths are 2.12, 2.39, 2.72 and 2.64 Å. After adding a Cu-P distance of 2.98 Å, there was a significant improvement of the fit parameters for calcined Bofe clay. However, at natural pH of contact solid-fluid, the main precipitation product on the clay surfaces seems to be copper(I) oxide. The EXAFS spectra recorded at pH 4.5 are almost identical, showing that the speciation is the same at all samples.

3.4 Mercury-Clay Complex

The fit of the experimental EXAFS data and the corresponding FTs at pH 4.5 for mercury(II) sample are given in Figure 4. For comparison purposes XANES spectrum of the mercury(II) oxide [HgO] that has a

chain structure with the bonds to the water molecules very tightly bound in linear fashion and four weak bonds to oxygen, as shown in Figure 4. The mercury(II) oxide spectrum is similar to the mercury(II) adsorbed clay at pH 4.5. Only one shell of light back-scattered around mercury at short bond distance, ≈ 1.65 Å, is observed in the FT, Figure 4. This shows that mercury(II) at this pH binds to oxygen in a linear fashion as previously found for adsorbed mercury(II) ion on goethite surfaces (Collins et al., 1999) and in solid mercury(II) oxide. It seems very likely that the mercury(II) is sorbed to the clay surface as a hydrolysis complex, since hydrated mercury(II) ions easily hydrolyze ($\text{pK}_a \approx 3.5$) depending on temperature and ionic strength and a precipitation of HgO does not occur.

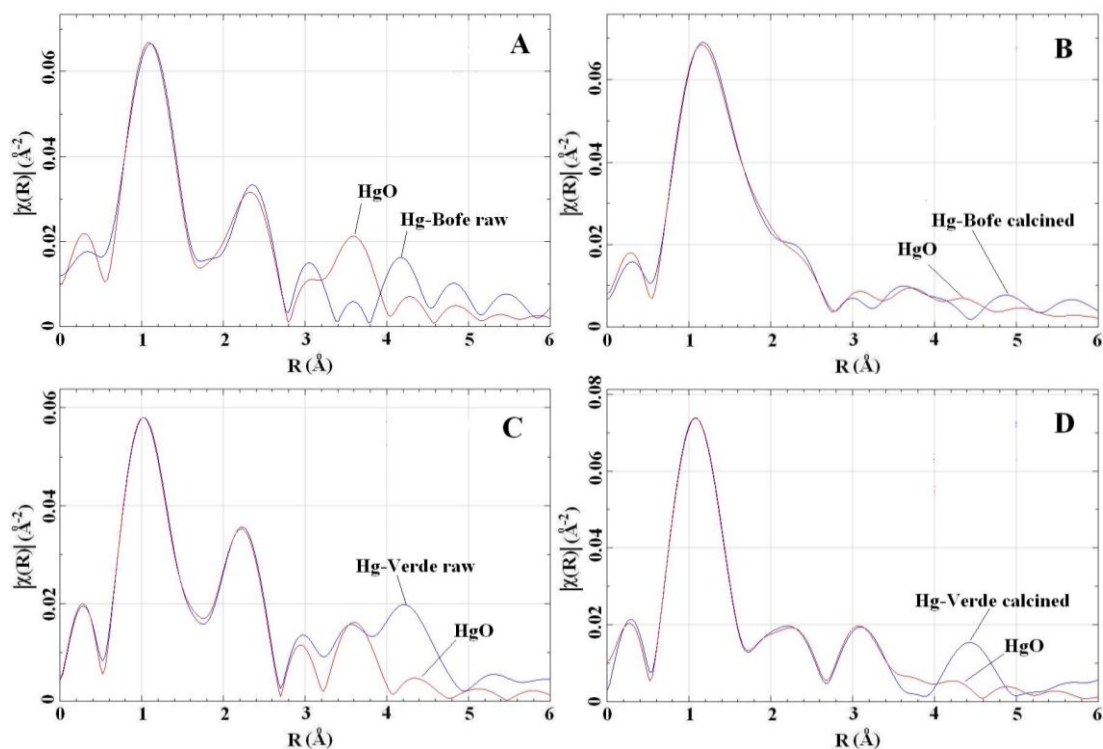


Figure 4: The EXAFS spectra of the mercury ions adsorption on (A) Bofe raw, (B) Bofe calcined, (C) Verde-lodo raw and (D) Verde-lodo calcined

The most relevant contribution to the EXAFS region of montmorillonite was recognized to Hg surrounded by six oxygen atoms. Two oxygen atoms are closer to Hg, at distances of 1.66, 1.91, 1.62 and 1.59 Å, respectively for Bofe raw, Bofe calcined, Verde-lodo raw and Verde-lodo calcined clays. The distance from Hg of the three remaining oxygen atoms is greater and reaches 2.40 Å. The short distances could be interpreted as indicators of Hg–O bonds in montroydite-like compounds, whereas the long distances can be attributed to Hg–O bonds in Hg–HO complexes. This hypothesis was also formulated by Collins et al. (1999) in studies of a goethite substrate. The lack of symmetry in the Hg coordination sphere is consistent with the two-steps release of the mercury at high temperatures (Brigatti et al. 2005). The EXAFS analysis also refines two Hg atoms at 3.17, 3.10 and 3.44 Å, from the central Hg atom, for Bofe calcined, Verde-lodo raw and Verde-lodo calcined, respectively.

4. Conclusion

Based on EXAFS investigation, it is possible to conclude that the structure of heavy metal ions (copper) on clay adsorbents does not depend primarily of calcinations in the structure. For copper ions on natural clay it was not possible to observe the occurrence of metal interaction mainly on hydroxyl groups. The FT functions generated from the Hg L-edge EXAFS spectra of Hg-rich Bofe and Verde-lodo, raw and calcined showed a good match in the peak positions and intensities of the experimental spectra for all the samples, compared with HgO (montroydite) as a model compound. For mercury and copper it was not possible to

distinguish if the interaction took place preferentially on hydroxyl groups, being necessary the utilization of this technique with others like FTIR and XPS together.

Acknowledgements

The authors thank FAPESP and CNPq for financial support and Brazilian National Synchrotron Light Laboratory (LNLS) for EXAFS analyses.

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