

AN EXAFS STUDY OF THE BINDING OF CHROMIUM, MERCURY AND COPPER ON NATURAL AND CROSSLINKED CHITOSAN FILMS

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Abstract

The nearest neighbouring atom and coordination environment involved in the heavy metal ion adsorption on chitosan films was provided using EXAFS measurements. It was prepared chromium, mercury and copper complexes on natural and crosslinked chitosan films and was obtained spectra of the distribution of neighboring atoms around the adsorbed central atom. All the spectra were performed in transmission mode and were collected around Hg (12284eV) L edge, Cr (5989eV) and Cu (8987eV) K edges. For chromium ions was possible observe that metal interaction is mainly on amino groups, however, for mercury and copper was not possible distinguish if the metal interaction takes place preferentially on amino or hydroxyl group.

Introduction

In the last years, environment contamination by heavy metals has gained much attention due to the significant potential health impact on the public. Chromium, mercury and copper are ions extremely toxic and used in different industrial applications. Several methods exist to remove toxic metals from aqueous solution such as ion exchange, reverse osmosis, adsorption, complexation and precipitation [1]. Adsorption is considered an effective and economical method for removal of pollutants from wastewater [2].

Chitosan, a linear polysaccharide based on glucosamine unit (Figure 1), has been described as a suitable biopolymer for removal of heavy metal ions from wastewater [3-10] since its chemical groups can act as chelation sites. 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.

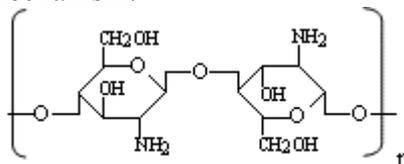


Figure 1 : . Molecular Structure of Chitosan

Sophisticated analytical techniques, like XPS [11], Mössbauer spectrometry [12], XANES and EXAFS [13], can be used to identify surface groups that are primarily responsible for binding metallic species and also the state of adsorbed metals. More recently, the technique of X-ray absorption fine structure spectroscopy (EXAFS) has been used to study the mechanism of metal binding by biopolymers [14]. Extended X-ray absorption fine structure spectroscopy (EXAFS) provides information on the coordination structure, like the number of atoms in the neighborhood of a determined coordination sphere (-NH₂, -OH), and the bond distance between heavy metal and chelation site. This technique presents several important advantages in studying local structures,

since is sensitive only to the short-range order and can probe 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. This makes it possible to be used directly to measure partial pair correlation functions around the targeted atoms in solution with a relatively small number of structural variables [15]. This interaction creates a wave function that can be Fourier transformed to give a pseudo-radial distribution function, where the major peak observed in the Fourier transform is the interatomic distance between target metal and coordination sphere, in this case, between heavy metals (chromium, mercury and copper) and functional groups of biopolymer.

This study was performed on natural and crosslinked chitosan films. Crosslinking with glutaraldehyde (GLA) or epichlorohydrin (ECH) were carried out in order to improve metal adsorption properties and to better understand the adsorption mechanism. Since glutaraldehyde binds to amino groups and epichlorohydrin binds preferentially to hydroxyl groups, it is possible to use both crosslinking processes to understand which chemical functionality is responsible for metal-chitosan interaction.

Extended X-Ray absorption fine structure (EXAFS) spectroscopy was used to provide information about the coordination environment and the nearest neighboring atoms involved in the heavy metal ion adsorption on chitosan films. Chromium, mercury and copper ions were chosen due to their toxicity, which depends mainly on their oxidation states. This approach provides valuable insight for explaining the adsorption mechanism exhibited by these heavy metal ions on chitosan films.

Material and Methods

Materials. Chitosan with molecular weight 9.90×10^5 g/mol was purchased from Sigma (USA), 82% deacetylated and commercial grade. All other chemicals (glutaraldehyde, epichlorohydrin, mercuric chloride, potassium dichromate, copper sulfate, mercuric oxide, chromium oxide, copper oxide, mercuric acetate and copper acetate) were of analytical grade. Aqueous solutions were prepared using Milli-Q ultrapure water.

Preparation and chemical modification of chitosan films. In order to obtain chitosan films the same procedure showed by Beppu (2003) [16] was used. The crosslinking treatment was performed as described by Vieira and Beppu (2006) [3-4].

Metal Adsorption. Metal adsorption was performed by soaking chitosan films in a 1000 mg/L solution of Hg(II), Cr(VI) and Cu(II) at pHs 5.0, 6.0, 4.0 for 60 h at 25°C. The Hg(II), Cr(VI) and Cu(II) solution were prepared using mercuric chloride, potassium dichromate, copper sulfate, respectively.

X-ray absorption fine structure spectroscopy (EXAFS) experiments. EXAFS experiments were 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 Hg (12284eV) L edge, Cr (5989eV) and Cu (8987eV) K edges. Each spectrum corresponded to an average of 3 independent scans. Standard compounds (mercuric oxide, chromium oxide, copper oxide, mercuric acetate and copper acetate) were used in order to distinguish the bond differences between the heavy metal and coordination spheres (N or O atoms).

Analysis of EXAFS data. The kinetic energy of the photoelectrons ejected from the chitosan samples and standard compounds were calculated based on edge positions of the metal of interest (12284, 5989 and 8987eV, for Hg, Cr and Cu) and converted to wave vector (k) space. This resulting EXAFS curve, which has dependence in module of wave vector (reciprocal space) is 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 neighboring atoms around the adsorbed central atom, which each obtained peak corresponds to a coordination sphere. For the treatment of EXAFS data, it was necessary to initially analyze a standard compound, which structural parameters were already known. All EXAFS data were analyzed using ATHENA[®] software (IFEFFIT package). This computational program could perform all transformations described early.

Results and Discussion

Chromium-Chitosan Complex. The EXAFS spectra of the chromium adsorption are showed in Figure 2 (left panel: raw absorption spectra without modeling adjustment, (k) space; right panel: Fourier transformed, real space). The Cr K-edge EXAFS spectra were taken up to 5989 eV. The experimental values for edge absorption, represented by the peaks in the absorption spectra in the Figure 2 (right panel) were 5992.6, 5992.98, 5992.56 e 6006.07 eV, respectively, for natural, epichlorohydrin and glutaraldehyde crosslinked chitosan, and Cr₂O₃ (standard compound).

The Fourier-transformed spectra show the radial distances of the coordination spheres having heavy metal atom as reference, with subtraction in lines of pre-edge and after-edge, normalization and background corrections. The FT curve for Cr₂O₃ compounds present three peaks at 1.6, 2.5 and 3.3 Å, where the first one arises from an oxygen shell (Cr-O), while the second one comes from a Cr type shell (Cr-Cr), the third one arising from both Cr and O atoms altogether [17-18].

Similar results were observed for natural and crosslinked films, with a stronger peak at about 1.3 Å and a weaker peak at about 1.7 Å. The opposite was observed for glutaraldehyde crosslinked chitosan.

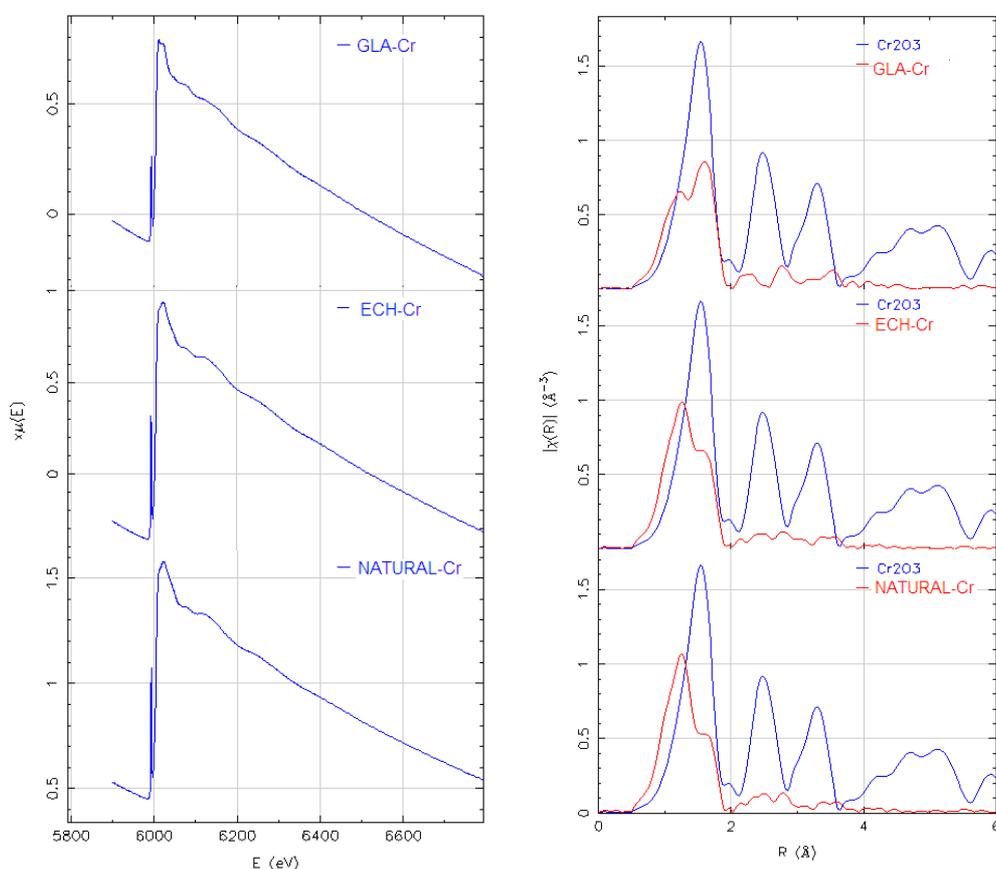


Figure 2 : The EXAFS spectra of the chromium ions adsorption

From the FT curve for natural chitosan (Figure 2), there is the first metal coordination sphere to a distance at about 1.3 Å and a second metal coordination sphere (in small proportion) to a distance at about 1.7 Å. These results indicate that the first coordination sphere is more important than the second, which occurs in a small scale. Similar profiles were observed for epichlorohydrin crosslinked chitosan. The distance of 1.7 Å, relative the second coordination sphere, is near the distance of oxygen shell (Cr-O), indicating that chromium adsorption take place in small scale with hydroxyl groups. After crosslinking with epichlorohydrin on chitosan structure the hydroxyl groups are unavailable and amino groups are free. Comparing the absorption spectra for natural and

epichlorohydrin crosslinked chitosan we can observe a similar profile, which indicates that interaction chromium/polymeric matrix, for both materials are the same type. In this case, the amino groups amino are accessible, indicating that interaction chromium/chitosan is mainly in these groups and in a less proportion in the hydroxyl groups.

Two peaks were observed for glutaraldehyde-crosslinked chitosan (Figure 2), but in this case, the second one was the strongest. The first metal coordination sphere occurs at a distance of 1.3 Å. This signal is probably related the Cr-N bond in the three cases. The second metal sphere coordination occurs at 1.65 Å, in the same distance of the second coordination sphere for the standard compound (Cr_2O_3), which occurs at 1.6 Å (Cr-O) in relation to the adsorbed atom. In this way, chromium adsorption on glutaraldehyde crosslinked chitosan takes place possibly in the oxygen of carbonyl groups, in bigger scale than natural and epichlorohydrin crosslinked chitosan, and possibly on the imino bounds (N=C) formed after glutaraldehyde crosslinking.

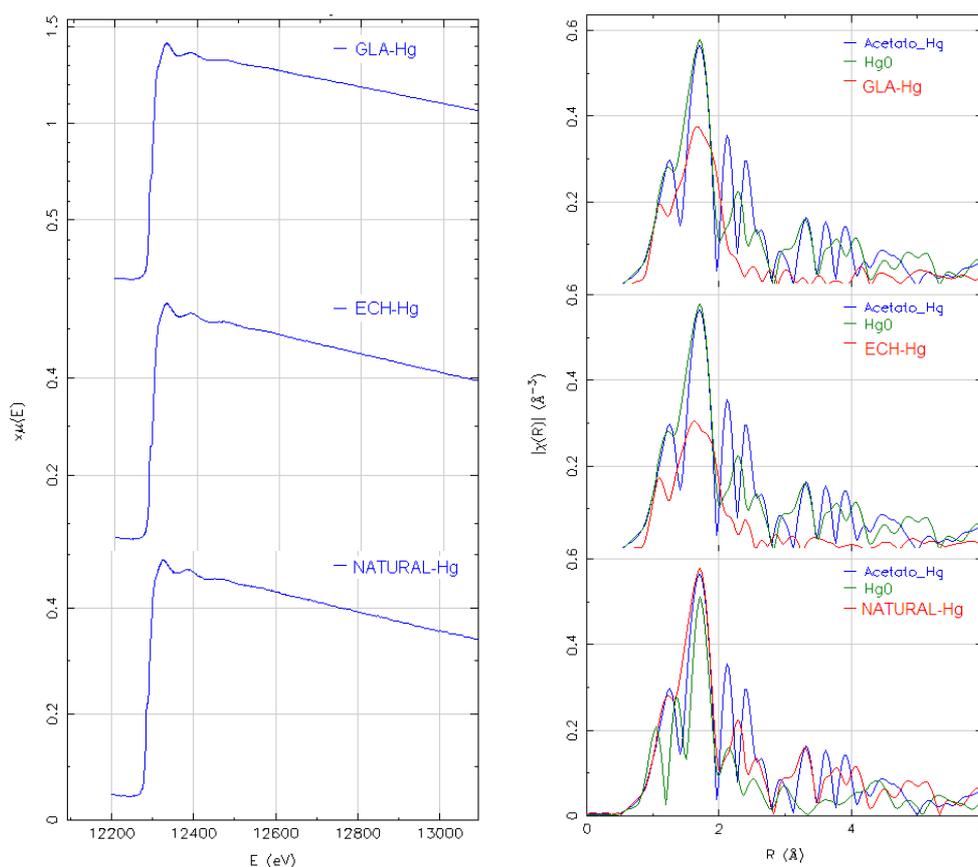


Figure 3 : The EXAFS spectra of the mercury ions adsorption

Mercury-Chitosan Complex. The EXAFS spectra of the mercury adsorption are showed in Figure 3 (left panel: raw absorption spectra without modeling adjustment, (k) space; right panel: Fourier transforms, real space). The Hg L-edge EXAFS spectra were taken up to 12284 eV. The experimental values for edge absorption, represented by the peaks in the absorption spectra in the Figure 3 (right panel) were 12293.2, 12283.8, 12284.1, 12282.2, 12281.7 eV, respectively, for natural, epichlorohydrin and glutaraldehyde crosslinked chitosan, HgO and $\text{Hg}(\text{CH}_3\text{COO})_2$ (standard compounds).

It was used two standard compounds, mercury oxide and mercuric acetate, which the last one present strongest and defined peaks. For mercuric acetate the first and second coordination sphere is related to Hg-O or O-Hg-O, the third Hg-C and the fourth Hg-Hg. For HgO there are three

defined peaks, the first one related Hg-O, the second one Hg-Hg and the last one Hg-O or Hg-Hg [19-20].

Analyzing the structure of natural chitosan (Figure 1), it is possible to observe that amino and hydroxyl groups are available and are the main adsorption sites. In the FT curve for natural chitosan was observed three peaks at $R < 2.0 \text{ \AA}$ and one fourth peak at about 2.1 \AA . For epichlorohydrin and glutaraldehyde crosslinked chitosan was observed only two peaks at $R < 2.0 \text{ \AA}$ and a decrease in the peak at about 2.1 \AA .

In EXAFS analyses nitrogen and oxygen atoms are hardly differentiated, because the bond length is very similar [14]. The three firsts peaks for natural chitosan can be associated to Hg-O, Hg-N, O-Hg-O or N-Hg-N. The fourth peak is near of the peak Hg-C for mercuric acetate, which can be assumed that this peak is referent to the backscattering carbon atoms in the fourth shell. In this shell the coordination number is probably small, because the corresponding peak amplitude is quite small.

The disappearance of one peak for epichlorohydrin and glutaraldehyde crosslinked chitosan indicates that crosslinking reaction takes place, blocking amino or hydroxyl group. In this case it was not possible distinguish if the mercury adsorption takes place preferentially on amino or hydroxyl groups, because was observed similar profiles for epichlorohydrin and glutaraldehyde crosslinked chitosan.

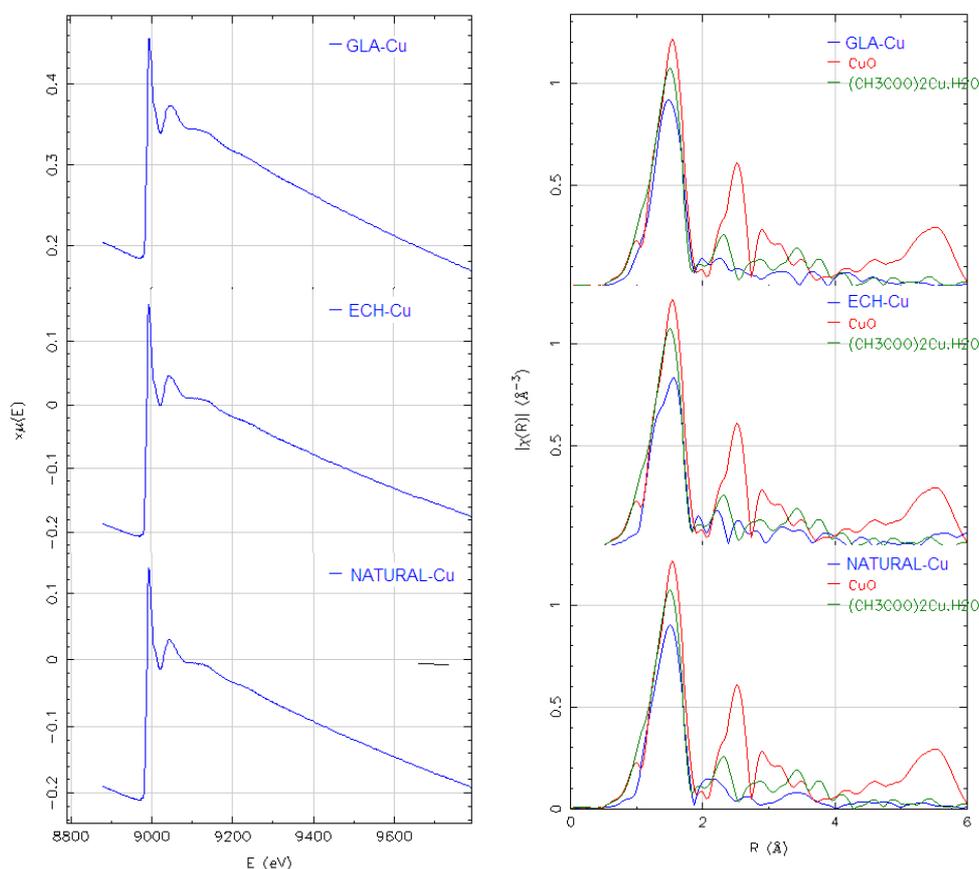


Figure 4 : The EXAFS spectra of the copper ions adsorption

Copper-Chitosan Complex. The EXAFS spectra of the copper adsorption are showed in Figure 4 (left panel: raw absorption spectra without modeling adjustment, (k) space; right panel: Fourier transforms, real space). The Cu K-edge EXAFS spectra were taken up to 8987 eV. The experimental values for edge absorption, represented by the peaks in the absorption spectra in the Figure 4 (right panel) were 8990.0, 8992.5, 8991.4, 8983.8, 8989.0 eV, respectively, for natural,

epichlorohydrin and glutaraldehyde crosslinked chitosan, and CuO and $(\text{CH}_3\text{COO})_2\text{Cu}\cdot\text{H}_2\text{O}$ (standard compounds).

Each peak in the absorption spectra represents one coordination sphere and its distance to the target atom. There are three stronger peaks located at about 1.5, 2.6 and 2.9 Å 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 acetate was observed a stronger peak at about 1.5 Å, corresponding Cu-O bond [20].

A strong peak was observed, in all the cases, at approximately 1.5 Å (first metal coordinate sphere) indicating that the copper on the adsorbent is bound to either an oxygen or nitrogen ligand. Brigatti et. al. (2004) [21] show for the glycylglycinatocopper(II) dihydrate complex that copper atoms are distanced of 1.95-1.97 Å from oxygen and 1.90-2.03 Å from nitrogen. In this work was observed practically the same signal in all the samples, either natural and crosslinked chitosan, indicating that adsorption takes place either on amino or hydroxyl groups, since is observed the same peak at about 1.9-2.1 Å.

Conclusions

Based on EXAFS investigation, it is possible to conclude that the structure of heavy metal ions (chromium, mercury and copper) on chitosan adsorbents depends primarily on chemical modification of polymeric matrix. For chromium ions could be observed that metal interaction is mainly on amino groups in a lower proportion than in the hydroxyl groups for natural and epichlorohydrin crosslinked chitosan. On the other hand, chromium interaction on glutaraldehyde crosslinked chitosan occurs mainly with the oxygen of carbonyl groups, and possibly on imino bounds. For mercury and copper was not possible distinguish if the metal interaction takes place preferentially on amino or hydroxyl groups, being necessary the utilization this technique together with others like FTIR and XPS.

Acknowledgements

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References

- [1] R.S. Juang, H.J. Shao, *Water Res.*, 36 (2002) 2999-3008.
- [2] J.C.Y. Ng., W.H.Cheung, G. Mckay, *J. Colloid Interf. Sci.*, 255 (2002) 64-74.
- [3] R.S. Vieira, M.M. Beppu, *Adsorption*, 11 (2005) 731-736.
- [4] R.S. Vieira, M.M. Beppu, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 279(2006) 196-207.
- [5] R.S. Vieira, M.M. Beppu, *Water Res.*, 40(8) (2006) 1726-1734.
- [6] E. Guibal, *Sep. Purif. Technol*, 38 (2004) 43-74.
- [7] M.M. Beppu, E.J. Arruda, R.S. Vieira, N.N. Santos, *J. Memb. Sci.*, 240 (2004) 227-235.
- [8] J.D. Merrifield, W.G. Davids, J.D. MacRae, A. Amirbahman, *Water Res.* 38(13) (2004) 3132-3138.

- [9] K.H. Chu, *J. Hazardous Mater.*, B90 (2002) 77-95.
- [10] W.S.W. Ngah, C.S. Endud, R. Mayanar, *React. Funct. Polym.*, 50 (2002) 181-190.
- [11] L. Dambiens, C. Guimon, S. Yiacoumi, E. Guibal, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 177 (2001) 203-214.
- [12] S.C. Bahtia, N. Ravi, *Biomacromolecules* 1 (2000) 413.
- [13] J.L. Gardea-Torresdey, K.J. Tiemann, J.G. Parsons, G. Gamez, I. Herrera, M. Jose-Yacaman, *Microchemical Journal* 71 (2002) 193-204.
- [14] N.V. Kramareva, A. Y.. Stakheev, O. P. Tkachenko, K.V. Klementiev, W. Grünert, E. D. Finashina, L. M. Kustov, *Journal of Molecular Catalysis A: Chemical* 209 (2004) 97–106.
- [15] J.L. Gardea-Torresdey, J.R. Peralta-Videa, G. de la Rosa, J.G. Parsons, *Coordination Chemistry Reviews* 249 (2005) 1797-1810.
- [16] M.M. Beppu, C.C. Santana, *Materials Science and Engineering C23* (2003) 651-658.
- [17] F.G. Requejo, J.M. Ramallo-López, R. Rosas-Salas, J.M. Domínguez, J.A. Domínguez, J.-Y. Kim, R. Quijada, *Catalysis Today* 107-108 (2005) 750-758.
- [18] M. L. Peterson, G.E. Brown, G.A. Parks, L.C. Stein, *Geochimica et Cosmochimica Acta*, 61 (1997) 3399-3412.
- [19] J.G. Parsons, M. Hejazi, K.J. Tiemann, J. Hrnning, J.L. Gardea-Torresdey, *Microchemical Journal* 71 (2002) 211-219.
- [20] C.R. Collins, D.M. Sherman, K.V. Ragnarsdottir, *Journal of Colloid and Interface Science* 219 (1999) 345-350.
- [21] M.F. Brigatti, S. Colonna, D. Malferrari, L. Medici, L. Poppi, *Applied Clay Science* 28 (2005) 1-8.
- [22] M. F. Brigatti, S. Coloma, D. Malferrari, L. Medici, *Geochimica et Cosmochimica Acta*, 68(4) (2004) 781-788.