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PO1-24**Distinct complexing trends of chitosan with toxic metals**

Maria Lasheras - Zubiate¹, Jose Maria Fernandez¹, Iigo Navarro - Blasco¹

¹*Departamento de Quimica y Edafologia, Universidad de Navarra, Spain*

Chitosan is the product of deacetylation of chitin, a natural homopolymer of *Beta*-(1-4) linked N-acetyl-D-glucosamine repeating units, which is known as the second most abundant biopolymer, after cellulose, among the biopolymers found in nature. The presence of amino groups in Chitosan increases its complexation capacity and has been investigated as an effective removing agent for several metals. A number of applications have been proposed for removing toxic species in water purification.

We have been able to prove that not only adsorption but also complexation of different metals (Pb, Cd, Mo, Cu, Zn and Cr) actually takes place in acetate buffer (pH=4) with Chitosans of different molecular weights and deacetylation degrees. Depending on the different electrochemical behaviour on mercury electrode of studied metals and the nature of the resulting complexes, diverse approaches have been used.

Chitosan molecular weight and concentration had been seen to play a key role in the Chitosan binding activity with Zn, Pb and Cd, as reported elsewhere[1]. Length of Chitosan chains influences the degree of complexation with both Cr and Mo, while Cu binding capacity remains independent of the molecular weight of the assayed polymers. The larger the polymer chain length the higher the number of amino group available for the retention of both Cr and Mo within the tridimensional structure of the acting ligand. This is consistent with a predominant intra-chain linkage of both metal atoms. On the contrary, in the case of Cu, an inter-layer binding mechanism is proposed as the main retention factor by Chitosan.

These studies will be applied to reduce toxicity from waste by the retention of these complexes within an inert cement matrix.

[1] M. Lasheras-Zubiate, J.M. Fernandez, I. Navarro-Blasco, Voltammetric evaluation of chitosan as an effective complexing ligand for the removal of toxic heavy metals. 59th Annual Meeting of the International Society of Electrochemistry (Sevilla 2008).

PO1-25**Effect of growing time on the chitosan content of cell wall of zygomycetes fungi**

Azam Jeihanipour^{1,2,3}, Zamani Akram^{1,2}, Keikhosro Karimi^{1,3}, Mohammad J. Taherzadeh¹

¹*School of Engineering, University of Boras, Boras, Sweden,* ²*Chemical Reaction Engineering, Chalmers University of Technology, Goteborg, Sweden,*

³*Chemical Engineering Department, Isfahan University of Technology, Isfahan, Iran*

Chitosan, deacetylated form of chitin with verity of industrial application, is produced in the cell wall of zygomycetes fungi by enzymatic deacetylation. Solubility of chitosan in acid solutions is the key factor in the purification process of this biopolymer. A new process has recently been developed for separation of chitosan from other components of the cell wall such as chitin and polyphosphates. The process was based on temperature-dependence solubility of chitosan in sulfuric acid. The cell wall was first treated with hot dilute sulfuric acid to dissolve the chitosan followed by cooling down for precipitation and recovery of chitosan from the solution. However, chitin is not soluble in sulfuric acid at any temperature and can be collected as hot acid insoluble material (HAIM). Polyphosphates were released in sulfuric acid as soluble phosphate in this process.

In the current work, extraction of chitosan from cell wall of three strains of

Distinct complexing trends of chitosan with toxic metals

Lasheras-Zubiarte M.*, Fernández J.M., Navarro-Blasco I.

Departamento de Química y Edafología, Universidad de Navarra, Spain

*mlashera@alumni.unav.es



Universidad de Navarra

INTRODUCTION

Chitosan is the product of deacetylation of chitin, a natural homopolymer of β -(1-4) linked N-acetyl-D-glucosamine repeating units, which is known as the second most abundant biopolymer after cellulose [1-3]. The presence of amino groups in chitosan increases its complexation capacity and has been investigated as an effective removing agent for several metals [4-6].

The aim of the present work is to prove the complexation of the metals Pb, Cd, Mo, Cu, Zn and Cr with chitosan. In order to show it, voltammetric measurements have proved useful [7]. Depending on the different electrochemical behaviour on mercury electrode of the studied metals and the nature of the resulting complexes, diverse approaches have been used. The effect of the molecular weight and concentration of the polymer on the binding of the metals has also been studied.

MATERIAL AND METHODS

Chitosans with different molecular weights (Sigma-Aldrich) were used in this study. The Certipure standard solutions containing 1000 ppm of the heavy metals Cr(VI), Cu(II), Zn(II), Mo(VI), Cd(II) and Pb(II) were purchased from Merck. Chitosan and metal solutions were dissolved in acetic-acetate buffer solution (pH=4).

Voltammetric measurements, both differential pulse anodic stripping voltammetry (DPASV) and differential pulse voltammetry (DPV), were performed with a Metrohm 746 VA Trace Analyzer coupled with a 747 VA Stand equipped with a static mercury drop electrode (SMDE).



RESULTS

We have been able to prove that not only adsorption but also complexation of different metals (Pb, Cd, Mo, Cu, Zn and Cr) actually takes place in acetate buffer (pH=4) with chitosans of different molecular weights.

To show complexation, current vs. metal concentration are plotted (Figure 1). In general, two linear portions are obtained: a first one with a lower slope, corresponding to the metal when complexed by the chitosan, and a second steeper branch indicative of free metal in solution.

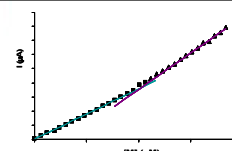
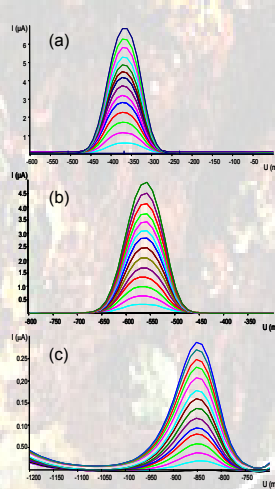
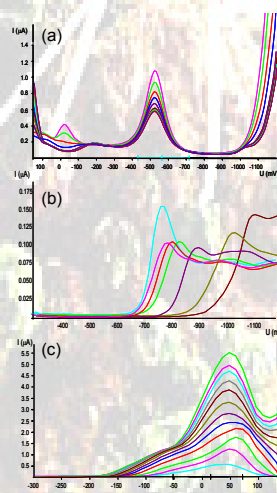


Figure 1: Titration curve of increasing concentrations of metal in a fixed concentration of ligand.



Complexation takes place in the case of Pb, Cd and Zn (Figure 2 (a), (b) and (c) respectively). The higher the molecular weight of chitosan, the larger the binding capacity observed for Pb and Zn. Longer chitosan chains involve a larger number of free available amino groups. Diluted chitosan solutions showed an increase of complexation capacity irrespective of the assayed molecular weight, due to the diminishing of steric hindrances as well as to the breaking of stabilizing hydrogen bonds within the structure of the chitosan molecule. This trend is not shown by Cd, which complexation seems to be independent of the concentration and molecular weight of the polymer.

Figure 2: Stripping voltammograms for increasing concentrations of Pb (a), Cd (b) and Zn (c) in chitosan.



Length of Chitosan chains influences the degree of complexation with both Cr and Mo (Figure 3 (a) and (b) respectively), while Cu (Figure 3 (c)) binding capacity remains independent of the molecular weight of the assayed polymers. The larger the polymer chain length the higher the number of amino group available for the retention of both Cr and Mo within the tridimensional structure of the acting ligand.

This is consistent with a predominant intra-chain linkage of both metal atoms. On the contrary, in the case of Cu, an inter-layer binding mechanism is proposed as the main retention factor by chitosan.

Figure 3: Stripping voltammograms of Mo (a), Cr (b) in increasing chitosan and of increasing concentrations of Cu (c) in chitosan.

CONCLUSIONS

- Not only adsorption but also complexation of different metals (Pb, Cd, Mo, Cu, Zn and Cr) actually takes place in acetate buffer (pH=4) with chitosans of different molecular weights.
- Chitosan molecular weight and concentration have been seen to play a key role in the chitosan binding activity with Zn and Pb but not with Cd.
- Length of chitosan chains influences the degree of complexation with both Cr and Mo, while Cu binding capacity remains independent of the molecular weight of the assayed polymers.
- A predominant intra-chain linkage for Cr and Mo is proposed. On the contrary, an inter-layer binding mechanism seems to be the main retention factor in the case of Cu.

ACKNOWLEDGEMENTS

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