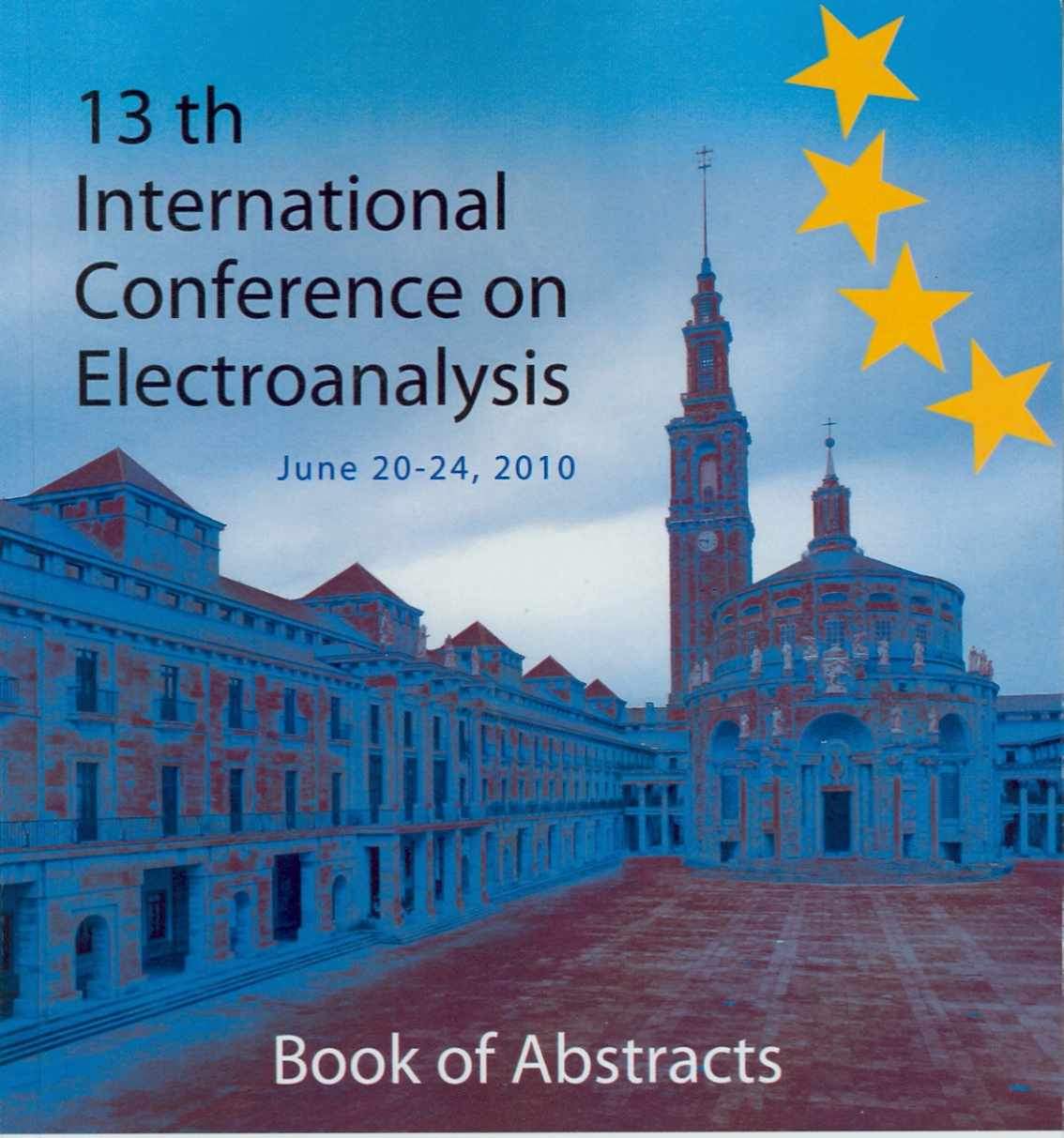
13 th International Conference on Electroanalysis

June 20-24, 2010



Book of Abstracts

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AN ETHERIFIED DERIVATIVE OF CHITOSAN AS AN IMPROVED COMPLEXING AGENT FOR SOLIDIFICATION/STABILISATION OF HEAVY METALS INTO CEMENTITIOUS MATRICES

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Chitosan is a natural widely available biopolymer and increasingly used for most diverse applications. Different chitosans of various molecular weight and deacetylation degrees have been previously checked as for their complexing activity towards selected target heavy metals, such as Zn, Pb, Cd, Cu, Mo and Cr [1,2]. Some rheological properties of cementitious matrices have been seen to improve upon incorporation of those biopolymers, such as water retention, setting time and consistency (through the flow table test). In this paper we report the different complexing patterns found for Zn and Pb when a chitosan derivative is used. These results will be discussed by comparison with the behaviour of the aforementioned non-modified chitosans.

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This is to certify that the contribution entitled

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AN ETHERIFIED DERIVATIVE OF CHITOSAN AS AN IMPROVED COMPLEXING AGENT FOR SOLIDIFICATION/STABILISATION OF HEAVY METALS INTO CEMENTITIOUS MATRICES

has been presented as a poster presentation at the 13th International Conference on Electoanalysis (ESEAC 2010)

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The Organizing Committee

A Derivative of Chitosan as an Improved Complexing Agent for Solidification/Stabilisation of Heavy Metals into Cementitious Matrices

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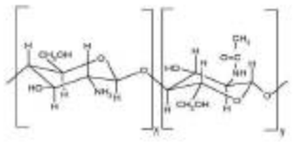
INTRODUCTION

Chitosan is the product of deacetylation of chitin, a natural homopolymer of ß-(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]. Previous work has been done and complexing activities of high, medium and low molecular weight chitosans (HMW, MMW and LMW) towards several heavy metals has been reported [7].



The aim of the present work is to use a derivative of chitosan (CD) of relatively low molecular weight (51,12 kDa) and check its complexing capacity with Pb and Zn at pHs over 7, where it is soluble, and to compare it with the aforementioned studies carried out with the non-modified chitosans.

MATERIAL AND METHODS

Chitosan Derivative (CD) was purchased from Heppe Medical Chitosan GmbH and used as such. The Certipure standard solutions containing 1000 ppm of the heavy metals Zn(II) and Pb(II) were purchased from Merck. Chitosan and metal solutions were dissolved in either 0.1 M HAc-/NaAc or 0.1 M Na_2HPO_4/ H_3PO_4 for pH = 7 whereas 0.1 M NH_4Cl/NH_3 buffer solutions were used for pH 8.25.

Differential pulse anodic stripping voltammetry (DPASV) measurements were performed with a Metrohm 746 VA Trace Analyzer coupled with a 747 VA Stand equipped with a static mercury drop electrode (SMDE).

RESULTS

Voltammetric studies

Titration curves were obtained by plotting stripping peak intensity current *vs.* added metal concentration (*Figure 1*). In general, two linear portions are obtained: a first one -with a lower slope- corresponding to the hindered metal accumulation onto the electrode , when complexed by the chitosan in solution, and subsequent diminished stripping signal, and a second steeper branch indicative of free metal in solution that undergoes accumulation/stripping in a normal fashion resembling that in the background buffer solutions.

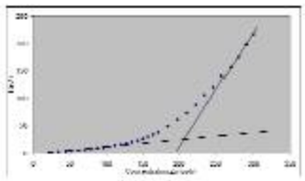


***Figure 1**: Typical titration curve of a 1 µM of ligand (CD) in pH 7 phosphate buffer with increasing concentrations of metal (Zn)*

Free accumulation/stripping: $M^{2+} + 2e^- + Hg \leftrightarrows M(Hg)^0$; $M(Hg)^0 - 2e^- \leftrightarrows M^{2+} + Hg$

Accumulation in presence of complexing ligand: $M_xCD + 2e^- + Hg \leftrightarrows xM(Hg)^0 + CD$

CD precipitates below pH 7, so that alkaline pHs had to be used for these studies. On the other side, extremely basic pHs –resembling the real cementitious media- interaction of metals with CD were not observed since both Zn and Pb will be mainly in the oxoanionic state (i.e. PbO_2^{2-} or ZnO_2^{2-}) Accordingly, pH range was limited by the insolubility of CD (pH = 7) and the existence of cationic forms for Pb abd Zn (pH ca. 8.25). Complexation was observed for both metals at both pHs (Figure 2). In all instances, a larger complexing capacity was observed for lower CD concentrations (0.05 and 0.1 µM), whereas higher CD assayed concentrations (0.5 and 1.0 µM) provided lower stoechiometries for the soluble complexes (see Table 1).

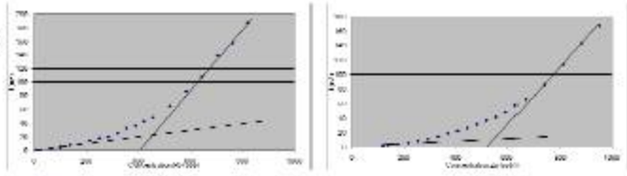
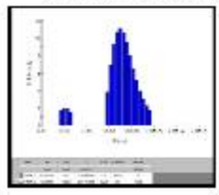
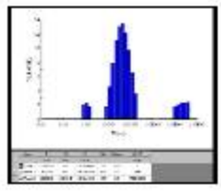


***Figure 2**: Titration curves for Pb in acetate buffer, pH 7, in the presence of CD 0.5 µM, and for Zn in ammonia buffer solution pH 8.25 in the presence of CD 1 µM.*

Dispersion Light Scattering (DLS)

DLS experiments carried out for a relatively concentrated sample of CD (10 µM) in the pH 8.25 NH_4Cl/NH_3 buffered solution showed the existence of a conglomerate responsible for the 100% mass with a diffusion coefficient of $1.94 \cdot 10^{-5}$ cm^2s^{-1}. Upon addition of Zn 200 µM this conglomerate increses its size and the diffusion coefficient decreases to $2.22 \cdot 10^{-6}$ cm^2s^{-1}.





			Concentration Chitosan (µM)			
Metal	pH	medium	0.05	0.1	0.5	1
Zn	4	acetic	/	40	20	9
	7	acetic	/	14	/	4
		Phosphate	/	7	3	3
	8	ammonia	/	12	/	4
Pb	4	acetic	/	24	12	6
	7	acetic	10	10	5	5
	8	ammonia	12	/	5	/

CONCLUSIONS

- Both Zn and Pb are complexed by CD at the assayed pHs.
- CD show lower stoichiometries than unmodified chitosans at pH = 4
- This findings are consistent with the much lower molecular weight of CD as compared with LMW, MMW and HMW Chitosans.
- A distinct conglomerate/complex between Zn and CD is confirmed by DLS experiments.

ACKNOWLEDGEMENTS

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