SIMULATED MODELING: CONTRASTING Ca/Mg AND M^{n+}-NATURAL ORGANIC MATTER COMPETITIVE COMPLEXATION IN WATER

G.O Bosire [a] , J.C. Ngila [a*]; J.M Mbugua[a]; T.A.M Msagati[a] and B.V Kgarebe[b]

[a]Department of Applied Chemistry, University of Johannesburg, PO Box 17011, Doornfontein 2028 Johannesburg, South Africa
[b]National Institute for Occupational Health Analytical services, 25 Hospital Street, Bramfontein, Johannesburg

*Corresponding author: Tel +27115596196; Fax +27115596425; Email: jcngila@uj.ac.za; nmusee@csir.co.za;orinajeff@gmail.com

ABSTRACT

Complexing capacities of calcium and magnesium with natural organic matter (NOM)/selected organic chelating agents, in the presence and absence of other major and trace cations in water, were studied by anodic and cathodic square wave stripping voltammetry techniques (ASWSV and CSWSV). Under predetermined and optimized physico-chemical parameters (pH, temperature and ionic strength), calcium-NOM complexation and competitive complexation by other elements of known concentration (Pb, Zn, and Cu) were determined. Voltammetric measurements showed competition between calcium and the other cations for the binding sites of humic substances at depositing, measuring and equilibrating potential of -2V and +1V and scan time of 150seconds. Two systems were complexed by known concentrations of NOM fractions (Humic acid (HA), 1, 2-dihydroxybenzene (CAT/catechol) and tannic acid (TA)): M^{n+}-NOM; M^{n+}-Calcium-NOM complexes at different pH conditions. Results show significant differences in peak currents in the order M^{n+}> Ca/M^{n+}-TA/HA/CAT > Mn^{2+}-TA/HA/CAT but differed depending on the metal species, type of humic chelant and pH. Visual Minteq and PHREEQC simulations show differences in distribution of scale causing species such as Ca^{2+}, $CaOH^{+}$, Mg^{2+} and $MgOH^{+}$ that are highly dependent on the pH and concentration. This paper presents results of part of the work aimed at providing simulated modeling alternatives in combating scaling as a consequence of cooling water used in industry. It equally provides an assurance on the re-use of the scarce water resources by simulated water experiments and models.

Key words: Natural Organic Matter (NOM); PHREEQC modeling; Humic acid, Tannic Acid, (TA), Catechol, Ca and Mg salts in water

INTRODUCTION

Physico-chemical changes in cooling water for a power generation plants can trigger scale formation in pipes carrying the cooling water. The precipitation involves mineral compounds mainly of Ca or Mg-carbonates or Ca-sulphate with the main culprit being $CaCO_3$ deposits. Natural Organic Matter (NOM) components (Croue, et al., 1999) act as chelants which aid to remove these cationic deposit-forming salts by forming stable soluble complexes. Filtration through a 0.45-µm membrane separates NOM into dissolved organic matter (DOM) and humin. Literature reports show that DOM is further evenly split into hydrophobic (humic) and hydrophilic (Non Humic) components. The two fractions of humic substances (HS); humic acid (HA) and fulvic acid (FA) have a high content of carboxylic groups and phenolic groups with HA having more aromatic groups. All acids are negatively charged at the pH of natural water due to the dissociation of the carboxyl groups (Croue, Korshin, & Benjamin, 1999).

$CaCO_3$ and other Ca salts precipitation reactions are inhibited by NOM in water by complexing Ca^{2+} in solution, thereby lowering the state of saturation. Phenolic and carboxylic acid functional groups are likely sites for Ca^{2+} complex forming bridges shown in Fig. 1(Hoch, Reddy, & Aiken, 2000).

Fig 1: Ca complexation and bridging

The ions of Ca^{2+} appear to be among the most strongly NOM-associating ions (Nebbioso, 2009). When Ca^{2+}, Mg^{2+} and Cu^{2+} are complexed together, Lu (Lu & Allen, 2002) suggests that Ca and Mg are preferably bound by carboxyl sites, especially at relatively high concentrations. The binding of Cu^{2+} and Ca^{2+} to a fulvic acid (FA) which simulates naturally occurring conditions, has shown that competition by the calcium ion affects the binding capacity of the Cu^{2+}–FA complexation (Iglesias, Lopez, Fiol, Antelo, & Arce, 2003). It has been observed under different studies that the NOM complexation with Ca is affected by a number of factors. The study therefore proposes to investigate complexing capacities and stabilities of alkaline earth metals (Ca and Mg) and NOM chelants under varying environmental conditions.

MATERIALS AND METHODS

Preparation of Humic Acid (HA), Tannic Acid (TA) and Catechol Solutions

Humic acid solutions (1000mg/L) were prepared by dissolving 1g of humic acid, tannic acid and Catechol (1, 2-dihydroxybenzene) in ultra-purely deionized water. Ultrapure water through 22.2µm, obtained direct from a Milli-Q-Plus water purification system (Millipore Corporation), was used to prepare all reference standards and test solutions. Fresh solutions were prepared prior to each experiment and stored in the dark at 4°C. The dissolution of humic acid was only possible in pH>7. The solutions containing 20 mg/L of Pb, Cu and Zn were prepared by diluting appropriate

amounts of 1000 µg/mL reference standard solutions (Sigma Aldrich, AR grade) in ultrapure water. 0.1 M stock solution of pure KNO_3 was prepared by dissolving an appropriate quantity of pure KNO_3 (Aldrich) in ultrapure water. A stock solution of catechol (Aldrich Chemical Company, 99% pure) was freshly prepared by dissolving solid catechol in ultrapure water prior to each experiment as catechol is degraded by air-oxidation. At the beginning of each test using electrochemical method, the test solutions were purged with ultra-high purity argon gas for 10 min. Copper, zinc, iron, lead and calcium metal solutions were prepared in 0.1M KNO_3 and dilutions made to obtain 200, 25, 20, 15, 10, 8, 4, and 1 mg/L of metal concentration in each case. The highest concentration (200 mg/L) was used to prepare 20mg/L used for complexation studies. The rest of standards 1-25 mg/L were used to prepare calibration curves in all cases. Humic substances and metal solutions were mixed together and the pH of the mixture was adjusted to 4 and 8 using 1 M NaOH.

Determination of complexing capacities

The Pb(II), Fe(II), Zn(II) and Cu(II) complexing capacities (CC) of metal–humic complexes were determined by adding increasing amounts of tannic acid, humic acid and catechol to 6ml of $20mgL^{-1}$ of Pb^{2+}, Fe^{2+}, Cu^{2+} and Zn^{2+} at pH 4 and ionic strength, I = 0.1 M (using 99.999% grade KNO_3.) Separately, these solutions were spiked with 50µL of 1000mg/L Ca^{2+} and relative complexation measured. This method is based on the assumption that metal-ligand complexes are formed in different ratios, and that the temperatures at which the complexing capacities are established do not vary. The runs were conducted in triplicate and average peaks were reported. Voltammetric measurements were performed on an autolab EWS.

Computation of free metal concentrations using voltammetry

The concentration relating to the peak current differences were calculated using the Randles Secvik Equation:

where i_p is the peak current in amps, A is the electrode area (cm^2), D is the diffusion coefficient ($cm^2\ s^{-1}$), c^o is the concentration in mol cm^{-3}, and n is the scan rate in V s^{-1}.

RESULTS AND DISCUSSION

Table 1 shows [$Zn_{unbound}$] as a function of the complexed Ca [Ca^{2+}-HA/CAT/TA], for pH values of 4 and 8 at I =0.1 M. Similar to other trace metals, Zn binding is pH dependent, and the total amounts of unbound Mn^{2+} relating to Ca complexation were found to differ under similar conditions.

Table 1. Differences in Zn complexing concentrations in Humic substance systems (1,2-dihydrobenzene, Humic Acid and Tannic acid are at 1000mg/L)

Zn				
Matrix	**pH8**		**pH4**	
	I_p^*	Pb_{Calc} (ppm)	I_p^*	Pb_{calc}
Zn	1.28E-04		4.25E-05	
ZnHA	8.91E-05		1.10E-05	

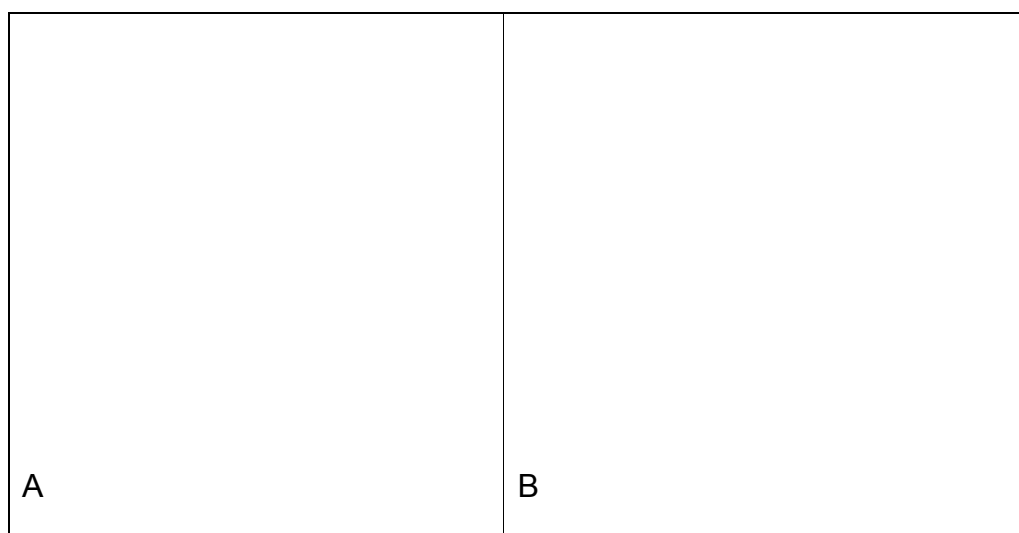|				
ZnCaHA	1.07E-04	**2.68**	3.60E-05	**3.74**
ZnCAT	1.26E-04		1.35E-05	
ZnCaCAT	1.09E-04	**-2.49**	2.35E-05	**1.50**
ZnTA	8.86E-06		8.07E-06	
ZnCaTA	5.07E-05	**6.27**	1.52E-05	**1.07**

Fig 1. :Anodic stripping voltammograms of Zn and Zn+Ca-NOM mixture binding at (A) pH 4 and (B) pH 8

The unbound Zn data show higher concentration values at pH 4 than pH 8 with humic acid and lower values at pH 4 than pH 8 with 1, 2 dihydrobenzene and tannic acid. Comparatively, Table 1 of our data shows only tannic acid favouring more unbound Pb in basic pH with both humic and 1,2 dihydrobenzene recording higher unbound Pb in acidic Media. Apart from competition for humic ligands, competitive interactions of H^+, inorganic Pb species, and major cations (Ca^{2+}, Mg^{2+}) with NOM will affect the pH and metal speciation(Pinheiro, Mota, & Benedetti, 1999).

CONCLUSION
Using PHREEQC, H^+, Ca^{2+}, $CaOH^+$, Mn^{2+}, MOH^+, $M(OH)_2$ species were obtained under the conditions and concentrations as in Table 1. The understanding of metal interactions with humic and other organic substances as presented herein, mainly as a function of changing labile metal concentrations under different pH, enables modeling of the speciation in cooling water systems. This in turn provides a quality assurance on water re-use, in addition to control of industrial scale. The findings of this study indicate that the presence of certain organic ligands naturally occurring in water may control the precipitation of alkali earth metals salts (notably Ca and Mg) responsible for scale formation in cooling water pipes.

REFERENCES
Croue, J. P., Korshin, G. V., & Benjamin, M. M. (1999). *Characterization of natural organic matter in drinking water*: Amer Water Works Assn.

Hoch, A., Reddy, M., & Aiken, G. (2000). Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades. *Geochimica et Cosmochimica Acta, 64*(1), 61-72.

Iglesias, A., Lopez, R., Fiol, S., Antelo, J., & Arce, F. (2003). Analysis of copper and calcium–fulvic acid complexation and competition effects. *Water research, 37*(15), 3749-3755.

Lu, Y., & Allen, H. E. (2002). Characterization of copper complexation with natural dissolved organic matter (DOM)—link to acidic moieties of DOM and competition by Ca and Mg. *Water research, 36*(20), 5083-5101.

Nebbioso, A., Piccolo, A. (2009). Molecular rigidity and diffusivity of Al3+ and Ca2+ humates as revealed by NMR spectroscopy. *Environmental Science & Technology, 43*(7), 2417-2424.

Pinheiro, J., Mota, A., & Benedetti, M. (1999). Lead and calcium binding to fulvic acids: salt effect and competition. *Environmental Science & Technology, 33*(19), 3398-3404.