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Thermodynamics of Cu^{2+}, Pb^{2+} and Cd^{2+} sorption onto low molecular weight chitosan using Isothermal Titration Calorimetry (ITC)

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Abstract: Chitosan and its derivatives possess valuable properties for its use as a sorbent for the removal of heavy metals from aqueous solution. In the present study, the thermodynamics of Cu^{2+}, Pb^{2+} and Cd^{2+} sorption onto low molecular weight chitosan (CS_8) using isothermal titration calorimetry (ITC) were investigated. Based on the ITC data, the stoichiometry data were 0.36±0.023, 0.813±0.015 and 0.029±0.006 for Cu^{2+}, Pb^{2+} and Cd^{2+}, respectively. The binding association constant (Ka) varied from (1.74±0.333) $\times 10^4 M^{-1}$ to (17.3±18.9) $\times 10^4 M^{-1}$. Also, all binding reactions to low molecular weight chitosan (CS_8) were enthalpically favored and the interaction between the sorbent and the metal ions were enthalpically not driven at 25 °C. Furthermore, free energy of reaction values were all determined to be negative indicating spontaneous reactions. In conclusion, the ITC instrument was successfully used to measure directly the stoichiometry (N), binding association constant (Ka), the enthalpy change (ΔH) and the entropy change (ΔS).

Keywords: Low Molecular Weight Chitosan, Isothermal Titration Calorimetry, Metal Ions, Binding

1. INTRODUCTION

Pollution of aqueous environments by metals is a global environmental issue due to their non-degradability and biomagnifications[1]. Examples of metal ions that can pollute the aqueous environments and have exhibited toxic effects at even very low concentrations include Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} Cr, Zn, etc[2]. Conventional techniques that have been used to remove metal ions from aqueous environments include chemical precipitation as metal hydroxide, electro-deposition, ion exchange and membrane separation, etc. The aforementioned techniques are often expensive and unsuccessful in removing heavy metal ions from aqueous environments[3]. Recently, the focus has been on various adsorbents that have metal-binding capacities and can remove unwanted metal ions from contaminated water at low cost. Chitosan, a derivative from N-deacetylation of chitin, a naturally occurring polysaccharide from crustacean and fungal biomass has been noticed to have high potential for adsorption of metal ions[4].

This is due to the presence of a large number of amine groups and hydroxyl groups on the chitosan chain. Chitosan has been used to remove various metals ions from aqueous solution[5-,8], but no research has been done on the use of isothermal titration calorimetry (ITC) for the thermodynamic studies of Cu^{2+}, Pb^{2+} and Cd^{2+} sorption onto low molecular weight chitosan(CS_8). ITC is a powerful technique to determine binding interactions of biomolecules. ITC needs no substrate immobilization or labelling and permits detection of the binding interaction in a computer-controlled mode at a constant temperature. The injection syringe stirs and titrates the ligand of attention into the macromolecule substrate in the instrument cell and because this is a chemical reaction, heat is either absorbed or evolved during the consecutive injections.

After the experimental run, software is used to integrate the area under these individual titrations to provide the heat of reaction value. Another significant aspect of ITC instrument is that it measures the enthalpy of binding directly and provides the binding constant and entropy of binding values as well. The kinetic and thermodynamic binding parameters are calculated by a single ITC experiment along with a reference titration. In this paper, kinetics and thermodynamic binding results for Cu^{2+}, Pb^{2+} and Cd^{2+} with low molecular weight chitosan (CS_8,) have been reported. This data allows us to draw some conclusions about the nature of the metal ions to low molecular weight chitosan that should aid future computational modelling studies.

2. MATERIALS AND METHOD

2.1. Materials: Chitosan (CS) (Molecular weight = 200 kDa, Degree of deacetylation = 95%) was bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), $CuCl_2.2H_2O$, Pb $(NO_3)_2$, $CdCl_2.2.5H_2O$ and all other chemicals and reagents were of analytical grade. Distilled water was used to prepare solutions.

2.2. Preparation of low molecular weight chitosan (CSn) (n = 8) using microwave: CS_8 was prepared in accordance with the literature described previously[9, 10]. The rationale was that small intermolecular distance enhances intermolecular interactions[11].

2.3. Characterization of the sorbents

2.3.1 Size Exclusion Chromatography (SEC): CS_8 molecular weight was known as reported in the previous literature[9, 12]. The molecular weight of CS_8 was determined through size exclusion

chromatography(SEC) using an RI K-2301 refractive index detector and TSK-GEL G4000 PWXL column (30cm × 7.5 mm). The solute was eluted with HAc/NH_4Ac buffer solution (pH 4.5) at a flow rate of 0.43 mL·min^{-1}.

2.4. Isothermal titration calorimetry (ITC): A VP-ITC isothermal titration microcalorimeter (MicroCal Inc., Northampton, MA) was used for the thermodynamics studies. All solutions were thoroughly degassed prior to the experimental trials to remove air bubbles. 1.0 mM of the ligand (Cu^{2+}, Pb^{2+} and Cd^{2+}) and 1.0 mM of the macromolecule (CS_8) were prepared and used for the ITC experiments. 1.0 mM of the macromolecule (CS_8) was placed in the reaction cell with a volume of 1.45 mL, and 5.0 mM of the ligand (Cu^{2+}, Pb^{2+} and Cd^{2+}) were placed in the ITC syringe with a volume of 250 µL.

Each titration consisted of an initial 2 µL injection (neglected in the analysis) followed by 29 subsequent 8 µL injections each of which were 16 s in duration and were programmed to occur at 210 s spacing at 25 ^oC with a stirring speed of 307 rpm. The ITC data was analyzed using the Microcal Origin v.7.0 software provided with the instrument, and then fitted using non-linear least-squares algorithm using a single-site binding model. Fitting of theoretical data to experimental yielded the equilibrium binding association constant (K_a), and the enthalpy change (ΔH) and entropy change (ΔS^o) of the reaction. The changes in the reaction free energy (ΔG^o) were calculated using the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. *Characterization of the sorbent*

3.1.1 Size Exclusion Chromatography (SEC): The size exclusion chromatography instrument determined the average molecular weight of the CS_8 to be 1401 Da.

3.2. Binding results: Titration of Cu^{2+}, Pb^{2+} and Cd^{2+} onto low molecular weight chitosan yielded the parameters for binding thermodynamics. In order to evaluate the experimental data, Origin 7.0 was used. 100-iterations technique to fit the data into a one-site binding model provided with the software. The software calculated from the binding curves and amount of heat generated the binding constants and enthalpies of the reaction. From that information, the entropies and free energies of binding were extracted.

Binding thermograms for copper (II) and lead (II) are presented in Figures 1 and 2, respectively. The copper (II)-low molecular weight chitosan interaction gave a binding constant of 4.24±2.11x 10^4M^{-1} with the highest enthalpy change of -23.86±1.87 kJ/mol. On the other hand, lead binding released much less heat to provide a 2-fold smaller binding constant for lead(II) of 1.74±0.333 x 10^4M^{-1} with enthalpy change of -8.811±0.23 kJ/mol.

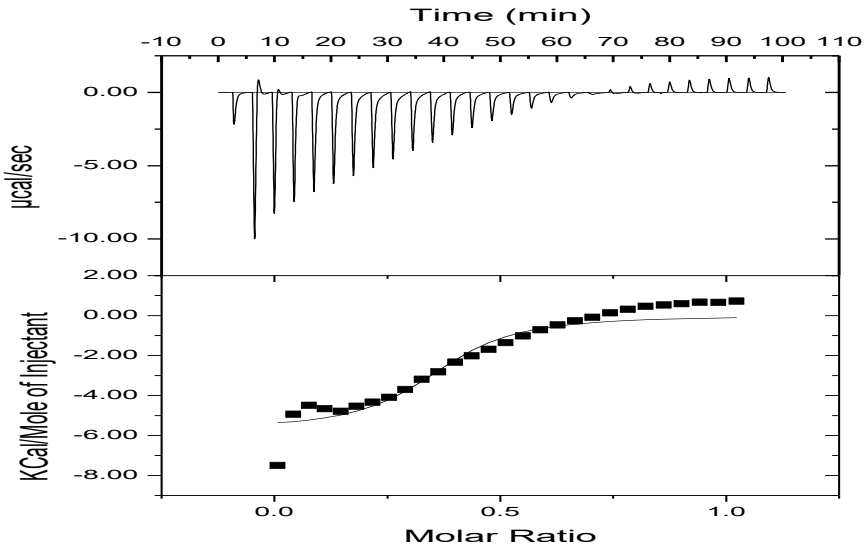

Fig. 1: Binding thermogram and isotherm for CS_8-Copper (II) interaction are given at the top and bottom, respectively.

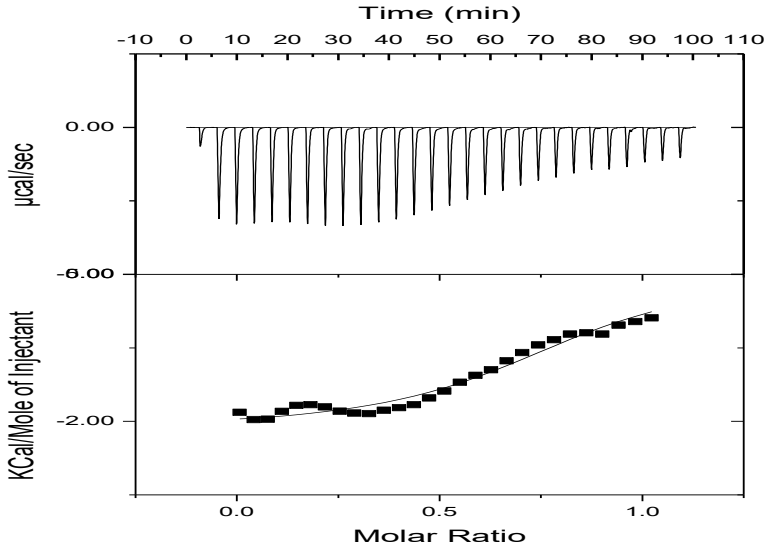

Fig. 2: Binding thermogram and isotherm for CS_8-Lead (II) interaction are given at the top and bottom, respectively.

The low molecular weight chitosan-cadmium (II) thermogram (Figure 3) showed a 4x increase in the binding constant of 17.1±18.9x 10^4M^{-1} compared to copper (II).

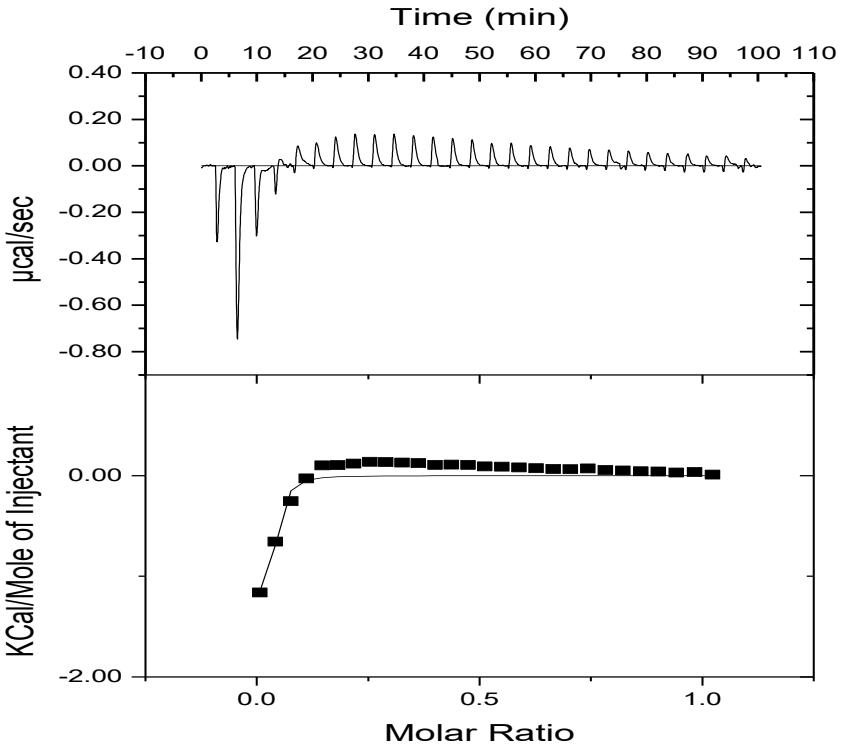

Fig. 3: Binding thermogram and isotherm for CS_8-Cadmium (II) interaction are given at the top and bottom, respectively

The overall order of binding affinities toward low molecular weight chitosan (CS_8) was determined to be as follows: Cd (II) >Cu (II) >Pb (II). The difference in magnitude of binding of low molecular weight chitosan (CS_8) with different metal cations is likely to be as a result of a combination of several factors, including the geometry of the metal complexes, ionic radii of the metal cations, valency of the metal, and hard-soft, acid-base considerations[13, 14, 15].

3.3. Thermodynamic interpretation: The stoichiometry data were 0.36±0.023, 0.813±0.015 and 0.029±0.006 for Cu^{2+}, Pb^{2+} and Cd^{2+}, respectively (Table 1). The binding association constant (Ka) varied from (1.74±0.333) ×10^4M^{-1} to (17.3±18.9) ×10^4M^{-1}. In this present study, all metal cation-low molecular weight chitosan interactions showed negative enthalpy of reaction at 25 °C, indicating that these interactions are all enthalpically favoured. Positive changes in the entropy of binding indicated that all metal cation-low molecular weight chitosan interactions were enthalpically not driven at 25 °C[14]. Furthermore, the negative changes in the free energy of reaction indicated that all metal cation-low molecular weight chitosan interactions were spontaneous[16].

Table 1: Thermodynamic Binding Parameters for low molecular weight chitosan-Metal Cation Interaction

Metal cation	Stoichiometry(N)	Binding association constant(Ka) x $10^4 M^{-1}$	Enthalpy change(ΔH(kJ/mol)	Entropy change(ΔS)(J /mol/K)	Gibbs free energy (ΔG)(kcal/mol)
Cu(II)	0.36±0.023	4.24±2.11	-23.86±1.87	0.029	-23.87±1.87
Pb(II)	0.813±0.015	1.74±0.333	-8.811±0.23	0.172	-8.86±0.23
Cd(II)	0.029±0.006	17.3±18.9	-5.98±1.54	0.269	-6.059±1.54

4. CONCLUSION

In this paper, ITC experiments were carried out to determine the thermodynamic parameters of low molecular weight chitosan-metal ion chelation reactions. Cadmium (II) was found to exhibit the strongest affinity towards low molecular weight chitosan (CS_8). Copper (II) was the next strongest cation. Lead (II) was found to show the weakest measurable affinity for low molecular weight chitosan chelation. Binding of Cu^{2+}, Pb^{2+} and Cd^{2+} to low molecular weight chitosan (CS_8) took place with negative enthalpy and free energy values. Binding of all of the heavy metal cations to low molecular weight chitosan (CS_8) was determined to be enthalpically driven with positive change in entropy values at 25 °C. The difference in magnitude of binding of low molecular weight chitosan (CS_8) with different metal cations is likely the result of a combination of several factors, including the geometry of the metal complexes, ionic radii of the metal cations, valency of the metal, and hard-soft, acid-base considerations.

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