

# Use of computational method to identify metal binding sites of chitosan as a tool to investigate the interaction mechanism of chitosan and heavy metals

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## Introduction

A bioadsorbent chitosan; a derivative of chitin polysaccharide composed of randomly distributed  $\beta$ -(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine (Cahyaningrum *et al.*, 2004) was reported by our group to be much effective as a drinking water purification agent as the percent removal of Cd(II), Pb(II) and Cr(VI) from drinking water by chitosan were 94%, 64% and 70% respectively under optimized conditions (De Silva *et al.*, 2014). It is widely known that chitosan can make complexes with certain metal ions as chitosan has different possible binding sites for metals (figure 1). But little attempt has been made to understand the interaction mechanism of chitosan and heavy metals. Hence the aim of this study was to simulate the IR spectrum of chitosan by DFT calculations and to identify the vibrational bands associated with the possible metal binding sites which can be used as a tool to investigate the interaction mechanism of chitosan and heavy metals.

## Methodology

All theoretical calculations reported in this study were carried out by use of the Gaussian 09 program package. Although chitosan is a polymer, a trimer shown in figure 01 was used to represent chitosan in all theoretical studies. First the structural parameters of the optimized structure of the chitosan have been obtained using electron density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP) and 6-31G (d) basis set employing in a gas phase model. Then the IR spectrum of the chitosan was simulated by using the computed frequencies of the optimized geometrical configuration of the trimer in gas phase. The experimental FTIR spectrum for chitosan was obtained from a Bruker Alpha-T spectrometer.

## Result and Discussion

The Optimized chitosan molecule (trimer) is shown in figure 2.

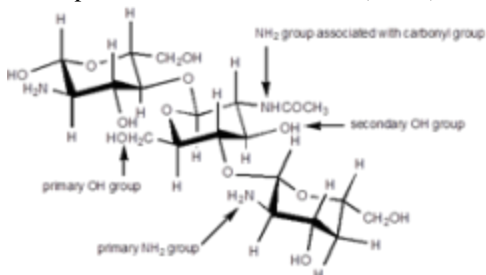


Figure 1: Possible metal binding sites of

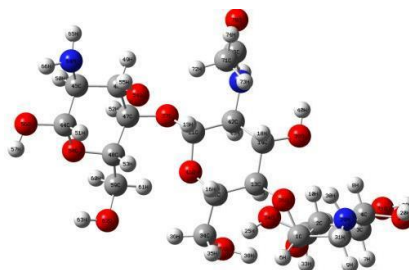


Figure 2: The Optimized chitosan molecule

chitosan.

with the labeled atoms (trimer)

It was clearly observed that the IR bands in simulated IR spectrum of optimized chitosan trimer (theoretical) show a similar pattern with those in FTIR spectrum of chitosan (experimental) for the range between  $400\text{ cm}^{-1}$  and  $4000\text{ cm}^{-1}$ . For instance, when the FTIR spectrum of chitosan (figure 3 (a)) measured in the  $1590\text{ cm}^{-1}$  -  $1800\text{ cm}^{-1}$  region is compared with computed IR spectrum of chitosan trimer (figure 3 (b)), it clearly indicates that the band patterns and their corresponding intensities of theoretically obtained IR spectrum are very much similar to that of experimentally obtained IR spectrum. Hence, it is clearly shown that simulated IR spectrum of chitosan by DFT calculations could be used to identify the vibrational bands in the close vicinity of metal binding sites and their corresponding vibrational modes. Therefore the vibrational assignment for the bands in the FTIR (experimental) could be easily obtained.

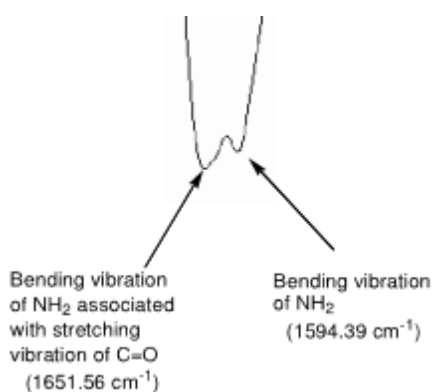


Figure 3 (a): IR bands in experimental spectrum in the region of  $1590\text{ cm}^{-1}$  -  $1800\text{ cm}^{-1}$

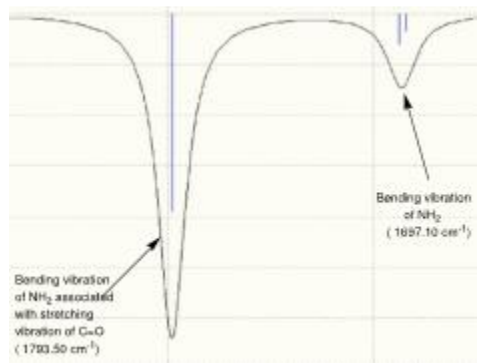


Figure 3 (b): IR bands in theoretical spectrum in the region of  $1590\text{ cm}^{-1}$  -  $1800\text{ cm}^{-1}$

Experimental and computed IR frequencies of selected bands are shown in table 1 and their corresponding vibrational assignments were successfully determined by the use of simulated IR spectrum are also tabulated in table 1.

Table 1 - Experimental and theoretical frequency values of selected IR bands of chitosan and their corresponding vibrational assignments.

Theoretical frequency value / $\text{cm}^{-1}$	Experimental frequency value / $\text{cm}^{-1}$	Assignment
3439.99 - 3767.34	3425.10	Stretching vibration of $\text{NH}_2$ and OH
1697.10	1594.39	Bending vibration of $\text{NH}_2$
1091.52	1089.54	Stretching vibration of C-O
1793.50	1651.56	Bending vibration of $\text{NH}_2$ associated with stretching vibration of C=O

Upon binding of metal with chitosan, the IR of the bonds (IR bands) in the close vicinity of the coordination site will be significantly shifted when compared with metal-free chitosan as the metal binding affects the normal vibration scheme of chitosan due to the formation of new chitosan-metal bond. For instance, according to figure 4, the bending vibration band of chitosan at  $1594.39\text{ cm}^{-1}$  was shifted to a higher frequency value upon binding of cadmium to chitosan indicating that

there is an interaction between the primary  $\text{NH}_2$  group of chitosan and the cadmium. Hence, the actual coordination sites of metal, in the formed metal-chitosan complex could be cognized by identifying the IR bands which are significantly shifted upon metal binding. Therefore, this may serve as an identification tool for determining the structural assignment of the formed metal-chitosan complexes.

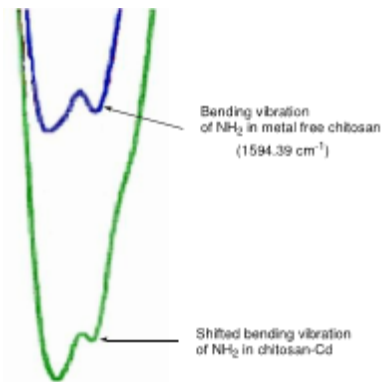


Figure 4: Experimental IR band shift of bending vibration of  $\text{NH}_2$  of chitosan upon binding with Cd

## Conclusion

By analyzing the theoretical IR spectrum of chitosan, the vibrational bands (bonds) in the close vicinity of the metal coordination sites and their corresponding vibrational modes could be clearly identified and hence those in the FTIR (Experimental) spectrum of chitosan could be correctly assigned. Further, the structural assignment of the formed metal-chitosan complex could be determined as there is a significant shift in the IR bands in the close vicinity of coordination sites upon metal binding. Hence this may serve as a diagnostic tool for determining metal binding preferences of bioadsorbents such as chitosan and might be other biological compounds.

## References

- Cahyaningrum, S.E., Herdyastuti, N. (2011). Sorption of  $\text{Mg}(\text{II})$  and  $\text{Ca}(\text{II})$  metal ions on chitosan-alginate membrane. Journal of Materials Science and Engineering. 1, 87- 92.
- De Silva, S.M., Fernando, W.T.I., Kannangara, A.T., Ubesena, J.G.P.S., Rajapakse, C.S.K. (2014). Determination of heavy metal adsorption capacity of chitosan and removal of heavy metals from drinking water using chitosan. Proceedings of Third International Symposium on Water Quality and Human Health: Challenges Ahead, Postgraduate Institute of Science (PGIS), University of Peradeniya, Sri Lanka. pp. 37.