

Preparation, Characterisation and Hg(II) Sorption Activity of Citralidene Chitosan

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Introduction

Chitosan is a non toxic, bio-degradable biopolymer produced by alkaline N-deacetylation of chitin, the most abundant natural polymer after cellulose .Chitin is present in the exoskeleton of crustaceans such as Crabs, Prawns, Shrimps, the cuticles of insects and the cell walls of fungi and is a cheap resource available in sea food industries. Chitosan consist of 2-amino -2-deoxy (1-4) β -D glucopyranose residues. It has many applications in biomedical, agriculture, waste water purification, environmental protection and biotechnology. Chitosan is soluble in acid pH range but insoluble in neutral and basic pH range.

Chitosan and its derivatives are capable of adsorbing a number of metal ions and its amino nitrogen can serve as chelation sites. Due to their high nitrogen content and porosity, chitosan based sorbents have exhibited relatively high sorption capacities for heavy metals such as Pb, Cd, Ni, Cu and oxyanions as well as complex metal ions. Since most of the effluents are acidic, chitosan itself cannot be used effectively because chitosan is soluble in acids. But its derivatives are effectively used for the treatment of wastes in acid solutions also.

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Mercury, the oldest metal known to man, may enter the environment at any point during mining, refining, geological erosion, manufacturing processes and industrial wastes. Hg interferes with the metabolism. It accumulate in the bone, kidneys and other intrrnal organs. Chitosan has been widely used for the removal of heavy metals from neutral and basic solutions. Since Chitosan is soluble in acidic media, attempts have been made by various researchers to chemically modify Chitosan so that the derivatives can be used in acidic effluents as sorbents. Here we have prepared a schiff base from chitosan and citral namely citralidene chitoan. The use of schiff base as sorbent also has environmental significance. The schiff base was characterized by SEM and FTIR and evaluated for its mercury (II) sorption capacity. Sorption experiments for the optimization of parameters viz: contact time, sorbent dose

and pH were done initially and then carried out the kinetics and equilibrium studies. The experimental data were applied to Langmuir and Freundlich models and kinetics parameters have been evaluated. Sorption of mercury on citralidene chitosan, CCD was confirmed by SEM, IR, XRD.

Materials and Methods

Materials

Chitosan with 85 percent degree of deacetylation and citral were purchased from Sigma Aldrich Co; USA and used as such. Mercury acetate was Merck grade. Methanol and acetic acid were also Merck quality. All other chemicals used were of analytical grade. All reagents were prepared in deionized water.

Preparation of schiff base

2g chitosan was dissolved in 50 ml 5percent acetic acid(v/v), 1.8 ml citral in 50 ml methanol was added to the viscous chitosan solution. Stirred for 8 hrs using a magnetic stirrer. Kept overnight. Filtered and washed with methanol. Distilled off methanol and acetic acid and dried at 50°C for 24 hrs.

Sorption experiments

Stock solution of 500 mg/L Hg (II) was prepared from mercury(II) acetate using deionized water. All other concentrations were prepared from this solution by dilution. Optimization of parameters viz; contact time, sorbent dose and pH were carried out initially. The effect of contact time on sorption capacity of the schiff base was studied in range of 1-4 hrs at initial concentrations of 400 mg/L at pH 6 with sorbent dose of 25 mg. The effect of sorbent dose on sorption capacity was studied by varying mass of the schiff base from 25mg to 100mg at an initial Hg(II) concentrations of 400 mg/L. (25ml). For pH studies the pH was varied by conc: HNO₃ and NaOH from 1 to 7 and was determined using a pH meter (Systronics make). All sorptions experiments were carried out by stirring 2h at a pH of 6 using a magnetic stirrer at moderate speed in 125 ml borosilicate glass stoppered bottle. Each experiment was duplicated under identical conditions. The aq:phase Hg(II) concentration was analysed with Shimadzu AA-6300 AAS instrument with slit width 0.7nm and wavelength 253.7nm.

For kinetic studies 400 mg/L Hg(II) solutions was stirred for 4 hours at room temperature (30°C). 1 ml of the sample was withdrawn in each hour, diluted and concentrations

were determined (q_t). The equilibrium studies were conducted using Hg(II) solutions of different initial concentrations ranging from 100 to 500 mg/L. All solutions were diluted properly to put down in the working range of AAS.

The amount of sorption at equilibrium q_e (mg/g) was obtained from the equation $q_e = [(C_i - C_e)V]/W$ where C_i is the initial concentration of Pb(II)/Hg(II) in the aq: phase in mg/L, V is the volume of the solution (L) and W is the weight of the schiff base used (g).

Results and Discussion

Characterization of Citralidene chitosan

In the Schiff base formation the amino group of chitosan condenses with the aldehyde group of Citral. The biopolymer Schiff base formed was yellow in colour, stable in air and insoluble in common organic solvents and in mineral and organic acids which shows the conversion of amino group into imine group. The FTIR spectroscopy was used to confirm the structure of the Schiff base. IR peaks at 1683.55 cm^{-1} and 1635.4 cm^{-1} indicate the formation of imine group (C=N). The FTIR spectra of Hg (II) loaded Schiff base indicated binding of Hg (II) through oxygen of -CHOH group and C=N group. The shifting of the band 1451.7 cm^{-1} in the Schiff base to 1456.96 cm^{-1} indicate the involvement of C=N in binding Hg(II). SEM images showed that the surface morphology of the Schiff base is different from that of chitosan. The Schiff base was more porous and has more surface area, and is capable of accommodating metal ions (Figures 1 and 2)



Fig 1. SEM-Chitosan

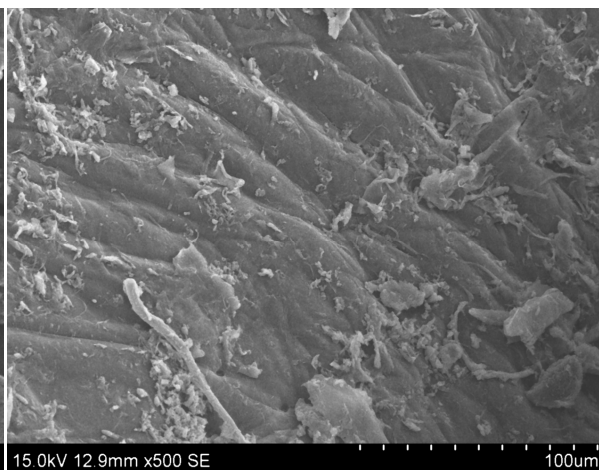


Fig 2. SEM-Citralidene chitosan

Effect of Contact time

Sorption capacity of schiff base was determined by varying the contact time from 0 to 6h. The results shows that sorption capacity increased sharply during the first hour, after that a slow increase were observed until it reaches saturation in 3h. The sorption capacity of the Schiff base in 3h was 294.51mg/g (Figure 3)

Effect of sorbent dose

Sorption experiments by varying adsorbent dose from 25 mg to 100mg shows that sorption capacity decreased with increase in weight of the sorbent. Maximum sorption observed (294.51mg/g) with a sorbent dose of 25mg.

Effect of pH

The metal ion removal from aqueous solutions is very much dependent on solution pH. Effluents from industries and urban discharges are having very high or low pH. So pH study on removal of metal ions is significant. Evaluated the sorption capacity of Schiff base for the sorption of Hg(II) at different pH values ranging from 1-7. Maximum sorption capacity was observed at pH6 (294.51mg/g). Low pH restricts the number of binding sites for sorption. All the sorption experiments were carried out at the optimum pH value of 6 (Figure 4)

Sorption Kinetics

The kinetics of sorption of Hg(II) on Schiff base indicated a rapid initial binding followed by a slow increase until a state of equilibrium was reached in 3h. After 3 hours no further change in concentration was observed. Sorption data were fitted to a pseudo second order kinetic model. The rate constant for Hg(II) was found to be $0.007 \text{ mg g}^{-1} \text{ h}^{-1}$, and sorption capacity q_e equals 300.03 mgg^{-1}

Sorption Isotherm

Sorption experiment at various concentrations were carried out and applied to Langmuir and Freundlich isotherm models. From linear Langmuir plot the maximum sorption capacity was found to be 352.11 mgg^{-1} with Langmuir constant K_L 0.0696 L/mg. Langmuir equilibrium parameter R_L falls between 0 and 1 which indicates that sorbent is suitable for Hg(II)

sorption(Figure5). The Freundlich constat $K_F = 38.41 \text{ mg}^{1-1/n} \cdot \text{g}^{-1} \text{L}^{1/n}$ and $1/n = 0.4607$. $1/n$ value between 1 and 0 indicate favourable sorption.SEM, IR and XRD images taken before and after adsorption confirmed the sorption (Figures 6,7 and 8)

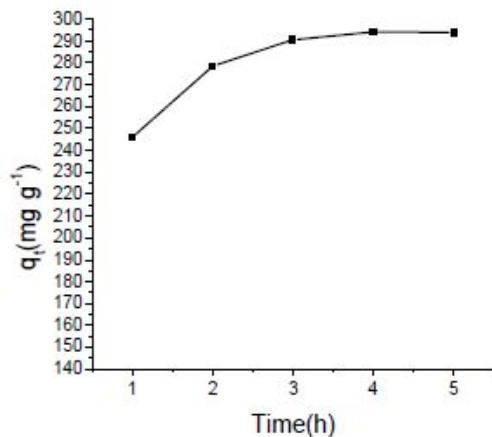


Fig 3. Effect of contact time

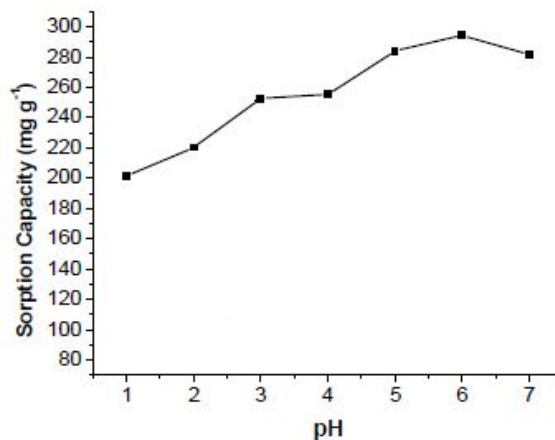


Fig 4. Effect of pH

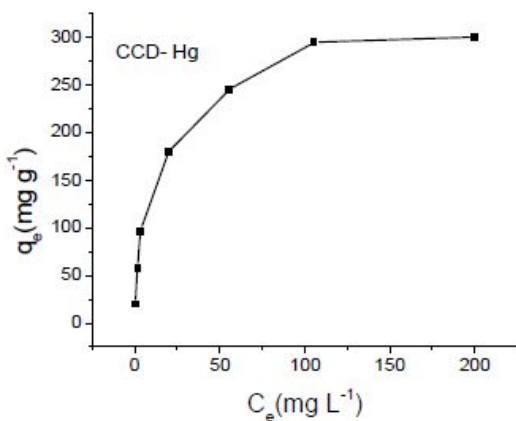


Fig 5. Sorption isotherm

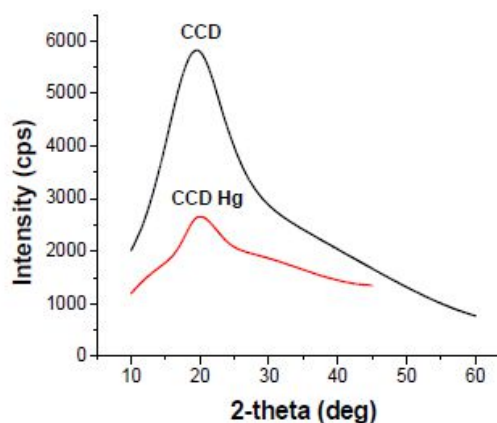


Fig 6. XRD comparison

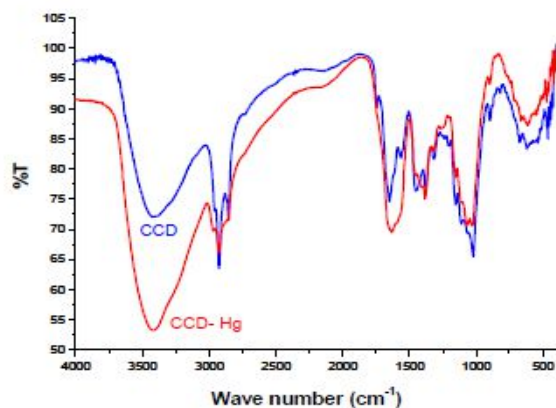


Fig 7. IR-comparison

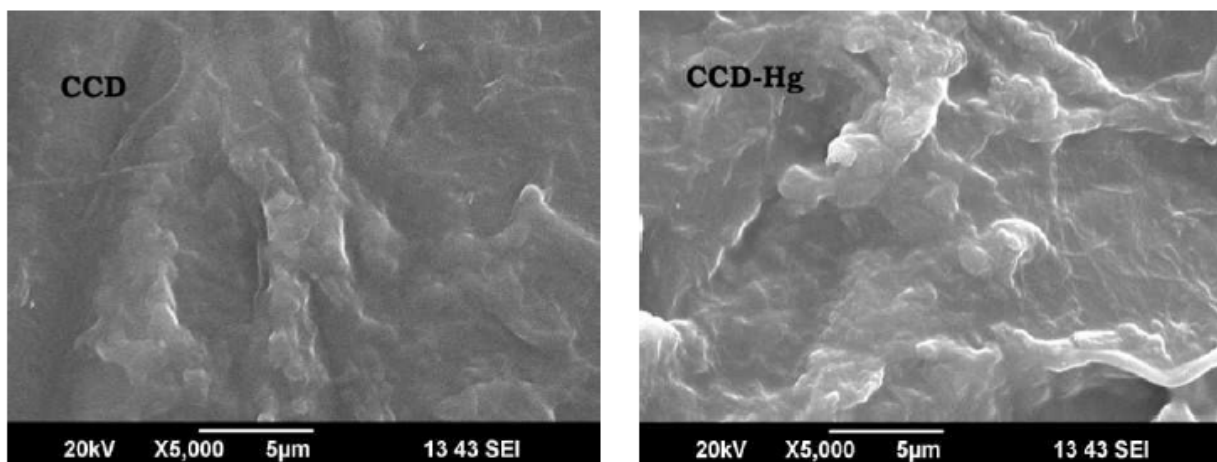


Fig 8. SEM-comparison

Conclusion

A Schiff base of chitosan with citral was prepared and characterized by Fourier Transform IR spectroscopy and Scanning electron microscopy. The Schiff base was evaluated for Hg(II) sorption. The sorption occurred and followed pseudo second order kinetics. Sorption data fitted to both Freundlich and Langmuir isotherms. The maximum sorption capacity was found to be 352.11 mg/g. Isotherm studies indicated that the Schiff base has different binding sites having different binding affinities. The sorption was spontaneous. Thus the Schiff base

from chitosan and citral, the citralidene chitosan was found to be an efficient, cheap and biodegradable sorbent for Hg(II).

References

1. Li.Y, Chen. XG,LiuN; Liu C.S; Meng X H;Yu L J; Kenedy J F Carbohydrate Polymers 2007, 67, 227-232.
2. E. Guibal, Sep. Purif.Technol 38(2004) 43-74.
3. R.A. Goyer in “ Hand book on Toxicity of Inorganic Compounds” eds. HG.Seiler, H.Sigel and Macel Dekker, NY, 1998, pp 359-382.
4. Helmut Sigel and Ashid Sigel.“Metal Ions in environment and biology”.J.Indian Chem. Soc. Vol. 77,Nov-Dec 2000 PP 501-509.
5. Ng JCY.Cheung, Wh Mc Kay G; 2003 Equilibrium studies for the sorption of lead from effluents using chitosan chemosphere 52, 1021-1030.
6. Ng J, C Y; Cheung.W H , Mc Kay G;2002 Equilibrium studies of the sorption of Cu(II) ion onto chitosan.J. Colloid interface Sci. 255 64-74
- 7 Ng JCY.Cheung, Wh Mc Kay G; 2003 Equilibrium studies for the sorption of lead from effluents using chitosan Chemosphere 52, 1021-1030
8. K R Krishnapriya; M Kandaswamy , A new chitosan biopolymer derivative as metal complexing agent, Synthesis Characterisation, and metal (II) ion adsorption. Carbohydrate Research 345 (2010) 2013-2022
9. Amit Bhatnager,Milka Sillanpää ‘ Application of Chitin and Chitosan derivatives for the depurification of water and waste water-A short review’.Advances in Colloid and Interface Science 152(2009) 26-38
- 10.Muniyappan Rajiv Gandhi,S.Meenakshi ‘Preparation,Characterisation of Silica gel/Chitosan composites for the removal of Cu(II) and Pb(II)-Int.J of Biological Macro.Mol.50(2012) 650- 657
11. Divya Chauhan, Meha Jaiswal, Nalini Sankaramakrishnan Removal of cadmium and hexavalent chromium from electroplating waste waer using thiocarbamoyl chitosan. Carbohydrate polymers 88 (2012) 670-675
12. Sankaramakrishnan.N; Dixit,A; Iyengar L;& Sanghi,R (2005). Removal of hexavalent chromium using a noval crosslinked xanthated chitosan . Bioresourse Technology 97

2377- 2382

13. Wang, F.Y.; Wang, H & Ma J. W. (2010) . Adsorption of cadmium (II) ions from aq: solutions by a new low cost adsorbent-Bamboo charcoal. *J. Haz Mat* 177, 300-306
14. Muzzarelli,R.A.A.(2011). Potential of chitin and chitosan bearing material for uranium recovery an inter disciplinary review *Carbohydrate Polymers*.84 54-63
15. Feng-Chin Wu, Ru-Ling Tseng, Ruey-Shin Juang. A review and experimental verification of using chitosan and its derivatives as adsorbents for selected heavy metals. *J. environ Manag* 91 (2010) 798-806
16. G . N. Kousalya, Muniyappan Rajiv Gandhi, S. Meenakshi . Sorption of chromium (VI) using modified forms of chitosan beads. *Int. J.Bio. Macr mol* 47 (2010) 308-315
17. Yawo-Kuo Twu, Hsin-1 Huang Szu-Ying Chang, San Lang Wang. Preparation and sorption activity of chitosan/ cellulose beads. *Carbohydrate polymers* 54 (2003) 425-430
18. Muzzarelli,RAA.(1973) *Natural chelatingpolymers*. Oxford Pergamon Press, 254.
19. Koide. SS. 1998 , Chitin-chitosan: properties, benefits and risks *Natr, Res.* 18 (6) 1091-1101.
20. Sigehiro Hirano, Hidemasa Hayashi, Some fragrant fibres and yarns based on chitosan. *Carbohydrate Polymers* 54 (2003) 131-136.
21. Ho YS &McKay G (1977) in L. Zhang & Y > Zhenhua (Eds.). *Proceedings of the Fourth China-Japan USA Symposium on Advanced Adsorption Separation Science and Technology* May 13-16 Guangehoid Chin p257. South China University of Technology press.