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ADSORPTION STUDIES OF Cd (II) WITH TANNIN-FORMALDEHYDE/ACETALDEHYDE RESINS DERIVED FROM *CAMELLIA SINENSIS* POWDER

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Abstract:
The adsorption study of Cd(II) ions on a low cost adsorbent such as tannins derived from tea powder is performed. Tannin formaldehyde/acetaldehyde resins based adsorbents were synthesized and their adsorption capacities were compared with virgin tea powder to remove the cadmium ion from aqueous solutions. The metal adsorption study was examined by AAS and EDS. All the methods show good agreement in results. Batch adsorption studies were carried out to examine the influence of various parameters such as initial pH, adsorbent dose, initial metal ion concentration, and time. The tannin-formaldehyde resins showed high adsorption capacity of Cd(II) ions in the range of pH 4–9, and a maximum adsorption capacity was observed at pH 6. The results indicate that tannin based tea powder can be converted into polymeric adsorbent such as tannin formaldehyde/acetaldehyde resins with simple chemistry and high selectivity, reusability and may be a promising substrate to entrap heavy metals from aqueous solutions..
Keywords: *Camellia sinensis*, adsorption, heavy metals, waste tea, tannins.

Introduction

In the past few decades water pollution due to heavy metals has become major cause of concern. The heavy metal ions are stable and persistent environmental contaminants, since they cannot be degraded or destroyed.[1] According to the World Health Organization (WHO), Cadmium is one of the most toxic pollutant due its low permissible concentration value less than 0.005 mg/L in drinking water.[2] Cadmium often discharged from a variety of industrial sources including electroplating, battery, mining, smelting, alloy manufacturing, pigments, nickel-cadmium and solar battery production.[3-4] It is well known that the industrial and municipal waste water always contaminated with heavy metal ions. Industrial waste constitutes the major source of various kinds of metal pollution in natural water.

Currently, methods used for waste water treatment such as reverse osmosis and nanofiltration[5], ion exchange[6,7], membrane processes, electrochemical techniques[8,9], chemical reactions, precipitation, coagulation/flocculation, sedimentation and adsorption.[10] All these methods may be ineffective or extremely expensive, when the metals are dissolved in large volumes of solution at relatively low concentrations.[11]

Among the waste treatment procedures, adsorption techniques are the most widely used and low-cost adsorbent alternatives are still need of the present. Therefore, numerous approaches have been studied by the researches to show that the use of low-cost adsorbent materials which can be easily obtained from industrial, agricultural or urban residues for recovery of heavy metals from contaminated industrial effluents has emerged as a potential alternative method over the conventional techniques. For example, some of the non-conventional low cost adsorbents recently used for the removal of heavy metals are apple residues[12], pine bark[13], hazelnut shell[14], banana pith, tree leaves, mandarin peels, rice polish[15-17], seeds of *Capsicum annuum*[18] and *Ceiba pentandra* hulls[19] etc.

Tea is one of the most consumed beverages in the world. Due to recent increase in tea consumption, a large amount of tea residue is generated. Most of the tea residues are burned or dumped into landfills. These tea residues contain a large percentage of polyphenols such as tannins, catechins, and lignins.[20-24] Functional phenolic groups of tannins, carboxylic groups of the pectins and the alcoholic hydroxyl groups of the celluloses can act as the active binding sites for metals.

Prime aim of the present study was to explore the feasibility of using tannins from *Camellia sinensis* residues obtained from tea-powder which further modified with formaldehyde/acetaldehyde to enhance the sorption properties of the adsorbent for the removal of cadmium..

Materials and Methods

Materials: Cadmium chloride monohydrate (CdCl2.H2O) analytical grade was procured from Thomas Baker, Mumbai, India. Acetaldehyde (35% solution), and 25% ammonia solution were purchased from Merck, India. Formaldehyde (37% solution) was obtained from Qualigens, India. All chemicals were used without further purification and distillation.

Stock cadmium solution of 100 ppm concentration was prepared by dissolving 0.1791 g of cadmium chloride in 1 L of deionized water. The metal concentrations such as 50, 40, 30, 20, 10, and 5 ppm were prepared by serial dilution method using stock solution.

Adsorbents

The tea powder contains catechins, polyphenols, amino acids, sugars, carbohydrates, lipids etc. Out of these, polyphenols were used as adsorbent obtained from the tea powder. The tea powder was extensively washed with distilled water to remove adhering dirt and water soluble components such as low molecular weight tannins, resins, reducing sugar, coloring agents etc. After that tea powder was treated with chloroform, to get free from chloroform soluble materials and dried under reduced pressure at 80 °C until a constant weight. Finally it was crushed and sieved to obtain a particle size lower than 0.5 μm.

The condensation of phenolic groups of tannins/polyphenols with formaldehyde/ acetaldehyde was performed using ammonia as a catalyst and scheme is depicted in scheme 1. Into a plastic container, 4 g of tea powder and 10 mL of 37% formaldehyde solution were added and stirred for five minutes. To this resulting solution, 20 mL of 25% ammonia solution was added, and continued the stirring for 5 min and kept as such mixture for 24 h. After that the reaction mixture was neutralized by 0.1 N hydrochloric acid and the obtained precipitate was washed with deionized water followed by drying at 80 °C for 10 h. under reduced pressure. Similar procedure was followed for acetaldehyde resin preparation. The monomer composition of tea tannin-formaldehyde (TF) and tannin-acetaldehyde (TA) resins using ammonia as catalyst is presented in Table 1 (Scheme 1).

Experimental

Adsorption studies were carried out by batch process. Resins were added to plastic flasks containing a known amount of metal solution of the desired concentration. The mixture was stirred in water bath at 100 rpm at temperature 25°C at different time intervals. The pH of solutions was adjusted by adding dilute solutions of nitric acid and ammonium hydroxide. The resins were separated by filtration through Whatman Filter paper No. 1 and the filtrates were analysed for residual cadmium concentration by atomic adsorption spectrophotometer (AAS, Varian Spectra model AA 200 FS) with an oxy-acetylene flame using cadmium hollow cathode lamp. The spectral slit width and the working wavelength were 0.7 and 228.8 nm, respectively. Atomic absorption standard of cadmium solutions supplied by the manufacture of instrument was used for calibration of instrument. The metal adsorbed on the resin was determined by using EDS (Bruker) technique.

Probable mechanism of metal adsorption scheme is depicted in Scheme 2. Metal uptake (*q*, mmol/g) was calculated using the equation 1.

$$\%\,\text{Adsorption} = \text{Final metal ion conc.} - \text{Initial metal ion conc.}$$

Preliminary experiments

Batch experiments were performed to determine the effect of various parameters (contact time and adsorbent dosage) on the adsorption of Cd^{2+} onto the adsorbents.

The effect of contact time on sorption of Cd^{2+} was obtained by placing the 50 mL of metal ion solution (100 mg/L) with different time intervals such as 5, 10, 20, 30, 60, 90, 120, 150 and 180 min with 0.2 g of adsorbents at room temperature and at constant pH (pH 6).

The effect of adsorbent dosage on sorption of Cd^{2+} was obtained by agitating 50 mL of metal ion solution (100 mg/L) with 0.05, 0.075, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4 and 0.5 g of adsorbent for 2 h at room temperature and at constant pH (pH 6).

Batch experiments were carried out to determine the effect of pH on the sorption of cadmium. This was performed by taking 50 mL of cadmium solution (100 mg/L) with 0.2 g of adsorbents for 2 h at different pH solution in the range of 4-9.

Results and discussions:

FT-IR analysis

In order to determine the functional groups which are responsible for metal uptake, FTIR analysis in solid phase was performed on the biomass prepared in a KBr disk. FTIR spectra were obtained for adsorbent solid samples before and after the biosorption process. As shown in Fig.1, the spectra display number of absorption peaks, indicating the complex nature of the material examined. The absorption peaks observed at 3385 cm^{-1} indicates hydroxyl groups, 2927 cm^{-1} can be assigned to the C-H stretching, 1651 cm^{-1} attributed to aromatic C-C bond, 1060 cm^{-1} can be assigned to the C-O stretching of alcohols and carboxylic acids. All these peaks observed after adsorption show an absorbance substantially lower than virgin sample and small differences in the frequency bands, suggesting the participation of these functional groups in the adsorption of cadmium by adsorbents (Figure 1).

Effect of adsorbent dose and time

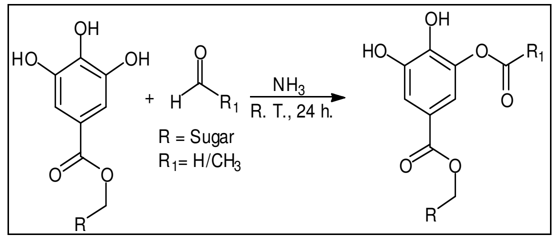
The adsorbent dose and time are the two important factors to study the adsorption process. EDS spectra of adsorbent without and with cadmium is shown in Fig. 2. It shows that cadmium ions are adsorbed on the TF resins. The adsorbent dose study reveals that there was rapid increase up to 200 mg of the adsorbent dose, thereafter no change in adsorption percent was observed as shown in Fig. 3. The graphical presentation of adsorption of cadmium ion with respect time is depicted in Fig. 4. The adsorption of Cd^{2+} was initially rapidly increased with time up to 120 min and then reached to equilibrium between the metal ion and the adsorbent.

Effect of pH

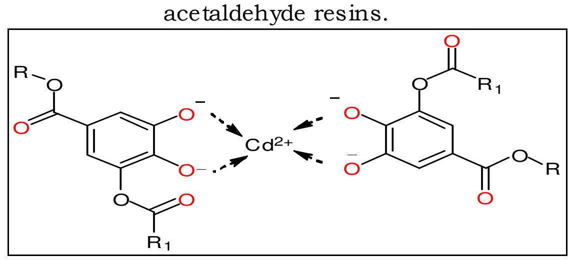
The pH of the aqueous solution is a crucial parameter which affects the adsorption process of metal.[25-27] Fig. 5 represents the effect of pH on the removal of cadmium ions at different pH. It can be seen that the adsorption capacity of cadmium (II) by tea resins is clearly affected by the pH, cadmium ion uptake increases with pH. This dependence of metal uptake on pH may be related to the functional groups of the biomass and/or the solution chemistry.[12,15] At pH below 8, cadmium is in its free ionic form (Cd^{2+}).[28-30] At higher pH, the lower number of H^+ ions and greater number of ligands with negative charges resulted in greater cadmium adsorption. For example, carboxylic groups (–COOH) are important groups for metal uptake by biological materials.[31,32] At pH higher than 3-4, carboxylic groups are deprotonated and become negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced. So in this study Cd^{2+} ions were more adsorbed around pH 6 (Figure 5).

Table 1: Monomer compositions of TF and TA resins

Resin code	Tannin / polyphenol (g)	Formaldehyde (mL)	Acetaldehyde (mL)	Ammonia (mL)
TF	4.0	10	--	20
TA	4.0	--	10	20



Scheme1: Synthesis of tannin-formaldehyde/ acetaldehyde resins.



Scheme 2: Possible mechanism of metal adsorption with tannin resin

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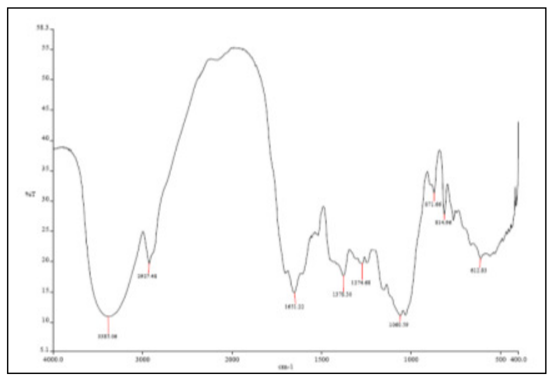
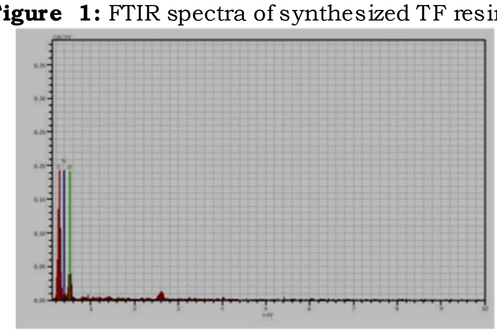
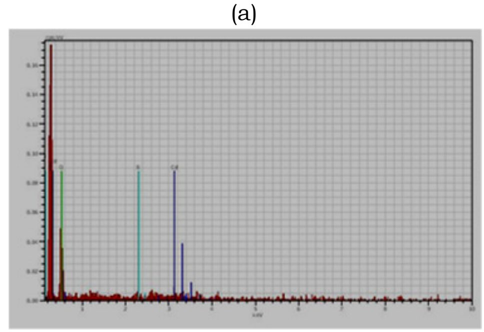


Figure 1: FTIR spectra of synthesized TF resins



(a)



(b)

Figure 2: EDS spectra without cadmium (a) and with cadmium (b) ions adsorbed on TF resins

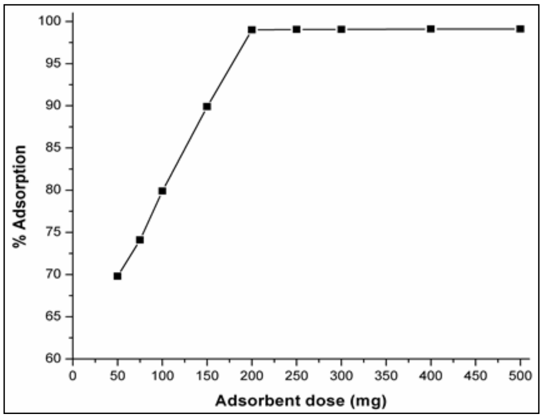


Figure 3: Effect of adsorbent dose on the removal of cadmium ions

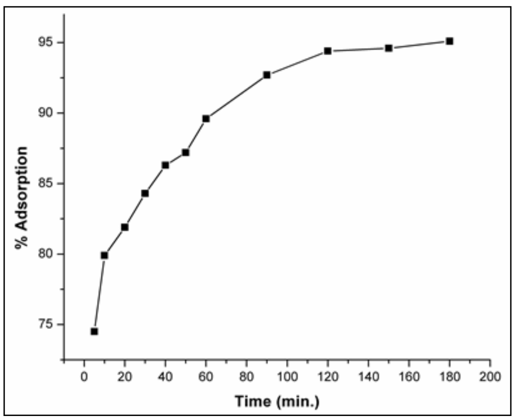


Figure 4: Effect of time on the removal of cadmium ions

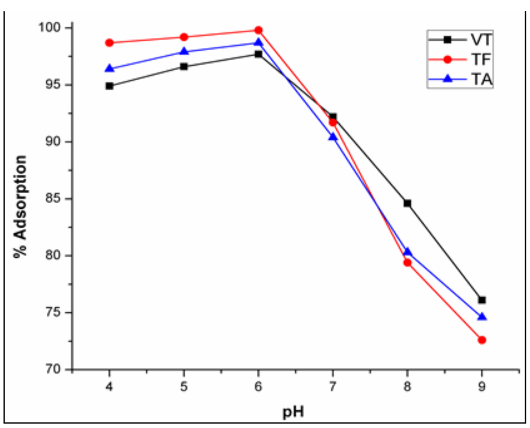


Figure 5: Effect of pH on removal of cadmium ions

Conclusion:

The results obtained in this study shows that tea tannin/ polyphenol formaldehyde /acetaldehyde resins can be considered as a potential biosorbent material for the removal of cadmium ions from aqueous solutions. The FTIR spectra of the biosorbent material shows that the adsorption capacity can be related to the carboxylic, alcoholic and the phenolic hydroxyl groups of the adsorbent. Cadmium uptake is strongly affected by pH. When the pH was increased from 2 to 6, the percentage of cadmium uptake was maximum and reached to 99% using TF resins at pH 6. This may be due to the proper size of cavity may have been generated by the resin which fits cadmium ion size. The adsorption kinetic is rapid and the equilibrium can be considered to be reached at 120 min at pH 6. It was demonstrated that the AAS and EDS results were quite agreement with both the methods. The results indicate that tea powder based materials can be converted into polymeric adsorbents such as TF/TA resins with simple chemistry and high selectivity, reusability and can be a promising substrate to entrap heavy metals from aqueous solutions.

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References:

1.Kaewsarn, P. & Yu Q. (2001). Cadmium (II) removal from aqueous solutions by pre-treated biomass of marine alga Padina sp. Environmental Pollution, 112: 209-213.

2.Mohan, D. & Singh, K. P. (2002). Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. Carbon, 36: 2304-2318.

3.Salim, R. Al-Subu, M. M. & Sahrhage, E. (1992). Uptake of cadmium from water by Beech leaves. J. Environ. Sci. Health, 3: A27, 603-627.

4.Cheung, C. W. Porter, J. F. & McKay G. (2000). Elovich equation and modified second-order equation for adsorption of cadmium ions onto bone char. J. Chem. Technol. Biotechnol., 75: 963–970.

5.Rouge, N. F. Dupont, A. Vidonne, A. Dejeu, J. Fievet, P. & Foissy, A. (2006). Removal of some divalent cations from water by membrane-filtration assisted with alginate. Water Res., 40: 1303-1309.

6.Dizge, N. Keskinler, B. & Barlas, H. (2009). Sorption of Ni(II) ions from aqueous solution by Lewatit cation-exchange resin. J. Hazard Mater., 167: 915-926.

7.Rafati, L. Mahvi, A. H. Asgari, A. R. & Hosseini, S. S. (2010). Removal of chromium (VI) from aqueous solutions using Lewatit FO36 nano ion exchange resin. Int. J. Environ. Sci. Tech., 7: 147-156.

8.Yuan, C. & Weng, C. H. (2006). Electro-kinetic enhancement removal of heavy metals from industrial wastewater sludge. Chemosphere, 65: 88-96.

9.Shah, P. & Murthy, C. N. (2013). Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal. Journal of Membrane Science, 437: 90-98.

10.Aguado, J. Arsuaga, J. M. Arencibia, A. Lindo, M. & Gascon, V. (2009). Aqueous heavy metals removal by adsorption on amine functionalized mesoporous silica. J. Hazard Mater., 163: 213-221.

11.Volesky, B. (Ed.) (1990). Biosorption of Heavy Metals. CRC Press, Boston, USA,

12.Lee, S. H. Jung, C. H. Chung, H. Lee, M. Y. & Yang, J. W. (1998). Removal of heavy metals from aqueous solution by apple residues. Process. Biochem., 33: 205-211.

13.Asheh, S. A. Banat, F. R. Omari, A. & Duvnjak, Z. (2000). Predictions of binary adsorption isotherms for the adsorption of heavy metals by pine bark using single isotherm data. Chemosphere, 41: 659-665.

14.Cimino, G. Passerini, A. & Toscano, G. (2000). Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. Water Res., 34: 2955-2962.

15.Annadurai, G. Juang, R. S. & Lee, D. J. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. J. Hazard. Mater., 92: (3) 263-274.

16.Pavan, F. A. Lima, I. S. Airoldi, C. & Gushikem, Y. (2006). Use of pokan Mandarin Peels as biosorbent for toxic metals uptake from aqueous solutions. J. Hazard. Mater., 137: 527-533.

17.Singh, K. K. Rastogi, R. & Hasan, S. H. (2005). Removal of cadmium from wastewater using agricultural waste “rice polish”. J. Hazard. Mater., A121: 51-58.

18.Ozcan, A. S. Tunali, S. Akar, T. & Kiran, I. (2005). Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of Capsicum annuum. J. Hazard. Mater., B124: 200-208.

19.Rao, M. M. Ramesh, A. Chandra Rao, G. P. & Seshaiah, K. (2006). Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. J. Hazard. Mater., B129: 123-129.

20.Brune, M. Rossander, L. & Hallberq, L. (1989). Iron absorption and phenolic compounds: Importance of different phenolic structures. European journal of clinical nutrition, 43: (8), 547-557.

21.Khanbabaee, K. Ree, T. V. (2001). Tannins: Classification and definition. Nat. Prod. Rep., 18: 641-649.

22.Martinez, S. (2002). Inhibitory mechanism of mimosa tannin using molecular modeling and substitutional adsorption isotherms. Materials Chemistry and Physics, 77: 97-102.

23.Bisanda, E. T. N. Ogala, W. O. & Tesha, J. V. (2003). Characterisation of tannin resin blends for particle board applications. Cement Concrete Composites, 25: 593-598.

24.Kollmann, F. P. Kuenzi, W. E. & Stamm, A. J. (Eds.), (1975). Principles of wood science and technology: II, Springer Verlag.

25.Ajmal, M. Khan, A. H. Ahamd, S. & Ahmad, A. (1998). Role of sawdust in the removal of copper (II) from industrial wastes. Water Res., 32: (10), 3085-3091.

26.Ajmal, M. Rao, R. A. K. Ahmad, R. & Ahmad, J. (2000). Adsorption studies on Citrus reticulata: removal and recovery of Ni(II) from electroplating wastewater J. Hazard. Mater., B79: 117-131.

27.Nuhoglu, Y. & Oguz, E. (2003). Removal of copper(II) from aqueous solutions by biosorption on the cone biomass of Thuja orientalis. Process Biochem., 38: 1627-1631.

28.Baes, C. F. & Mesmer, R. E. (Eds.), (1986). The Hydrolysis of Cations, Krieger Publishing Company Malabar, Florida, pp. 40-65.

29.Ma, W. & Tobin, J. M. (2004). Determination and modelling of effects of pH on peat biosorption of chromium, copper and cadmium. Biochem. Eng. J., 18: 33-40.

30.Pagnanelli, F. Petrangeli, M. P. Toro, L. Trifoni, M. & Veglio, F. (2000). Biosorption of metal ions on Arthrobacter sp. biomass characterization and biosorption modeling. Environ. Sci. Technol., 34: 2773-2778.

31.Norton, L. Baskaran, K. & McKenzie, T. (2004). Biosorption of zinc from aqueous solutions using biosolids. Adv. Environ. Res., 8: 629-635.

32.Kratochvil, D. & Volesky, B. (1998). Advances in the biosorption of heavy metals. Trends Biotechnol., 16: 291-300.