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*Chemistry*

# PREPARATION AND CHARACTERIZATION OF BIOSORBENT FOR TREATMENT OF WASTE WATER

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## Abstract

Biosorption is considered as good alternative methods for treatment of waste water containing trace amount of metal ions. It works with interaction between a solid phase (sorbent) and a liquid phase (solvent) containing dissolved species to be sorbed (sorbate i.e. metal ions). In recent decades, the study of low cost biosorbents has been intensified for efficient metal binding. In this context, different biosorbents have been explored for removal of heavy metals. In this study an efficient and low cost biosorbent has been prepared from consumed tealeaves by amination. The biosobent is characterized by its elemental analysis and also analyzed for its major constituents. The introduction of amino group is indicated by Bohem titration values and $pH_{pzc}$ values. It is further characterized by SEM images, FTIR spectra, XRD spectra and thermal analysis. The biosorbent has been then used for removal of Zn (II).

**Keywords:** *Biosorbent, zinc, SEM images, amination*

## Introduction

Biosorption emerges as an attractive alternative to conventional methods for treatment of waste water containing trace amount of metal ions. Biosorption is removal of metals, metalloids, compounds and particulates from solution by using biological materials (Volesky 1990a). It offers several advantages over conventional treatment methods including cost effectiveness, efficiency, and minimization of chemical or biological sludge and regeneration of biosorbent with possibility of metal recovery (Southichak 2006).

It involves an interaction between a solid phase (sorbent) and a liquid phase (solvent) containing dissolved species to be sorbed (Ahalya 2003). The higher affinity of the sorbent for sorbate species is the cause for attachment towards the sorbent and removed thereby different mechanism (Volesky 2004). This process continues till equilibrium is established between the amount of solid, bound sorbate species and its portion remaining in the solution (Volesky 2004). The sorbent's affinity for the sorbate determines the distribution of sorbate between solid and liquid phase (Volesky 2004).

In last few decades, the study of low cost biosorbents that have efficient metal binding capacity has been intensified. In this regards, different biosorbents have been explored for removal of heavy metals (Sud 2008). They include algae, fungi, bacteria, agricultural waste and waste from industries Recently, the research work has been focused on treatment of waste water by the use of agricultural bio-waste as adsorbent (Sud 2008). The process utilizes inactive bio-waste to bind and concentrate heavy metals from waste water by purely physico- chemical process. These agricultural bio-waste are inexhaustible, cost-effective and nonhazardous materials which can be easily disposed by incineration (Ghimire *et al*. 2002). In this study a biosorbent will be prepared using consumed tealeaves [CT]. The aminated consumed tealeaves [ACT] will characterized by various spectral and analytical methods to see if it could be used for removal of Zn (II).

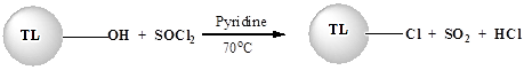
## Materials and Methods

### Preparation of biosorbent

A biosorbent was prepared by using consumed tealeaves. The procedures used for preparation of biosorbent are similar to those earlier reported (Shrestha *et al*. 2012). It involves two steps. The

first step is chlorination by using thionyl chloride, in which the – OH group is substituted with – Cl group. In the second step, the –Cl group is substituted with amino group by using ethylenediamine. The reaction schemes are represented in figure 1.

Step I




Step II

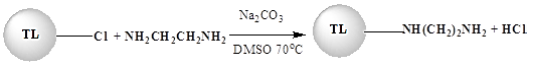



***Figure 1.*** Amination of consumed tealeaves by using ethylenediamine.

The biosorbent was chemically analyzed to quantify the amount of acidic and basic functional sites on its surface, before and after amination. Boehm titration was used as a typical method to quantify acidic and basic functional sites on the surface of biosorbent. The method involved neutralization of surface acidic sites with a base, sodium hydroxide and surface basic sites with an acid, hydrochloric acid. The total acidic sites could be calculated from the amount of NaOH consumed by the adsorbent in neutralization reaction between the adsorbent and NaOH. Similarly, the basic sites could be calculated from the amount of HCl consumed by adsorbent in neutralization reaction between the adsorbent and HCl. Scanning Electron Microscope (SEM) images were used to examine the surface morphology of the biosorbent.

Thus prepared biosorbent was used for removal of Zn (II) from aqueous solution. Adsorption experiments were studied using batch equilibrium experiment. The experiments were performed at $25^0$ C using 20 ml metal solution and 25 mg of adsorbent. The reaction mixtures were shaken in a mechanical shaker for 24 h at 150 rpm. The optimized adsorption parameters were contact time, initial concentration and pH of the solution. After adsorption the solutions were filtered and were analyzed for metal ions concentration using atomic absorption spectroscopy (Chemito AA 202, AAS). During the experiment, pH of the solution was maintained using nitric acid and sodium hydroxide solution and 2-[4-(2-hydroxymethyl)-1-piperazinyl] ethanesulfonic acid [HEPES] was used as buffer. All the chemicals used were of AR grade and double distilled water was used for the experimental work.

## Results and Discussion

### Elemental analysis

The amount of carbon, nitrogen and sulphur in raw and aminated tea leaves are depicted in table 1. The amounts of nitrogen as well as sulphur are increased after amination as shown in the table.

***Table 1.*** % of carbon, nitrogen and sulphur in consumed tealeaves before and after amination

| Adsorbent | Carbon | Nitrogen | Sulphur |
|---|---|---|---|
| CT | 47.17 | 1.03 | 0.29 |
| ACT | 51.59 | 9.52 | 5.18 |

The major constituents present in the biosorbent are given in Table 2.

***Table 2.*** % of the major constituents of consumed tealeaves

| Adsorbents | Lignin | Cellulose | Hemicellulose |
|---|---|---|---|
| CT | 28.70 | 22.33 | 11.37 |

The acidic functional sites on the surface of adsorbent before amination, were found to be 1.8 meq/g, which was slightly decreased to 1.4 meq/g after amination in ACT. The basic functional sites were found to be 0.9 meq/g before amination, which was increased to 3.3 meq/g after amination. The increasing basic functional group indicates the introduction of basic amino groups on the surface of the biosorbent.

### Scanning Electron Microscope (SEM) analysis

SEM image of consumed tealeaves is shown in figure 1(a). Its surface morphology is fibrous in nature as it contains cellulose, hemicelluloses and lignin as the main constituents. After amination, the fibrous nature of the biosorbent surface was destroyed and irregularly distributed pores were formed and the surface of biosorbent becames rough as shown in figure 1 (b). This morphological change indicates the required modification onto the surface of biosorbent. The surface of biomaterials after amination was full of cavities that are essential to enhance the metal binding capacity of the adsorbent.

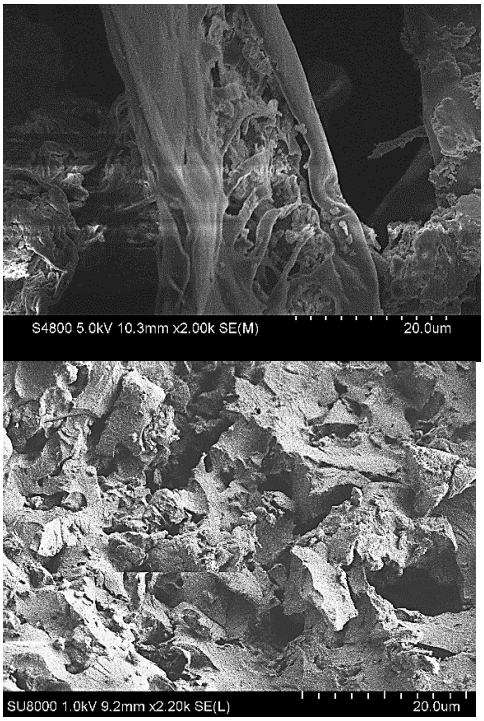



***Figure 1***. SEM images of (a) CT top and (b) ACT bottom.

## FTIR analysis

The spectra are complex due to various functional groups present on the surface of biomaterial. In the spectrum of CT, peaks are observed at 3382, 2924, 1646 and 1071 $cm^{-1}$. The strong band at 3382 $cm^{-1}$ is due to OH stretching, 2924 $cm^{-1}$ is due to aliphatic CH stretching in $CH_3$, $CH_2$ and CH group, 1646 $cm^{-1}$ is due to C=O or C=C stretching and 1071$cm^{-1}$ is due to C – O stretching.

The spectrum exhibits some significant changes after amination of the biosorbent. The broad and strong band ranging from 3130 – 3666 $cm^{-1}$ in ACT, may be due to overlapping of OH and NH stretching. Peaks around 1650 $cm^{-1}$ are in N – H bending range. Peaks at 1065 $cm^{-1}$ assigned to C – N stretching vibration. The spectra of aminated biomaterials have shown the presence of amino groups on their surface indicating the changes after modification.

## XRD analysis

The amorphous nature of biosorbent is highly suitable for metal adsorption (Kurita, 1979). The XRD spectra of CT and ACT are shown in figure 2. In XRD profile strongest reflection appears at $2\Theta = 21^{o}$. This broad peak indicates the lesser crystallinity of biosorbent.

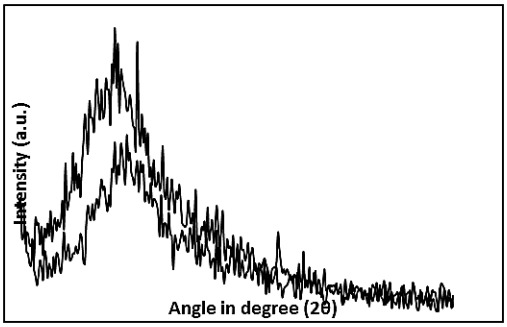



***Figure 2.*** XRD spectrum of CT and ACT.

## Thermogravimetric analysis

The thermal stability and degradation behavior of consumed tea leaves was evaluated by TGA under nitrogen atmosphere. The TGA curve is shown in Figure 3, in which the biosorbent degrades in two stages. The first stage begins at about 100°C with weight loss of 5-10%, which is due to loss of residual or physically adsorbed water molecules. The second stage degradation occurs with rapid weight loss at 230-560°C reaching a maximum value at 485°C.

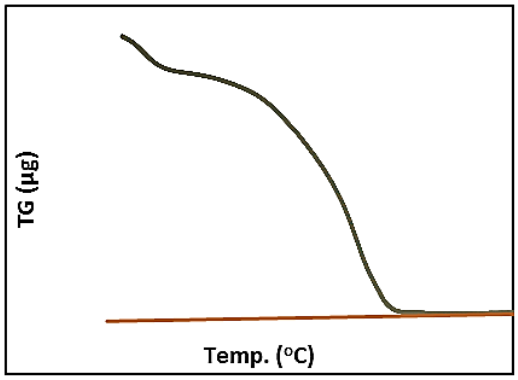



***Figure 3.*** Thermal analysis of ACT.

## Zeta potential

The zeta potential i.e. $pH_{pzc}$ of biomaterial is an important character that determines the nature of the surface of biomaterial. It is the pH at which surface of biomaterial has net electrical neutrality. The zeta potentials of consumed tealeaves are positive at pH < 5.9 and negative at pH > 5.9. It indicates that the surface of biosorbent becomes positive below pH 5.9, while it becomes negative

above pH 5.9. After amination, the $pH_{pzc}$ value shifts towards higher pH ranges. The increase in $pH_{pzc}$ values after amination is due to protonation of amino groups introduced onto the surface of biosorbent. Hence increase in $pH_{pzc}$ values further confirms the successful amination onto the surface of biosorbent.

All the chemicals used were of AR grade and double distilled water was used for the experimental work. The maximum adsorption for Zn (II) was found to be 30.08 mg/g. The adsorption value is comparable with the values obtained for other biosorbents.

## Conclusion

A new and efficient biosorbent has been prepared by using consumed tealeaves. To enhance the adsorption capacity the biosorbent was aminated. The prepared biosorbent was characterized by elemental analysis, cellulose, hemicelluloses and lignin analysis, Boehm titration, SEM image, FTIR spectra, XRD spectra, thermal analysis and its $pH_{pzc}$ value. The experimental results shows that the biosorbent has been successfully aminated. This biosorbent can be used for removal of heavy metals, which are highly toxic.

## Acknowledgements

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## References

Ahalya N., Ramachandra T.V. and Kanamadi R.D. 2003. Biosorption of heavy metals. *Res. J. Chem. Environ.* **7** (4): 71-79.

Ghimire K.N., Inoue K., Makino K. and Miyajima T. 2002. Adsorptive removal of arsenic using orange juice residue. *Sep. Sci. Technol*. **37** (12): 2785-2799.

Kurita K., Sannan T. and Iwakura, Y. (1979). Studies on chitin-6, binding of metal cations. *J. Applied Polymer Sci.* **23**: 511-515.

Shrestha B., Homagai P.L., Pokhrel M.R. and Ghimire K.N. 2012. Exhausted tealeaves – a low cost bioadsorbent for Lead (II) and zinc (II) removal from their aqueous solution, *J. Nep. Che. Soc.* **30** (2): 124-129.

Shriner R.L., Hermann C.K.F., Morrill T.C., Curtin D.Y. and Fuson R.C. 1998. *The Systematic Identification of Organic Compounds*. 7th ed. Wiley, New York. Pp.324.

Southichak B., Nakano K., Nomura M., Chiba N., Nishimura O. and Phragmites A. 2006. A novel biosorbent for the removal of heavy metals from aqueous solution. *Water Res*. **40:** 2295-2302.

Sud D., Mahajan G. and Kaur M.P. 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - a review. *Biores. Techol.* **99** (14): 6017-6027.

Volesky B. 2004. Equilibrium biosorption performance. *In*: *Sorption and biosorption* (ed. Volesky B.), BV-Sorbex, Inc., Montreal, Canada http://biosorption.mcgill.ca/publication/ book/6.1-4w (103-16).

Volesky B. 1990. Biosorption and biosorbents. *In: Biosorption of Heavy Metals*. Boston, USA, CRC Press. Pp. 3-5.