# Removal of Hg (II) from contaminated water on the bark powder of *Syzygium Cumini*

**Shashikant Kuchekar[*], Monali Patil[*], Haribhau Aher[*], Bhaskar Zaware [**]and Vishwas Gaikwad [***]**

[*]Principal, Women's College of Home Science & BCA, Loni (Kd), Tal. Rahata, Dist. Ahmednagar, MS, 413713, India.
[**]Principal, New Arts, Commerce and Science College, Ahmednagar, MS, 413713, India.
[***]Principal, KTHM College, Nashik, Dist. Nashik, MS, 422002, India.

*shashi17@gmail.com

***Abstract***

*Mercury is a toxic pollutant present in industrial effluent is responsible for environmental pollution. The current work focuses on removal of Hg (II) from contaminated water using a natural biosorbent, Syzygium cumini bark powder. Investigations have been made to study various factors such as biosorbent concentration, initial metal concentration, agitation time, pH, temperature for the maximum removal of Hg (II) from contaminated water. Also an FTIR study of Syzygium cumini was done before and after adsorption process to intervene the functional groups responsible for Hg (II) ion adsorption. The optimum pH for maximum efficiency of adsorption of Hg (II) was found to be 7.2. The adsorption process was exothermic in nature. About 97 % removal of Hg (II) ion was obtained at 20 mg/L of absorbate and 2.5 gm of biosorbent concentration respectively. The study suggests biosorbent used are capable of removing Hg (II) ion at significant capacity*

Keywords: Adsorption, *Syzygium cumini*, mercury metal, FTIR spectra

---



**Introduction**

Industrialization and Urbanization often lead to an increase in the discharge of toxic metals into the environment. The Uncontrolled discharge of waste waters from different industries is a major environmental concern encountered in many parts of the world.[1] Contamination of the environment with heavy metals has increased behind the recommended limit is harmful to all life forms.[2,3,4] Mercury is one of the most toxic environmental contaminants, which even at low concentration is harmful. WHO recommended the maximum concentration 0.001 ppm for drinking water. The Hg (II) ion can cause respiratory failure, kidney injury, chronic diseases, central nervous system disorders, brain damage and severe environmental pollution.[5] Traditionally heavy metal waste removal has been accomplished using methods as ion exchange[6], reverse osmosis, chemical precipitation[7], electrodialysis.[8] These techniques have many disadvantages high capital investment, operating cost, incomplete metal recovery and generation of toxic sludge.[9] Recently adsorption technique has emerged as effective, alternative and inexpensive over the traditional methods for heavy metal removal.[10,11,12] Despite of the advantages of adsorption, the major obstacle for its industrial application is the very high price of adsorbent. With the objective, in this study natural and abundant plant material *Syzygium cumini* bark powder is studied as biosorbent for the removal of mercury from contaminated water. *Syzygium cumini* is the widely used medicinal plant in the treatment of various diseases particularly diabetic. It is as an antidiabetic plant since it became commercially available several decades ago. The bark of *Syzygium cumini* contains polyhydroxy, polyphenyl groups of tannin, which are though to be the active species in the process of adsorption. The current study is an attempt in a way to find out an alternate, low-cost green biosorbent. The main objective of this study was to explore the effects of various parameters such as biosorbent concentration, metal ion concentration, agitation time, pH, temperature. FTIR studies of *Syzygiym cumini* before and after Hg (II) adsorption shows the functional groups responsible for the adsorption.

## Materials and Methods

Preparation of Syzygium cumini bark for adsorption

*Syzygium cumini* barks were collected in bulk from local area. The collected barks were washed with distilled water to remove dust and soluble impurities. Dried in sunlight for 3-4 days. The dried barks were crushed, grinded using grinder. The grinded powder stored in air tight container for further use.

Chemicals and equipments

All the chemicals used were of analytical grade. The stock solution of Hg (II) 1000 mg/L was prepared by dissolving 0.338 gm of $HgCl_2$ into deionized water to obtain the required concentration. The prepared working solutions were used for adsorption studies. A pH meter was employed for pH measuring. pH of solution was adjusted using 0.01 N HCL and 0.01 N NaOH solution. The FTIR spectra of unloaded biosorbent and Hg (II) loaded biosorbent were taken using KBr pellets at 4000-650 $cm^{-1}$ using thermo-scientific spectrophotometer.



Biosorption method

In this study adsorption experiment was carried by taking 2.5 gm of *Syzygium cumini* in 100 ml flask in 30 ml 20 mg/L mercury solution and was shaken in an orbital shaker at 130 rpm, samples were withdrawn at different time intervals. In order to study the effects of different parameters we varied biosorbent concentration, metal ion concentration, agitation time, pH, temperature on the removal of mercury. The percentage removals of mercury were determined complexometrically using equation as,

$$\% R = (Co - Ce) / Co \times 100$$

Where R is percentage removal, Co, Ce expressed in mg/L are the initial and equilibrium concentrations of metal ion in solution respectively.

## Results and Discussion

### Effect of biosorbent concentration

The effect of biosorbent concentration on biosorption efficiency for Hg (II) ion was investigated. The outcome indicates that the percentage removal of Hg (II) increases by varying the biosorbent concentration from 0.5 to 3.0 gm (Table 2). Figure 1 showed 2.5 gm biosorbent dose is sufficient for optimal Hg (II) ion removal whereas beyond 2.5 gm decreasing trend was observed. This is owing to the increase of biosorbent mass (more surface area available for adsorption) that would result in greater availability of reactive groups.[13]

**Effect of increasing concentration of mercury on adsorption**

The influence of initial metal ion concentration in the solution on the adsorption capacity and removal efficiency for *Syzygium cumini* bark shows that the metal uptake mechanism is particularly dependent upon initial metal ions concentration.[14] The study was carried out using metal concentration in the range of 20-100 mg/L at 2.5 gm of biosorbent at 130 rpm. It is because the sufficient adsorption sites are available at low concentration but at higher concentration Hg (II) ions are greater than adsorption sites available.[15]

**Effect of agitation time**

It is observed that adsorption of mercury ion removal was investigated using agitation time at regular interval of 15 min upto 150 minutes using 2.5 gm biosorbent dose at 130 rpm shown in Table 4.The contact time needed for Hg (II) ion solutions to reach equilibrium was 120 minute, after that no significant change was observed. The maximum biosorption of metal ion may be due to the presence of large number of accessible binding sites and the affinity of the functional groups as well as the mode of interaction between the metal ion and biosorbent.[16]

**Effect of pH**

The experiment was conducted using 20 mg/L of initial Hg (II) solutions at initial pH values ranging from 3.2 to 8.2. It was seen that removal of Hg (II) ions was low at low pH and increased with increasing pH of solution. Maximum 98 % Hg (II) ion removal was found at 7.2 pH beyond this, decreasing Hg (II) ion removal was reported in Figure 4. The influence of pH can be related with electrostatic repulsion where its decrease will be associated with reduction of positive charge density on the sorption sites resulting in an enhancement of metal biosorption.[17]

**Effect of temperature**

The effect of temperature on the mercury removal was varied in the range of 10 to 60 $^{o}$C with an initial mercury ion concentration 20 mg/L, pH 7.2 with biosorbent concentration of 2.5 gm and agitation speed 130 rpm. Adsorption reactions are normally exothermic so adsorption capacity increases with decrease of temperature. In this study, maximum equilibrium adsorption capacity for Hg (II) ions was reached at 40 $^{o}$C. At higher temperature 40-60 $^{o}$C, decreasing in adsorption capacity showed that the processes of Hg (II) adsorption are exothermic (Figure 5). The decrease of adsorption at higher temperature may be due to damage of active binding sites in the biosorbent.[18]

## FTIR Characterization

FTIR technique is an important to analyze the characteristic functional groups present on the surface of Syzygium cumini loaded and unloaded shown in Figure 6 and 7 respectively. The peak approximately at 1016.89 $cm^{-1}$, 1225.58 $cm^{-1}$ is due to presence of C=O stretch of OH of carboxylic acid. The peak obtained at 1315.80 $cm^{-1}$, 1458.13 $cm^{-1}$, 1508.14 $cm^{-1}$ and 1617.19 $cm^{-1}$ corresponds the presence of N-H (amide), C-H (alkane), and C=C (aromatic), C-F (alkyl halide) and C-N (amine) functional groups respectively are found to be involved in biosorption process. Viberations noticed at 2916.65 $cm^{-1}$, 2848.26 $cm^{-1}$ respectively are caused due to the presence of symmetric and asymmetric CH stretching of aliphatic acids. From FTIR spectra of mercury loaded biosorbents, it was observed that there was a shift in wave numbers of some peaks associated with loaded mercury. There was a decreased shift from 1458.13 $cm^{-1}$ to 1425.04 $cm^{-1}$ for mercury loaded. Also some metal binding groups present on surface of biosorbents get shifted shortly or disappeared after mercury loading. FTIR study before and after adsorption revealed the functional groups like hydroxyl, carbonyl, amide and carboxyl were involved in metal ion adsorption onto biosorbent surface.



## Conclusion

The current study shows that *Syzygium cumini* was an objective biosorbent for the adsorption of mercury. The adsorption of mercury (II) ions by *Syzygium cumini* was reasonably fast and reached equilibrium at 120 minutes. It is found that the maximum removal occurs at initial Hg (II) ion concentration of 20 mg/L at pH 7.2 with an biosorbent concentration 2.5 gm. FTIR Spectra provides the presence of functional groups responsible for sorption of mercury. The main advantage of this study is the higher sorption capacity of *Syzygium cumini* effectively used for the removal of mercury.

## Acknowledgement

Authors are thankful to the Management PRESS, Loni for providing necessary facilities in department of Analytical and Food chemistry laboratory, Women's College of Home Science and BCA, Loni.

## References

1. Attahiru S., Shiundu M., Wambu W., Removal of Cr (III) from aqueous solutions using a micaceous poly-mineral from Kenya, *Int. J. Phys Sci*., **7,** 1198-1204 **(2012)**
2. Gaur N., Flora G., Yadav M., Tiwari A., A review with recent advancement on bioremediation–based abolition of heavy metals, *Environ. Sci. Process Impacts.*, **16,** 180-193 **(2014)**
3. Dixit R., MalaviyaD., Pandiyan K., Singh VB., Sahu A., Shukla R., Singh BP., Rai JP., Sharma PK., Lade H., Bioremediation of heavy metals from soil and aquatic environment: An overview of principles and criteria of fundamental processes, *Sustainability.*, **7,** 2189-2212 **(2015)**
4. Tak HI., Ahmad F., Babalola OO., Advances in the application of plant growth–promoting rhizobacteria in phytoremediation of heavy metals, In Reviews of Environmental Contamination and Toxicology; Springer: New York, NY, USA., 33-52 **(2013)**
5. Awual R., Hasan M., Eldesoky G.E., Khaleque A., Rahman M.M. and Naushad M., Facile mercury detection and removal from aqueous media involving ligand impregnated conjugate nanomaterials, *Chemical Engineering Journal.*, **290**, 243-251 **(2016)**
6. Feng D., Aldrich C., Tan H., Treatment of acid mine water by use of heavy metal precipitation and ion exchange, *Minerals Engineering.*, **13(6),** 623-642 **(2000)**
7. Matlock M.M., Howerton B.S., Atwood D.A., Chemical precipation of heavy metals from acid mine drainage, *Water Research.*, **36(19**), 4757-4764 **(2002)**
8. Mohammadi T., Moheb A., Sadrzadeh M., Razmi A., Modeling of metal ion removal from wastewater by electro-dialysis, *Seperation Purification Technology.*, **41(1 ),** 73-82 **(2005)**
9. Celaya R.J., Noriega J.A., Yeomans J.H., Ortega L.J., Ruiz-Manriquez A., Biosorption of Zn (II) by Thiobacillus ferrooxidans, *Bioprocess Engineering.*, **22(6),** 539-542 **(2000)**
10. Wang J.L., Chen C., Biosorbents for heavy metals removal and their future. *Biotechnology Advances.*, **27(2),** 195-226 **(2009)**
11. Wang X.J., Xia S.Q., Chen L., Zhao J.F., Chovelon J.M., Nicole J.R., Biosorption of cadmium (II) and lead (II) ions from aqueous solutions onto dried activated sludge, *Journal of Environmental Sciences.*, **18(5),** 840-844 **(2006)**
12. Krishnani K., Meng X., Christodoulatos C. and Baddu V., Biosorption mechanism of nine differerent heavy metals onto biomatrix from rice husk, *Journal of Hazardous Materials.*, **153**, 1222-1234 **(2008)**
13. Kumar P.Y., King P., Prasad V.S.R.K., Zinc biosorption on *Tectona grandis* L.f. leaves. Biomass: Equilibrium and kinetic studies, *Chemical Engineering Journal*., **124 (1),** 63-70 **(2006)**
14. Saeed A., Akhter M.W. and Iqbal M., Removal and recovery of heavy metals from aqueous solution using papaya wood as a new

biosorbent, *Seperation and purification Technology.*, **45**, 25-319 **(2005)**

15. Ajmal M., Rao RAK.,, AnwarS., Ahmad J. and Ahmad R., Adsorption Studies on Rice Husk: Removal and Recovery of Cd (II) from Wastewater, *Bioresource Tech.*, **86**, 147-149 **(2003)**
16. Sanchez AG., Ayuso EA., DeBlas OJ., Sorption of heavy metals from industrial waste water by low cost mineral silicates, *Clay Miner.*, **34**, 469-477 **(1999)**
17. Bhattacharya AK., Mandal SN., Das SK., Adsorption of Zn (II) from aqueous solution by using different adsorbents, *Chem. Eng. J.*, **123**, 43-51 **(2006)**
18. Romera E., Gonzalez F., Ballester A., Blazquez M.L. and Munoz J.A, "Comparative Study of Biosorption of Heavy Metals Using Different Types of Algae," *Bioresource Technology.*, **98(17),** 3344-3353 **(2007)**

Table1 Investigated experimental conditions

| Parameters | Investigated *S.cumini* values |
|---|---|
| Biosorbent conc. | 0.5-3.0 |
| Initial conc of mercury (mg/L) | 20-100 |
| Agitation time (min) | 15-150 |
| pH | 3.2-8.2 |
| Temperature | 10-60 |

Table 2 Effect of biosorbent conc on the removal of mercury

| Adsorbent amount (gm) | % Removal |
|---|---|
| 0.5 | 23.12 |
| 1.0 | 46.10 |
| 1.5 | 68.28 |
| 2.0 | 84.33 |
| 2.5 | 97.00 |
| 3.0 | 88.50 |



Table 3 Effect of initial ion conc on the removal of mercury

| Initial ion conc ( mg/L) | % Removal |
|---|---|
| 20 | 96.84 |
| 40 | 90.68 |
| 60 | 84.52 |

| | |
|---|---|
| 80 | 75.36 |
| 100 | 68.21 |

Table 4 Effect of agitation time on the removal of mercury

| Agitation time (min) | % Removal |
|---|---|
| 15 | 61.05 |
| 30 | 74.10 |
| 45 | 81.05 |
| 60 | 86.15 |
| 90 | 92.63 |
| 120 | 98.00 |
| 150 | 97.90 |

Table 5 Effect of pH on the removal of mercury

| pH | % Removal |
|---|---|
| 3.2 | 62.18 |
| 4.2 | 77.15 |
| 5.2 | 89.12 |
| 6.2 | 95.33 |
| 7.2 | 98.00 |
| 8.2 | 93.10 |

Table 6 Effect of temperature on the removal of mercury

| Temperature ($^{o}$C) | % Removal |
|---|---|
| 10 | 75.10 |

| | |
|---|---|
| 20 | 89.47 |
| 30 | 94 |
| 40 | 98.94 |
| 50 | 85.10 |
| 60 | 74.23 |

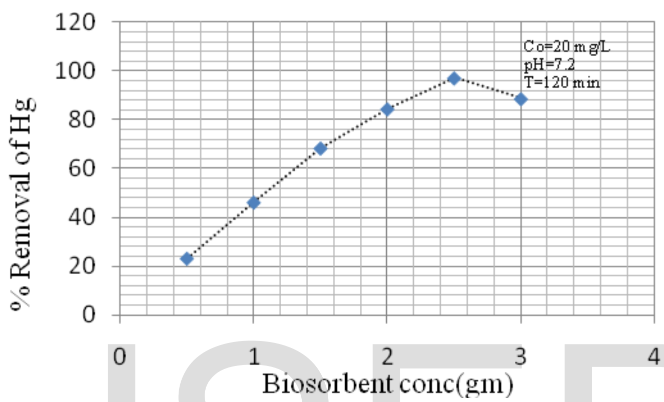


Figure 1: Dependence of biosorbent conc. on mercury adsorption



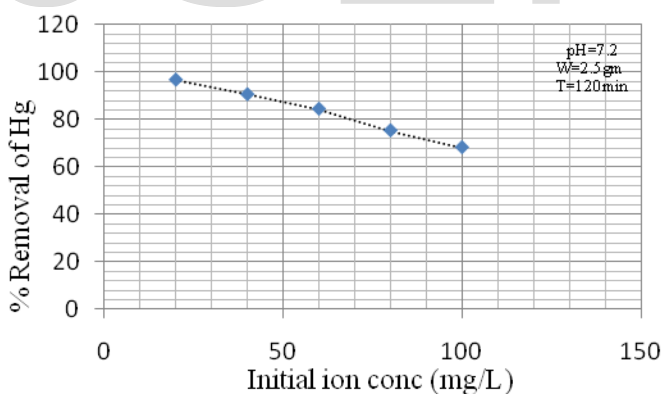


Figure 2: Variation of initial metal conc of mercury adsorption

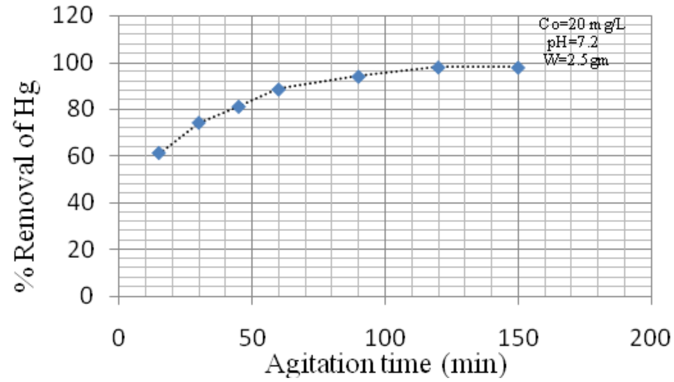


Figure 3: Effect of agitation time on adsorption of mercury

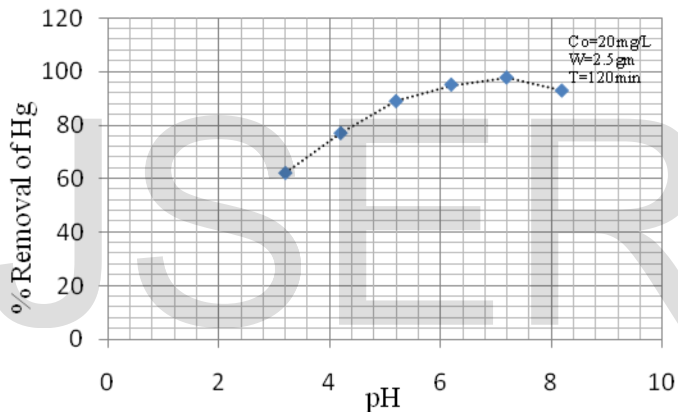


Figure 4: Adsorption of mercury as a function of pH

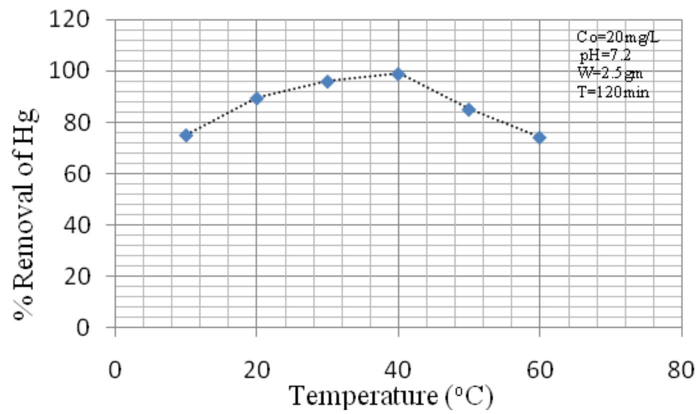


Figure 5: Influence of temperature on mercury adsorption

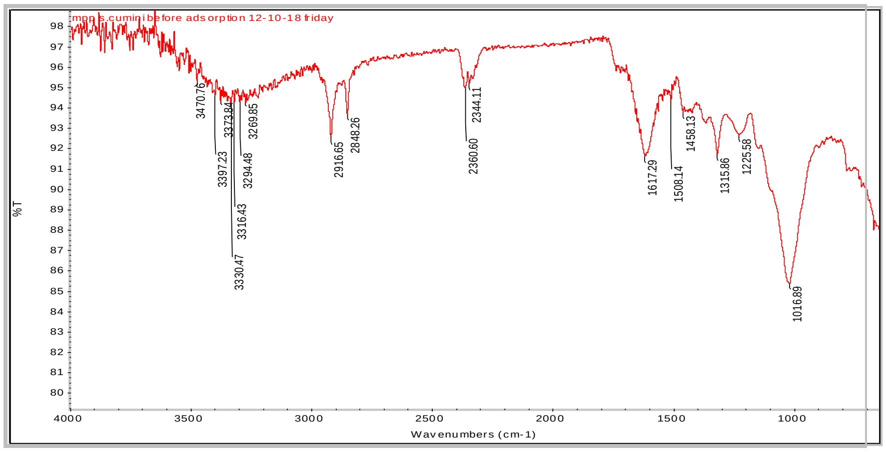


Figure 6: FTIR spectra before mercry adsorption on *Syzygium cumini*

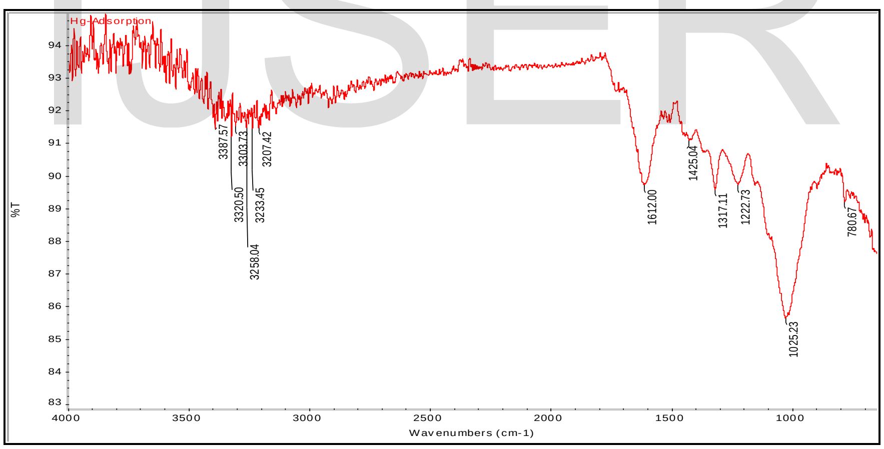


Figure7: FTIR spectra after mercury adsorption on *Syzygium cumini*