Synthesis And Characterization of Plant Mediated Natural Adsorbent Using *Punica Granatum* Stem and Its Application in Removal of Heavy Metal Co (Ii)

Harshal S. Kharde[1], Sandeep R. Gadhave[1]*, Abhijit B. Kadlag[2], Nikita S. Aher[3], Priya S. Kote[3], Gayatri S. Kote[3]

[1]*Assistant Professor, Department of Chemistry, Padmashri Vikhe Patil College of Arts, Science and Commerce, Pravaranagar, Maharashtra, India.*
[2]*Research Associate, Dr. Reddy's Institute of Life Sciences, Hyderabad, Telangana, India.*
[3]*Post Graduate Student, Department of Chemistry, Padmashri Vikhe Patil College of Arts, Science and Commerce, Pravaranagar, Maharashtra, India*
**Corresponding Author: srgdrug@gmail.com*

---***---

ABSTRACT – Removal of heavy metals ions from wastewater is of prime importance for a clean environment and human health. *Punica granatum* were used to remove zinc, chromium and cobalt from industrial wastewater. *Punica granatum*, was synthesized into particle in the removal of cobalt metals ions. A batch absorption study was carried out with parameters including the effect of pH (pH 5), adsorbent dose (0.5gm) ,the concentration of metal ion (100ppm), the effect of temperature (40°c) characterization on study of the before cobalt metal ion adsorption and after lead metal ion adsorption was conducted. Energy Dispersive X-ray spectroscopy (EDX), Fourier transforms infrared spectroscopy (FTIR).

Key Words: Cobalt, Adsorbent, Characterization, Synthesis, Removal

1. INTRODUCTION

Heavy metals are a serious environmental contaminant because they are environmentally persistent, have high toxicity and have a tendency to accumulate in body tissues. Because of this, environmental regulations compel industries to reduce the concentration of heavy metals in their waste water to within safe levels.[1] Heavy metals are natural components of the Earth's crust and can enter a water supply by Industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. They cannot be degraded or destroyed but tend to bio-accumulate and thus causing an increase in its concentration in a biological organism over time, compared to its amount in the environment [2]. In the eco-system and based on the biological role, the heavy metals can be classified as essential heavy metals including copper, zinc, and Ferric5, and also non-essential heavy metals such as cobalt mercury, lead, and cadmium. [3] The heavy metals most frequently found in our environment are cadmium (Cd), chromium (Cr), copper (Cu), cobalt (Co), nickel (Ni), Zinc (Zn), manganese (Mn), and lead (Pb). These tend to accumulate in the environment, they are unstable and ofen toxic, so they pose a threat to all living creatures. Heavy metals, hazardous compounds, and dyes abound In industrial discharges. Heavy metals are thought to be the most dangerous because of their potential to accumulate heavy metals are thought to be the most dangerous because of their potential to accumulate in human bodies and cause signifcant illnesses and physical problems. Many methods for removing heavy metals and dyes from water have been proposed recently, including chemical precipitation, ion-exchange, adsorption, membrane filtration, photocatalytic degradation, and electrochemical technologies. [4] The amputation of heavy metals from numerous sources of wastewater has reportedly been accomplished using commercial activated carbon, zeolites and biomass-derived adsorbents like peanut shells , banana peel, dry tree leaves, rice husk, tea and coffee waste , coconut shell powder, Papaya seed ,pomegranate peels. Nevertheless, some problems, including the need for a prolonged reaction time, excessive calcination temperature, inadequate stability, short reusability, a low surface area, etc. restrict most of the available adsorbents. As a result, it is crucial to create low-cost adsorbents with a large surface area utilizing straightforward synthesis techniques. [5] Pomegranate (*Punica granatum L.*) belongs to the Punicacea family. The cultivation of pomegranate is native to the Middle East and was later known in the Mediterranean. Pomegranate peels are rich in tannins. They have been used traditionally for their medicinal properties as anticancer, anti-inflammatory, antioxidant and antihelminthic. [6] In this research pomegranate peel powder is utilized as an efficient adsorbent for the removal of cobalt metal ions through the aqueous solution cobalt metal ions in its divalent and trivalent state in excess can result for toxicity. [7] However, most of these methods resulted in removal of metal ion, low selectivity, high operational cost, high consumption of reagents, energy and generation of secondary pollutants besides, it was revealed that these techniques when applied, some of them are usually incapable of meeting the discharged standards limits for heavy metals concentrations ranging between 0.1 and 3 mg/L.[8] A search for a low cost and easily available adsorbent has led to the investigation of materials of agricultural products as well as industrial byproducts which are considered as potential metal sorbents. The utilization of these low cost adsorbent for the treatment of wastewater make it more valuable. [9] These methods were mainly categorized as chemical, physical and biological methods. These conventional methods included ion exchange, membrane filtration, precipitation, coagulation and flocculation. [10] In adsorption process, an adsorbent is usually required. It is in the light of this that agricultural-waste-based biochar is eco-friendly and cost-effective adsorbent. [11]In the present study the process is optimized by treating untreated ppm with stock solutions of lead, copper, cadmium, cobalt ,and zinc. After the process has been optimized different chemically treated ppm is treated with tanneries effluents collected from different tanneries. [12]

2. MATERIALS AND METHODS

- **Collection of plant material**: Pomegranate stems is easily available and collected from Nimgaon Jali, Sangamner Taluka, Maharashtra state (India).
- **Synthesis of Natural Adsorbent**: Plant material of *punica granatum* was dried in sunlight for 1-2days. Then these shell dry in oven. After drying, powdered and transfer in oven for 2 days. Weighing 20 gm powder, add 100ml distilled water for digestion. Again wash with distilled water for 7-8 times. Filter this residue, place in oven for drying 2 days.
- **Preparation of Adsorbate**: For this study, cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) were used as Adsorbate. A stock solution of cobalt (II) chloride hexahydrate was prepared by dissolving 0.2015 gm quantity in 500ml distilled water. The stock solution was finally diluted to obtain standard solution.

3. RESULT AND DISCUSSION

Characterization of Natural Adsorbent punica granatum Fruit Peel:

a. FTIR Analysis:

Fourier Trasform infrared spectroscopy for the extract *punica granatum* fruit peel. Identifies its diverse array of bioactive phytochemicals, including carbohydrates, alkaloids tannins, flavonoids, and phenols, by analyzing the adsorption of infrared light. The resulting FTIR spectrum shows peaks at specific wavenumber, each corresponding to the vibrational modes of different functional group allowing for the identification and characterization of these compounds in various parts of the plant such as peels, seeds, or flowers. The analysis spectrum of peels extract shows various peaks of functional groups which due to the presence of biomolecules and the phytoconstituents capped on the surface of the synthesized nanoparticle. Identifies functional groups within its complex structure, confirming the presence of bioactive compounds such as phenols, carbohydrates, and tannins. Fourier Transform Infrared (FTIR) spectroscopy uses infrared light to probe the sample. The infrared light causes molecules within the sample, such as those in pomegranate peel, to vibrate at specific Frequencies. Different chemical bonds within the sample absorb specific frequencies of infrared light. The FTIR instrument measures the frequencies that are absorbed or transmitted by the sample. This data is then transformed into a spectrum that acts as a unique "fingerprint" for the material. Confirms the presence of bioactive compounds like flavonoids, tannins, and phenols, which are responsible for pomegranate's medicinal properties. Helps characterize the composition for processes like bioethanol or biodiesel production.

Spectral Data for analysis

Peak position (cm^{-1})	Functional Group / Assignment
3920.42cm^{-1} to 3823.46cm^{-1}	O −H stretching frequency (alcohol)
3333.34cm^{-1} to 3823cm^{-1}	C−H Stretching frequency of phenolic OH (alcohol, phenol)
2926.67cm^{-1} to 2362.58cm^{-1}	C−H stretching frequency (alkane)
1715.84cm^{-1} to 1606.35cm^{-1}	C=O stretching frequency (amide)
1444.35cm^{-1} to 1320.99cm^{-1}	C=O stretching frequency (alkenes)
1216.84cm^{-1}	C=O stretching frequency (alcohol, ester, acid)
1016.44cm^{-1} to 755.94cm^{-1}	C−H stretching frequency (benzene, alkenes)

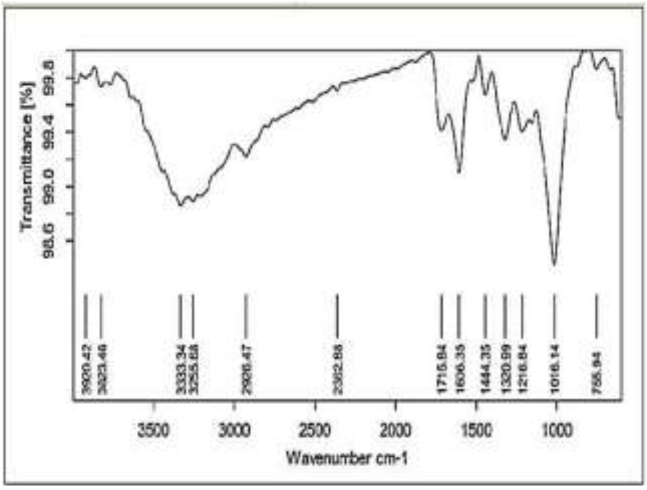


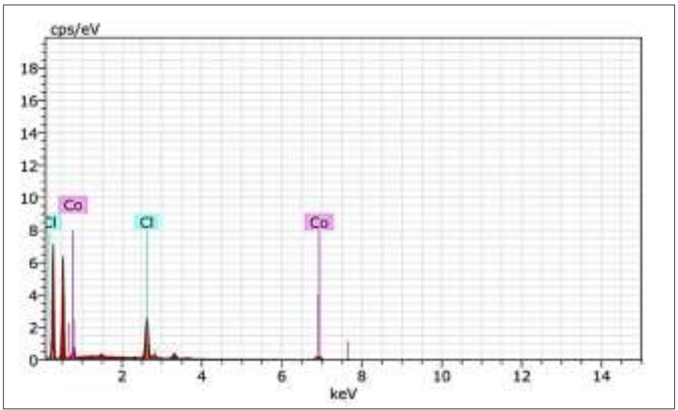
Fig 1: FTIR Spectrum of Punica grantanum fruit peel powder

b. EDX Analysis:

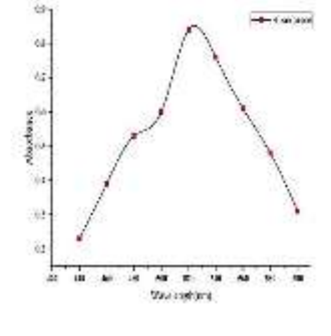
The highest contribution is from Chlorine (Cl, ~13.07wt.%) → This indicates that your material is oxide-rich (probably a metal oxide surface).
Cobalt (Co~9.72wt.%) → Present in a small but significant amount. It may come from a mineral or a compound in the material.

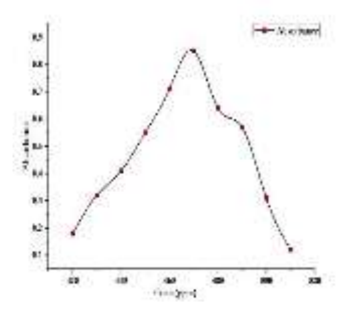
"The EDX analysis of the sample shows a dominant presence of chlorine (13.07wt.%), confirming that the material is largely composed of oxides. Cobalt (9.72wt.%) was also detected, which may indicate the presence of potassium compounds or minerals. The peaks in the spectrum correspond to the characteristic X-rays of these elements, with chlorine showing the highest intensity.

Fig 2. EDX analysis of after removal of Co(II) metal ion adsorbent



c. UV Visible





UV Visible Spectra of Plant extract of *punica grantanum* show maximum absorbance at 510 nm	UV Visible Spectra of aqueous solution of Co(II) show maximum absorbance at 470 nm

Removal of Heavy Metal Co(II)

a. Effect of Adsorbent dosages: In this study, after transferring 10 ml of cobalt chloride solution having concentration of 20, 40, 60, 80,100 ppm is taken in 100 ml conical flask and adsorbent dose is varied 0.5g with keeping all other Conditions constant. The outcome obtained indicates that the absorbance of cobalt increases with increasing concentration dose at 0.5g, absorbance of cobalt decreases. The maximum absorbance of cobalt was observed 0.57with an adsorbent dosage of 0.5g. It is seen that the initial increase in absorbance of cobalt may be due to increase in surface area of the sorbent, thus making it probable that the cobalt ions are adsorbed on to the adsorption sites.

b. Effect of pH: The pH plays an important role on the sorption of adsorbents on the surface of Adsorbate. pH is one of the most important factor that influences surface charge of the adsorbent, degree of ionization and speciation on Adsorbate. In order to establish the effect of pH on the adsorption of cobalt ion on *punica granatum* fruit peel, different pH values were carried out in the range of 2 to 4 or a constant 0.5g *punica granatum* fruit peel dose and initial metal ion concentration of 20, 40, 60, 80,100 ppm for a period of 60 minutes. It is seen that absorbance of cobalt ion shows an increasing trend with increasing pH from 2 to 4. Beyond pH 5, the adsorption was not carried out due to the formation of precipitate at acidic medium. In this study it has been seen that with increased pH, the absorbance of adsorption of Cobalt increased. At low pH, there might be occupation of the negative sites by the H+ which gives to the reduction of the vacancies for the metal ions and it causes decrease in the metal ion adsorption.

c. Effect of Temperature: Temperature is one of the most important factor for the adsorption of cobalt. In this study, the effect of temperature on the cobalt removal was studied in the range of 10-50°C with an initial metal ion concentration 20, 40, 60, 80,100 ppm at pH 4, with 0.5 g adsorbent dose. The solutions were kept for about 60 minutes with 150 rpm shaking. The cobalt removal increased significantly to absorbance 0.57 as the operating temperature was raised to 40°C and minimum 0.5 at 10 °C. Beyond 40°C there is no increase in absorbance of cobalt. When the temperature rises, the pores enlarge and more surfaces will be available for the adsorption of Cobalt (II) ions. At high temperature pores size changes, desolation of cobalt ions and increase in intra particles diffusion it increases the adsorption of cobalt.

d. Effect of Initial metal ion concentration: Initial concentration of metal ions is a crucial parameter as it offers the driving force for overcoming the mass transfer resistance of metal ions between the aqueous and solid phase. The Cobalt (II) ion uptake is particularly reliant on the initial metal ion concentration. The effect of change in adsorption efficiency with initial ion concentration (Table 2). In this experiment initial ion concentration was varied from 20 ppm to 100 ppm treated with 0.5g *punica granatum* fruit peel dose, at pH 4 for 60 minutes. The graph plotted showed that the concentration increase then absorbance also increases. Adsorption of Cobalt(II) removal using *punica granatum* fruit peel increases from 0.11 to 0.57 on increasing initial Cobalt (II) ion concentration up to 100 ppm. The results indicate that the metal ion uptake tends to saturate as the initial concentrations increased. At higher concentration, metal ion diffuses to the adsorbent surface by Intraparticle diffusion and the hydrolysed ions diffuse at a slower rate decreasing the absorbance.

Table 2. Effect of metal ion concentration on absorbance of Cobalt(II)

Concentration (ppm)	Absorbance before adsorption	Absorbance after adsorption
20	0.16	0.11
40	0.33	0.22

60	0.40	0.34
80	0.64	0.47
100	0.80	0.57

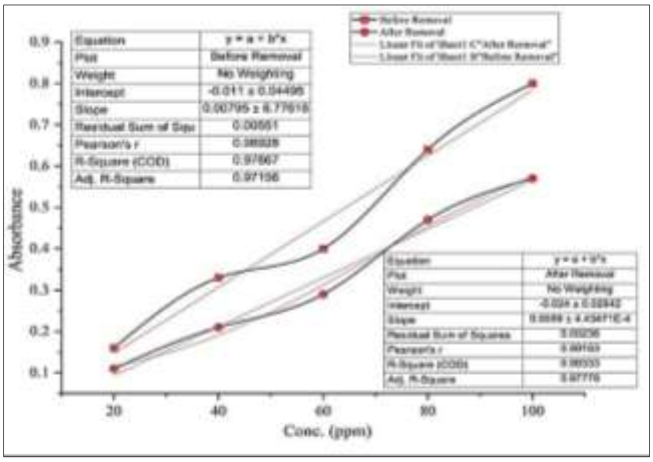


Fig 4.2: Removal of Heavy Metal Co(II) show after and before removal absorbance

4. CONCLUSIONS

The green synthesis of natural adsorbent using pomegranate shell residue was confirmed by the formation of a brownish residue. UV-Visible analysis of pomegranate shell extract show maximum absorbance 510 nm, and 470 nm for aqueous solution of Co(II) metal ion. The EDX analysis of the sample shows a dominant presence of Cl is 13.07 wt.%, confirming that the material is largely composed of oxides., Co is 9.72 wt.% was also detected, which may indicate the presence of chlorine compounds or minerals. A trace level of Co(II) is 0.51 wt.% is observed. The conc. of aqueous solution Co(II) is 20, 40, 60, 80, 100 ppm. Absorbance of before removal of Co (II) is 0.16, 0.33, 0.40, 0.64, 0.80. After removal of Co (II) absorbance is 0.11, 0.22, 0.34, 0.47, 0.57.Slope and R^2 of before removal of Co(II) is 0.00795 ± 6.77618 and 0.97156 And Slope and R^2 of after removal of Co(II) is 0.0059 ± 4.43471E-1 and 0.98922. The EDX was confirmed the presence of Cobalt(II) is 9.72%.

REFERENCES

1. B.A.M. Al-Rashdi, D.J. Johnson, N. Hilal (2012) Removal of heavy metal ions by nanofiltration a centre for Water Advanced Technologies and Environmental Research (CWATER). http://doi.org/10.1016/j.desal.2012.05.022
2. Nirav P. Ravala, Prapti U. Shah, Nisha K. Shah (2016) Adsorptive removal of nickel(II) ions from aqueous environment: A review, Journal of Environmental Management 179 (2016) 20 http://dx.doi.org/10.1016/j.jenvman.2016.04.045
3. Bashar Qasim (2024) Simultaneous Determination of Lead and cadmium in Environmental Samples Using Zinc-diethyldithiocarbamates ,Baghdad Science Journal https://doi.org/10.21123/bsj.2024.5749
4. Dipesh Chandra, Md. Tamzid Hossain Molla, Md.Abul Bashar, Md. Suman Islam & Md. Shameem Ahsan (2023) Chitosan-based nano-sorbents: synthesis, surface modifcation, characterisation and application in Cd (II), Co (II), Cu (II) and Pb (II) ions removal from wastewater, scientific reports https://doi.org/10.1038/s41598-023-32847-3
5. Mesfn Yimer, Shaguf Naz Ansari, Biniyam Abdu Berehe1, Krishna Kanthi Gudimella, Gangaraju Gedda,Wubshet Mekonnen Girma, Nazim Hasan and Shadma Tasneem (2024) Adsorptive removal of heavy metals from wastewater using Cobalt-diphenylamine (Co-DPA) complex, BM chemistry https://doi.org/10.1186/s13065-024-01128-z
6. H. Saada,, F. Charrier-El Bouhtoury, A. Pizzi, K. Rode, B. Charrier, N. Ayeda, (2021),Characterization of pomegranate peels tannin extractives ,Industrial Crops and Products 40 (2012) 239–246. http://doi:10.1016/j.indcrop.2012.02.038
7. Harshal S Kharde1, Champa Maurya2, Haribhau R Aher3, (2024), Removal of Cobalt Metal Ion from Aqueous Solution using Punica granatum Stem Powder as biosorbent, Journal of Advanced Scientific Research. https://doi.org/10.55218/JASR.2024150402
8. Jonas Bayuo, Kenneth Bayetimani Pelig-Ba1,Moses Abdullai Abukari, Adsorptive removal of chromium(VI) from aqueous solution unto groundnut shell, Applied Water Science (2019) 9:107. https://doi.org/10.1007/s13201-019-0987-8
9. H. Saeed, F. S. Chaudhry, S. Rehman, Z. Rashidl, A. Ijaz, J. A. Awan, (2016), Removal of Toxic Metallic Ions Cr(VI), *Punica granatum* Cu(II), Ni(II), Co(II) and Cd(II) from Waste Water Effluents of Tanneries by Using (Pomegranates) Membrane , Iranica Journal of Energy and Environment 7(1): 52-57. https://doi.org/10.5829/idosi.ijee.2015.07.01.08
10. Rusol Maki, Bashar Qasim(2023), Potassium Hydroxide Activated Peanut Shell as an Effective Adsorbent for the Removal of Zinc, Lead and Cadmium from Wastewater, Journal of Ecological Engineering, 24(1), 66–78. https://doi.org/10.12911/22998993/15600
11. S. J. Cobbina1, A. B. Duwiejuah, A. K. Quainoo, (2018), Single and simultaneous adsorption of heavy metals onto groundnut shell biochar produced under fast and slow pyrolysis, International Journal of Environmental Science and Technology, https://doi.org/10.1007/s13762-018-1910-9
12. Muhmmad Arslan Hameed, Shahid Rehman, (2020), Pomegranate Peel Treated With Different Chemicals as Novel Biosorbent of Heavy Metals such as PB, CD, From Tanneries Effluents, Journal of Advanced Chemical Engineering. https://doi.org/10.35248/2090-4568.20.10.194

BIOGRAPHIES

Dr. Harshal Sukhalal Kharde
Assistant Professor, Department of Chemistry, Padmashri Vikhe Patil College of Arts, Science and commerce, Pravaranagar. Maharashtra, India