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Chemo-thermal Treatment of *Tribulus tresstris* to Enhance Its Sequestering Potential for Adsorption of Some Heavy Metals from Aqueous Media: Kinetic and Thermodynamic Study

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Abstract

The plant based renewable biosorbents have extensively been investigated for removing water pollutants. The present study describes the sequestering of metal ions by exploiting a low cost biomaterial derived from *Tribulus tresstris* as sorbent. The batch equilibrium studies have been carried out both with raw and chemically/thermally treated biomaterial as a function of pH, contact time, shaking speed and shaking time to decide the effectiveness of biosorbent. The sorbent was activated chemically by utilizing 0.1M HCl and 0.1M K_2CO_3. A close muffle furnace was used for thermal treatment of the sorbent. The adsorption capacity was enhanced to 25% by thermal treatment and 54% by chemical treatment because of increase in pore volume and surface area. The greatest sorption was found for particle size of 200 μm with a 0.5 g dosage at pH 6 for 20 min at shaking speed 100 rpm. The FT-IR and SEM study was performed to discover the adsorption capacity of various functional groups and their binding mechanism. The adsorption data demonstrates that Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were very much fitted to describe the adsorption behavior.

Keywords: Biosorption, Metal ions, *Tribulus tresstris*, Freundlich, Langmuir and Dubinin–Radushkevich isotherms.

Introduction

Metallic species discharged to our ecosystem by different mechanical and innovative exercises of individuals and industries enter into food chain and cause irreparable continuous damage to natural ecosystems. Aside from scattered wellsprings of metals, expansive convergences of heavy metals enter in the environment from industrial activities due to inefficiencies built in technological activities. Life of individuals in addition to animals is being antagonistically influenced by the exceptionally harmful pollutants [1]. Today the major ecological pollutants are heavy metals (Co, Hg, Zn, Cr, Pb, As, Cu, Ni, Cd, and Sn), and radioactive metals (Am, U, Th, Ra) [2]. Various ventures like mining, refining, metal electroplating, manures and pesticides enterprises release substantial metals containing waste to ecosphere. Other critical sources of such kind of heavy metal wastes are photography, electrolysis, leather industries and nuclear installations. These metals are polluting the environment and posing a direct danger to human well being. The presence of toxic

metals in the aqueous media above the tolerance levels is responsible for accumulative poisoning cancer, and brain damage. The compounds of lead are very toxic to humans and cause adverse health effects such as anemia, encephalopathy, hepatitis, and nephritic syndrome. Hence it is essential to remove these metal ions from wastewater before being discharged into an aquatic environment [3]. There are various conventional methods like precipitation, oxidation reduction, ion exchange, filtration, electro chemical processes, evaporation, reverse osmosis and membrane separation for this purpose. However, these methods are considered to have several disadvantages such as low selectivity, high cost, incomplete separation, high energy consumption and generation of toxic byproducts. The problems can be overcome by bio-sorption of metal ions on selected bio-sorbents. In this way, expulsion of these metals from wastewater is more efficient and economical. Bio-sorption of heavy metals is not just single mechanism based anyway it is influenced by several mechanisms that differ qualitatively and quantitatively according to the species used and their processing. A large number of bio-materials have been investigated to remove pollutants from aqueous media [4].

The sorption relies on the presence of various types of functional groups such as $-NH_2$, $-OH$, $-COOH$, $-CONH_2$, $-SH$ which are available in bio-sorbent for sequestering the overwhelming metal ions [5, 6]. In any case, the presence of such useful groups sometime does not ensure their availability for sorption, might be because of steric hindrance or conformational %. The current study deals with investigation of the bio-sorption potential of *Tribulus tresstris* as bio-sorbent because it is wide spread plant and cheap.

Materials and Methods
Preparation of biosorbent

Tribulus tresstris (TT) was collected from the vicinity of Sargodha, Punjab, Pakistan and was authenticated in the Department of Botany, University of Sargodha. The plants were washed with distilled water for removal of various impurities, followed by drying at 110° C. The dried plant material was crushed and sieved to achieve particles of different sizes, i.e. 50, 100 and 200 μm.

Chemical treatment of tribulus tresstris (CATT)

The 10 g sample of uniform particle size was mixed with 20 mL 0.1M HCl and filtered. Then sorbent was treated with 0.1 M K_2CO_3 solutions and finally repeatedly washed with distilled water to remove residual HCl and K_2CO_3. The neutralized sample was dried and stored for further use.

Thermal treatment of tribulus tresstris (TATT)

The thermal activation of samples was performed utilizing Closed Muffle furnace (Phoenix, Sheffield, England 1983) at temperature extending from $100 - 200 \ ^{\circ}C$ and heating rate of 10 $^{\circ}C$/min under nitrogen stream of 500 mL/min for 5 h to increase the surface area of biosorbent.

Scanning electron microscopy (SEM)

By focusing a light energy of electron, a variety of signals are produced at the surface of solid sample. The SEM image gives data about morphology/composition, compound structure and crystalline nature of sample.

Fourier transform infrared (FTIR) spectroscopy

IR spectra of raw and treated bio-sorbent sample were recorded by KBr pellets technique using FT-IR spectrophotometer (prestige 21 Shimadzu). A significant change in the intensity and frequency of the functional groups on adsorbent surface was observed by FT-IR analysis of raw and activated samples [Fig.1-3]. This technique is a fast and non-destructive for identification of molecules using very small amount of sample [7].

Analysis of metal ions

AAS (Atomic Absorption Spectrometer, AA-6300 SHIMADZU) was used to analyze the metal ions in the solution. The concentration of metal ions was determined by their λ max values prior and then afterward each addition of bio-sorbent. For a typical metal ion, the light source utilized was a hollow cathode lamp with their current value 15 Ma. The analyses for each metal cation was carried out in triplicate and mean qualities were adjusted.

Results and Discussion
FTIR analysis of raw TT CATT and TATT

FT-IR spectrum of raw TT indicates that the structure of TT is relatively complex due to presence of several functionalities. The FT-IR spectra of raw TT and activated TT are shown in Fig.1-3. FT-IR spectra of raw TT and CATT are not much different which shows that treating biomass with mild acids does not induce significant changes in surface structure.
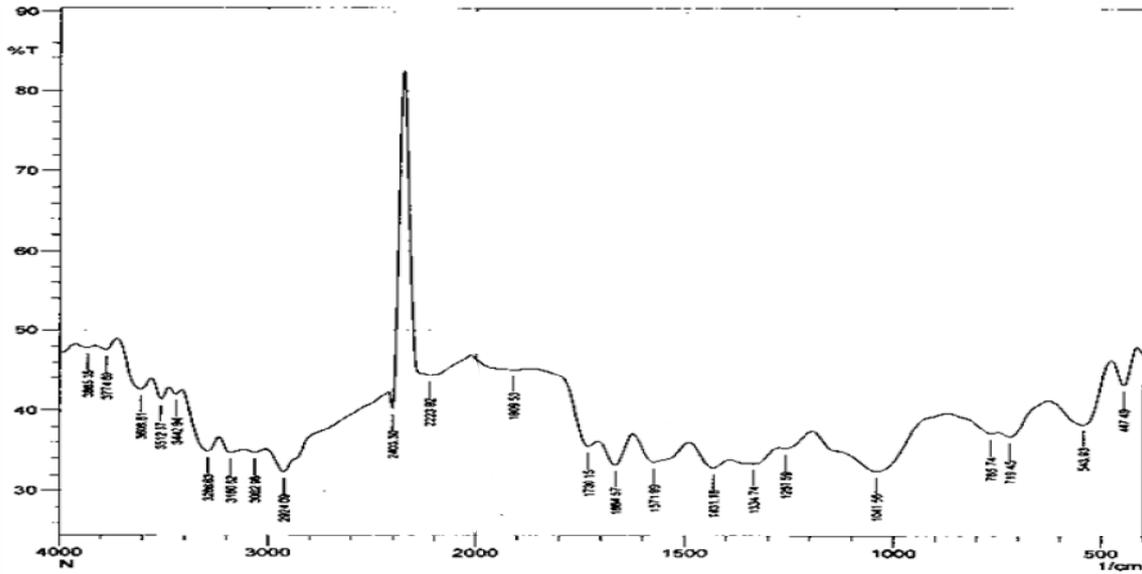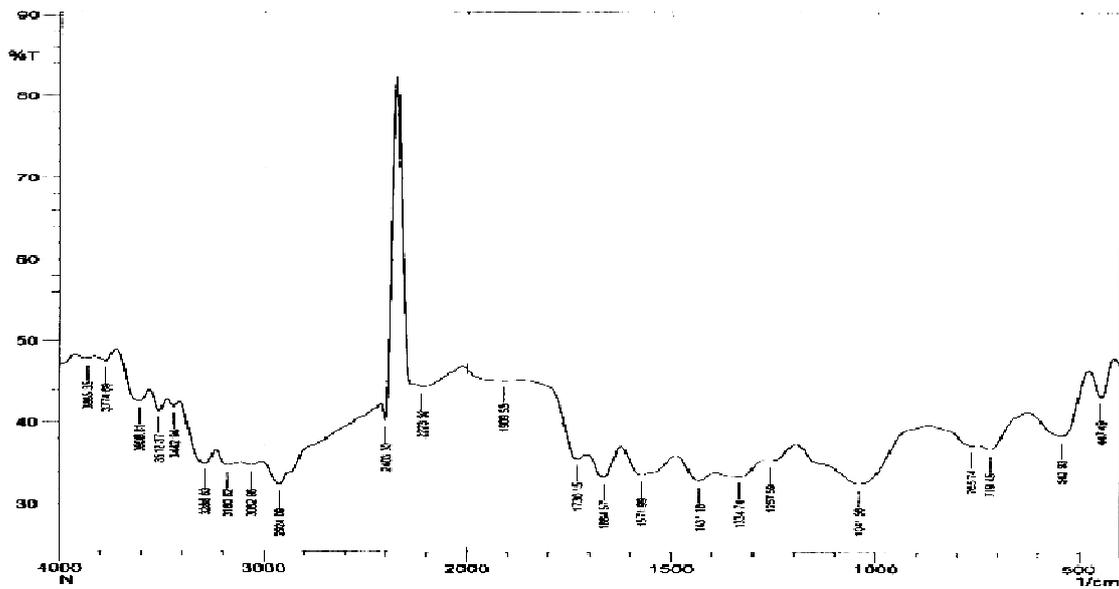

Figure 1. **FT-IR Spectrum of Raw TT**
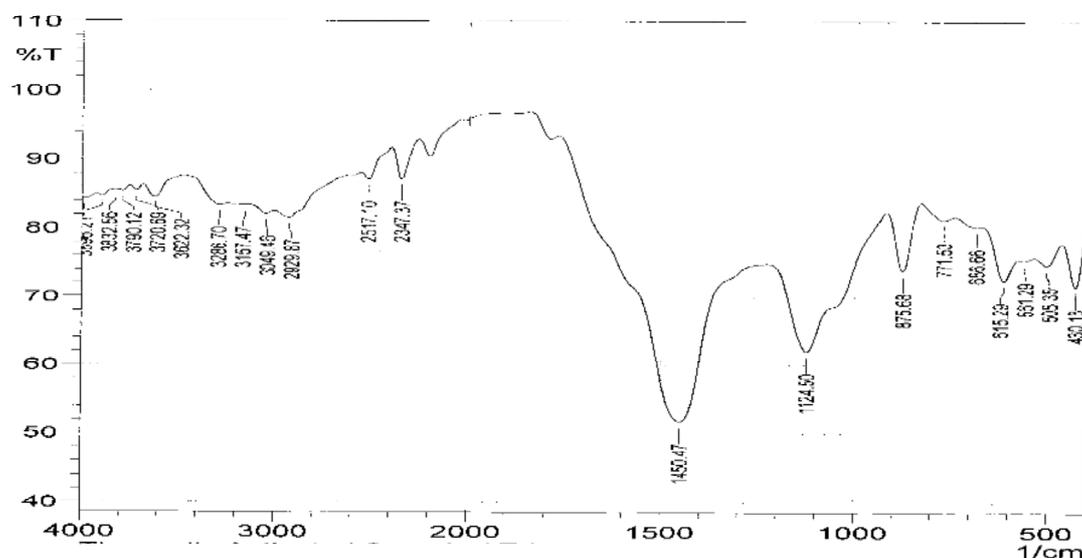

Figure 2. **FT-IR spectrum of CATT**

Figure 3. **FT-IR spectrum of TATT**

A peak around 3296.35 cm^{-1} in raw TT, indicating free and hydrogen bonded –OH functional groups normally found in cellulose. This shifting of peak in activated sample to 3290.56 cm^{-1} shows deformity in the structure of –OH groups more suitable for adsorption (Table 2). The % peak at 3057.17 cm^{-1} in raw sample, can be weak stretching to stretched aromatic =C-H, and C=C groups. However, it is shifted to 3037.89 cm^{-1} in activated samples which can be attributed to deformation in structure, better for adsorption. In thermally treated samples, these peaks become weaker and shifted to 3049.46 cm^{-1} attributed to deformation however; lesser as compared to chemically activated peak at 2918.30 cm^{-1}, indicates –C-H stretching of alkanes for methylene or methyl groups while it's appearance at 2916.37 cm^{-1} and 2920.23 cm^{-1} in chemically and thermally activated samples respectively, suggesting minute changes.

The C=O peak is visible around 1734.01 cm^{-1} can be attributed to lignin aromatic groups with its shift to 1674.21 cm^{-1} in CATT sample which might be due to conjugation in the carbonyl functionalities. This conjugation may be due to adsorption in CATT sample.

The peaks around 1039.63 cm^{-1} and 1029.99 cm^{-1} indicate silyl ether linkage (Si-O-Si)

in raw as well as CATT sample, while appearance of peak at 1103.28 cm^{-1} can be assigned to Si-O-C linkage. More prominent peaks are seen in raw sample as compared to activated sample, as adsorption potential might have been reduced in untreated sample due to strong vibrational frequencies (Table 2).

Table 2. **Absorbance study of treated and untreated samples of TT.**

Adsorbent	-OH	C=C, =C-H	-C-H	C=O	Si-O-Si	Si-O-C
Raw TT	3296.35	3057.17	2918.30	1734.01	1039.63	--------
CATT	356290	3037.89	2916.37	1674.21	1029.99	1103.28
TATT	3288.63	3049.46	2920.23	--------	----------	1104.29

Scanning electron microscopy (SEM)

The SEM pictures of raw and treated sample are shown in Fig. 4-5. An expansion in pore volume was seen in activated material. An increase in the percentage of activated carbon was found in treated samples being best wellspring of bio-sorption. This study is useful for investigating the metal binding to sample. It actually decides the change that happens in surface morphology. After metal binding, changes happen in cell wall composition which gives best information about the distribution of various elements on the sample surface. This system is likewise utilized for qualitative estimation of surface structure [8].
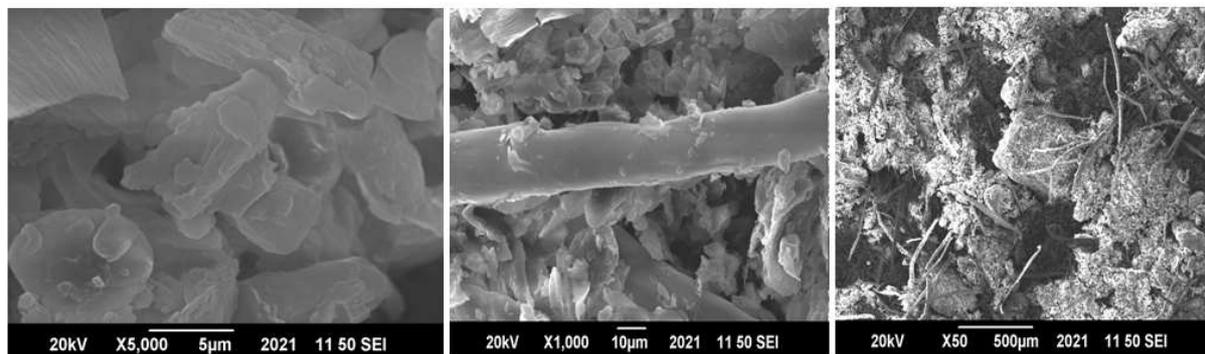
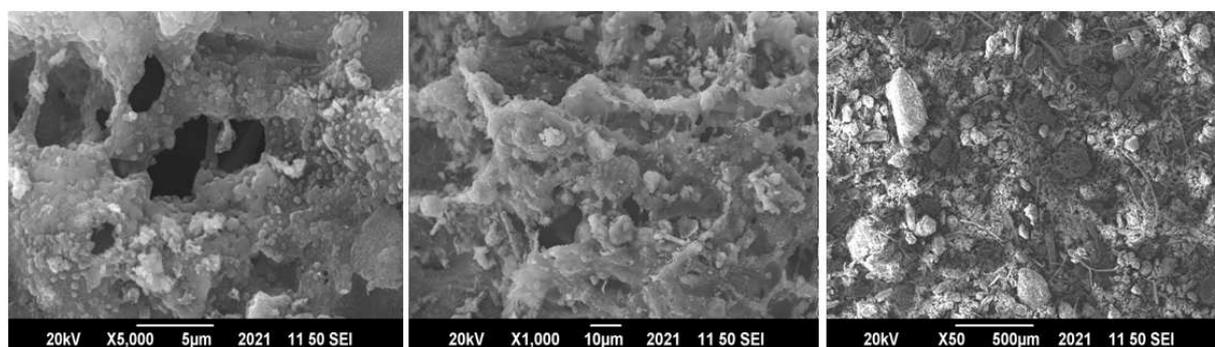*Figure 4.* **SEM images of raw TT (L →R) at 50 and 100 and 200 μm**

Figure 5. **SEM images of TATT (L→R) at 50, 100 and 200 μm**

Measurement of porosity

The pore capacity of sample was determined by centrifugation method [9]. Approximately 10 g of treated sample was immersed in deionized water and centrifuged at 1300 G. The centrifuged sample was accurately weighed and then dried again for about 18 h at 100 ^{o}C and reweighed. The water retention value was calculated using equation,

WR (%) = 100 × Centrifuged weight - Dried weight/dried sample

The WR (45 %) was calculated by sample of particle size 200 μm and maximum WR value (64%) was detected for thermally treated sample of same particle size. Therefore this sample was selected for adsorption of metal ions; where RW may increase because of interaction of these metal ions with different groups of activated sample. Therefore, the adsorption percent was increased up to more than 90 %.

Effect of sorbent particle size on percent sorption

The effect of sorbent particle size on % sorption was used to determine the adsorption potential of various metal ions, e.g. Pb, Ni and Co [Fig. 6]. Three different sized samples, e.g. 50, 100 and 200 μm were used for this purpose. The maximum sorption potential was found for particle size of 200 μm. Therefore, further studies were conducted using the sorbent of particle size 200 μm. This increase in sorption potential can be attributed to increase in surface area (Fig. 6).
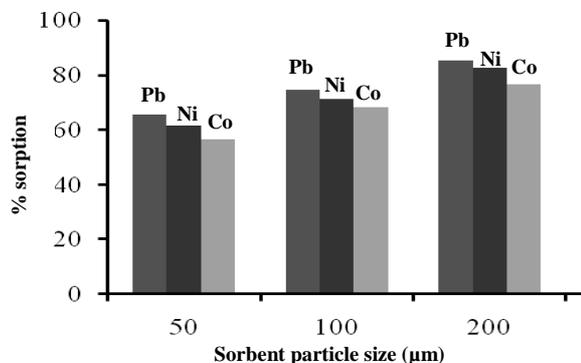

Figure 6. **Effect of sorbent size on sorption**

Effect of chemical and thermal treatment on sorption

The effect of thermal and chemical activation on the efficiency of activated TT is shown in Fig.7.The sorption capacity was increased to 25% in TATT and 54% in CATT. This increase was due to increase in pore volume and surface area of sample that ultimately increased the sorption potential.
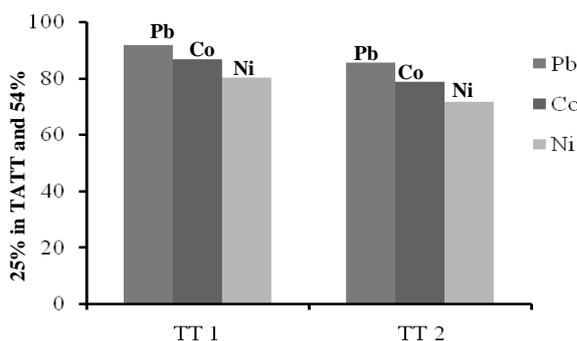

Figure 7. **Effect of chemical & thermal treatment on sorption**

Effect of pH on % sorption

The pH has a vital role on sorption of metal ions in the sorption process. The pH range of 1-10 was elaborated to study its effect on the sorption of Pb, Co and Ni at shaking time 20 min 100 at rpm shaking speed. Studies were carried out by taking 0.5 g of sorbent in solution of metal ion with concentration of 12 ppm. The sorption potential was increased by increasing the pH up to 6 and decreased slightly after pH 6 and then became constant (Fig.8).Therefore pH 6 was considered to be optimum condition for maximum sorption.
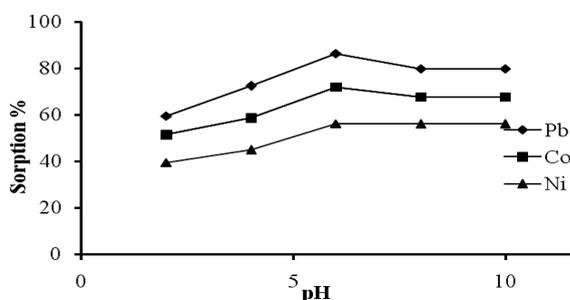

Figure 8. **Effect of pH on % sorption**

Effect of contact time on % sorption

It was seen that the rate of sorption was increased by increasing the contact time until the equilibrium was achieved. Initially a rapid increase in sorption shows extra cellular binding, no further increase indicates the possibility of monolayer coverage by metal ions on the surface of adsorbent [10]. By keeping the same conditions as for pH study, effect of contact time (5-40 min) was noted (Fig. 9) and for the maximal sorption of metal ions 20 min were found to be optimal. The maximum sorption of Pb, Co and Ni ions observed was 89.45%, 82.47% and 75.85% respectively.
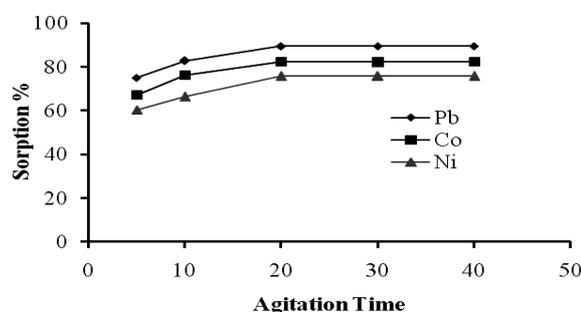

Figure 9. **Effect of contact time on sorption**

Effect of shaking speed on % sorption

The sample material was shaken in order to enhance the interaction between the adsorption site of bio-sorbent and metal ions in the solution. By taking the sample under same condition, effect of shaking speed from 25-200 rpm was noted (Fig.10) and sorption was increased by increasing shaking speed and became maximum at 100 rpm. It was found that by increasing the shaking speed, the turbulence increases which in turn increases the metal adsorption ability.
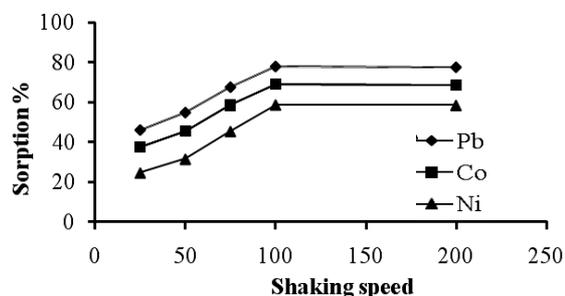

Figure 10. **Effect of shaking speed on sorption**

Effect of sorbent dose on % sorption

The effect of adsorbent dosage on adsorption of metal ions was studied using different doses in the range, 0.1–0.9 g/100 mL (Fig. 11). The metal ion concentration in each case was recorded and it was found that adsorption efficiency is highly dependent on quantity of adsorbent added. Maximum removal of ions was recorded at dose 0.5 g and it was expected that as the concentration of adsorbent was increased, more active sites became available for metal ions uptake. Similar bio-sorbent dose behavior for all metal ions for adsorption was observed on various adsorbents. At higher adsorbent dosage efficiency was decreased, which can be explained by the partial aggregation of adsorbent that results in the decrease in an effective surface area hence lower metal ions uptake [11]. Therefore, the optimum dosage was selected as 0.5 g.
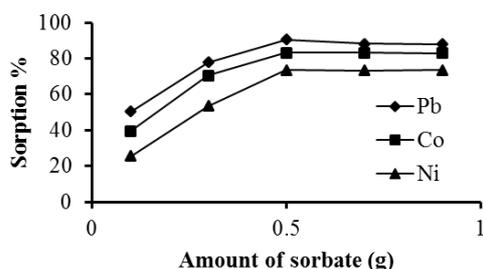

Figure 11. **Effect of sorbent concentration on sorption %**

Biosorption isotherms

The bio-sorption process is evaluated by the analysis of equilibrium data. The sorption isotherms obtained from equilibrium indicate relationship between the sorbate and its amount accumulated on the sorbent surface. Freundlich and Langmuir bio-sorption process was evaluated first time by Dubinin-Radushkevich models.

Freundlich isotherm

The Freundlich isotherm is expressed in eq-1

$$\text{Log } C_{ads} = \log C_m + 1/n \log C_e \qquad \text{(eq-1)}$$

Where, adsorption capacity and intensity is represented by constant parameters C_m and n. A plot of log C_{ads} and log C_e gives a straight line (Fig. 12). From this plot log C_m can be deduced from intercept however, value of n can be obtained from the slope. The energies and distribution sites are assumed as exponential and the surface of biomass is considered as heterogeneous in this isotherm [12].
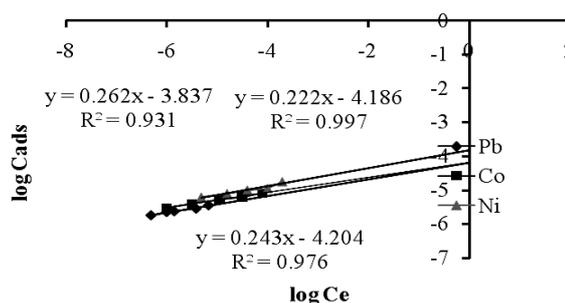

Figure 12. **Freundlich plot for Pb, Co and Ni, TT = 0.5 g, [Pb] =0.02-0.01x 10^{-4} M, [Co] = 0.03-0.87 x 10^{-4} M, [Ni] = 0.11-1.02 x 10^{-4} M, Agitation time = 20 min, Agitation speed = 100 rpm, T = 25 °C.**

In the plot log C_e versus log C_{ads} for Pb, Co and Ni a straight line is shown in Fig. 15. The values of 1/n were found to be 0.24, 0.22 and 0.26 for Pb, Co and Ni respectively from slope of the straight line. These values being <1 indicate that better sorption at a low concentration of sorbate while values of C_m were deduced from intercept are shown in Table 3.

Table 3. **Freundlich constant for Pb, Co, and Ni.**

Freundlich Isotherm Constants			
Sorbate	Cm (m mol g⁻¹)	R²	n
Pb(II)	0.0624	0.976	4.1087
Co(II)	0.0651	0.997	4.2042
Ni(II)	0.1383	0.925	3.8952

Langmuir isotherm

Langmuir isotherm gives information about maximum adsorption in the form of single layer of the sorbate molecules on the surface of bio-sorbent. It gives an idea about the energy involved in the process of desorption and found to be constant showing that after attachment on the surface the site of the adsorbate is not changed

[13]. The mathematical form of Langmuir isotherm is given in equation eq-2

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \qquad \text{(eq-2)}$$

This is the linear form of equation. In this equation metal ions attached to the surface (mg/g) are expressed by $qe(C_{ads})$, and metal ions concentration (mgL^{-1}) at equilibrium is given by Ce, Q_o and b are the constants which express the maximum capacity of absorbance and energy. A plot of Ce/qe and Ce gives a straight line at a given temperature (Fig.13). The R_L an equilibrium parameter is basically dimensionless quantity explained by *eq-3* is an important property of the isotherm.

$$R_L = \frac{1}{(1 + bC_o)} \qquad \text{(eq-3)}$$

The favorability of isotherm can be deduced from R in the way as, if (*R*>1) the type of isotherm is unfavorable, if (*R*= 0) % is linear, it is favorable if (0 < *R* <1) and is irreversible if (*R* = 0) [14]. Langmuir considered sorption process as a chemical phenomenon [14].
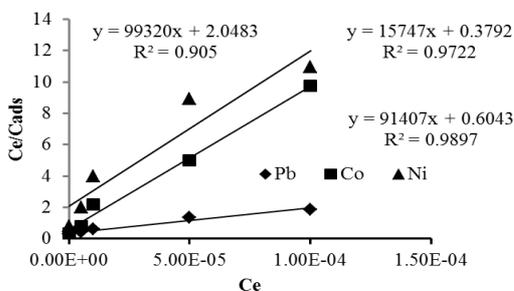
Figure 13. **Langmuir plots for Pb, Co and Ni, TT = 0.5 g, Pb = 0.02-0.01 x 10^{-4} M, Co = 0.03-0.87 x 10^{-4} M, Ni = 0.11-1.02 x 10^{-4} M, time = 20 min, speed = 100 rpm, T = 25 °C**

The plots of Log Ce/Cads versus Ce for Pb, Co and Ni are shown in fig 4.13. These plots gave straight lines and the values of various parameters deduced from graph are tabulated in Table 4. These values show that the bio-sorption process is well obeyed by Langmuir model. The values of R_L are ranged between 0.07-0.25, 0.05-0.56 and 0.11-0.70 for Pb, Co and Ni, respectively.

These values fulfill the criteria of (0 < *R* <1), which indicates that TT is well suitable for the bio-sorption of divalent cations like Pb, Co and Ni. The Langmuir model also suggests that each sorbate ion is confined to a specific sorbent site which cannot interact and move across the neighboring molecules [15].

Table 4. Langmuir parameters for Pb, Co and Ni.

Langmuir Isotherms Constants			
Sorbate	*C_m (m mol g^{-1})*	*R^2*	*n*
Pb(II)	0.038096	0.983	1280313.142
Co(II)	0.008424	0.987	191904.9126
Ni(II)	0.018499	0.918	36466.58895

Dubinin-radushkevich isotherm

D-R isotherm was used to evaluate equilibrium data from equation (eq-4).

$$\text{Ln } C_{ads} = \ln X_m - BE_2 \qquad \text{(eq-4)}$$

Where C_{ads} and X_m are sorbed concentration and maximum sorption capacity at the sorbent surface and B is a constant related to sorption energy and E is Polanyi potential (eq-5).

$$E = RT \ln (1 + 1/C_e) \qquad \text{(eq-5)}$$

If a straight line is obtained by plotting ln Cads against E_2 it is considered as D-R isotherm. The slope gives the value of B while values of X_m can be deduced from intercept. The D-R isotherm model finds good application as being very simple its applicability in the concentration ranges from trace to saturated solutions. E is considered as Polanyi potential required to remove ions from sorption space. The volume where sorption takes place near to sorbent surface is fixed according to D-R isotherm. If value of E falls in the range of 8-16 KJ/mol, the sorption can be considered as ion exchange process, if E< 16 KJ/mol then it might be due to contribution of physical forces and if E > 16 KJ/mol then it can be considered as chemical process. The straight line in the plot of ln Cads versus E_2 indicates that D-R isotherm is well obeyed by all concentrations of Pb, Co and Ni (Fig. 14). The slope and intercept of the straight line gives the values of B and X_m, which are given

in Table 5. The sorption energy values of E were found to be 18.13, 17.82 and 16.22 (KJ mol^{-1}) for Pb, Co and Ni respectively showing sorption as a chemical process.
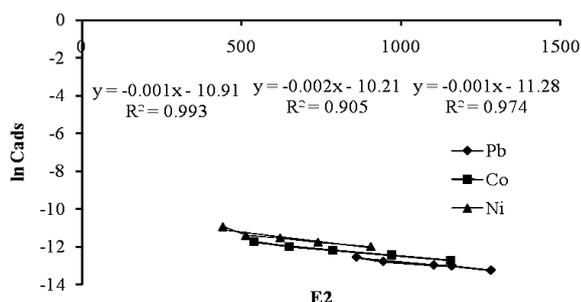
$$E = 1/\sqrt{2\beta} \qquad (eq\text{-}6)$$

Figure 14. **D-R sorption isotherms of Pb, Co and Ni, TT = 0.5 g, Pb = 0.02-0.01 x 10^{-4} M, Co = 0.03-0.87 x 10^{-4} M, Ni = 0.11-1.02 x 10^{-4} M, shaking constant time = 20 min, shaking speed = 100 rpm, T = 25 °C**

Table 5. **D-R isotherm for Pb, Co and Ni on TT.**

Sorbate	D-R Isotherm		
	X_m (m mol g^{-1})	R^2	B
Pb(II)	0.01259	0.974	0.0015
Co(II)	0.01819	0.993	0.0016
Ni(II)	0.0366	0.905	0.0019

Morris-Weber isotherm

M-W model explains intra-particle diffusion sorption process. It is expressed in equation as

$$q_t = R_{id} \cdot t^{1/2} \qquad (eq\text{-}7)$$

Where qt is referred as concentration of sorbed ions (m mol/g) against time t. R_{id} is the intra-particle diffusion rate constant. Sorption mechanism can be predicted by this model for TT by plotting qt verses $t_{1/2}$. In case of a straight line obtained passing through the origin then sorption mechanism can be considered as the diffusion process. The value of R_{id} can be deduced from the slope of the straight line. The results of M-W isotherm are given in Fig.15 and Table 6. Since, the straight line is not passing through origin suggesting that diffusion is not only rate limiting step for the bio-sorption of Pb, Co and Ni [16].

Table 6. **Morris-Weber constant for Pb, Co and Ni.**

Sorbate	M-W Isotherms	
	R_{id}	R^2
Pb(II)	0.410388	0.758
Co(II)	3.260176	0.798
Ni(II)	10.66554	0.803
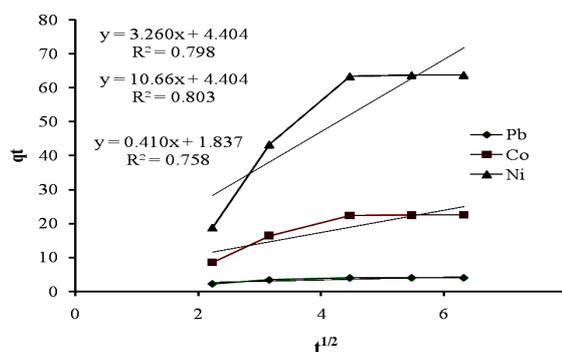
Figure 15. **Morris-Weber isotherms for Pb, Co and Ni, Pb = 0.006 x 10^{-4}, Co = 0.03 x 10^{-4}, Ni = 1.11 x 10^{-4}mol L^{-1}, TT = 0.5, pH = 6, T = 25 °C**

Conclusion

This paper reports that the bio-sorbent potential of TT for removing the heavy metals from aqueous media. The bio-sorption capacity of TT was evaluated considering several effects, e.g. dose rate, contact time, pH, speed of shaking, sorbent size and chemical and thermal treatment. FT-IR spectroscopy revealed the presence of various functional groups present on bio-sorbent surface and SEM revealed the surface morphological changes of bio-sorbent. It was concluded from this study that TT can act as bio-sorbent and can be used for waste water treatment at industrial level to remove the toxic metal ions.

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