Original Research Articles

Equilibrium Isotherm Study for Removal of Mn (II) from Aqueous Solutions by Using Novel Bioadsorbent *Tinospora cordifolia*

ABSTRACT

The removal efficiency of *Tinospora cordifolia* from manganese containing aqueous solutions was investigated. The effect of adsorbent dosages, pH of solution, initial Mn (II) concentration and contact time was investigated using a batch adsorption technique. The optimum pH for Mn (II) adsorption was found as 4.0 for *T. cordifolia*. Results were analyzed by the Langmuir and Freundlich isotherm models using linearized correlation coefficient. The characteristic parameters for each isotherm have been determined. The Langmuir model agrees very well with experimental data than the Freundlich isotherm model. According to Langmuir isotherm, the monolayer saturation capacity (Q_{max}) is 24.69 mg/g at temperature (25±2°C). The FT-IR analysis indicated the involvement of hydroxyl (-OH), aliphatic (-C-H), and carbonyl group (C=O) chelates in metal binding. The biomass was then used for the removal of Pb(II) in synthetic and real wastewater samples from a coal-mine acid industrial wastewater. This study indicated that the biomass of *T. cordifolia* can be used as an effective and environmental friendly adsorbent for the treatment of Mn (II) containing aqueous solutions.

Keywords: Adsorption; Manganese; *Tinospora cordifolia*; FTIR; Wastewater

1. INTRODUCTION

The contamination of water by heavy metals through the discharge of industrial wastewater is a worldwide environmental problem. Heavy metals may come from various industrial sources such as electroplating, metal finishing, metallurgy, chemical manufacturing, mining, battery manufacturing, textile industries etc. Manganese is usually present in groundwater as a divalent ion (Mn^{2+}) and it is considered a pollutant mainly because of their organoleptic properties [1]. Removal of toxic heavy metals including manganese from industrial wastewater has been practicing for several years [2]

Among the toxic heavy metal ions which are present in water, its potential health hazard to aquatic animals and human life, metals such as Pb, Cd, Cr, V, Bi, As, Ni, Hg and Mn are very toxic. Mn (II) concentration in excess of the drinking water standard can result in the formation of oxide deposits in pipelines, discoloration of water and impart an unpleasant metallic taste [3]. The 1958 WHO *International Standards for Drinking-water* suggested that concentration of manganese greater than 0.5 mg L^{-1} or 500 µg L^{-1} would markedly impair the portability of the water [4]. The permissible limit for Mn (II) in wastewater is 2 mg L^{-1} according to [Environment (Protection) Rules VI, 1986] [5].

Toxicity of manganese causes psychological and neurological disorders, pneumonia, bronchitis, nose and throat infection, increased respiration, hyposexuality, tremor of the fingers, muscular rigidity, chronic bronchitis and decrease liver activity. Manganese ethylene-bis-dithiocarbomide is found to be carcinogenic and causes cancer. Divalent manganese has been found to be 2 to 3 times more toxic than trivalent form[6].

At present, a number of technologies can be used to remove heavy metals from the contaminated water such as filtration, chemical precipitation, ion exchange, membrane separation, electro remediation methods etc. However, most of this method might not be efficient in removing heavy metals at very low concentrations and could be relatively expensive, these methods are also not effective due to their secondary effluent impact on the recipient environment [7]. Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater and ground water [8]. Biosorption of metals by biomass has been much explored in recent years. This novel approach is competitive, effective and cheap [9]. Biosorption is a physical-chemical process, simply defined as the removal of substances from solution by biological material, this is a property of both living and dead organisms (and their components) and has been heralded as a promising biotechnology because of its simplicity, analogous operation to conventional ion-exchange technology, apparent efficiency and availability of biomass and waste bio-products [10]. In past years there are various adsorbent were used for removal of Mn (II) in ground water and wastewater including Fly ash [11], Activated carbon [5], Cow Bone Charcoal [12], *Sargassum filipendula* [13], Birbira (*Militia Ferruginea*) [7], Synthesized Chitosan [14], *Nymphaea alba* [15], Activated carbon derived from local agro-residue [16], *Prosopis cineraria* leaf [2], Activated carbon [17], Banana Peel [18] etc.

In the present investigation, the potential of a plant biomass has been assessed for the removal of manganese ion. The effects of various parameters have been studied and the results are presented in this paper.

2. MATERIALS AND METHOD

2.1 Biomass

In this study stem part are used in plant biomass *Tinospora cordifolia*. *T*. *cordifolia* (TC) is a large extensively spreading glabrous, perennial deciduous twiner with succulent stems and papery bark it belongs to family Manispermeace[19].

2.2 Collection and Preparation of the Biosorbent

Biomass was collected from the different areas of Chhattisgarh in India. The collected biomass was dried under sun and cleaned manually. It was washed with distilled water to make it free from dust and impurities. The residual material so obtained was dried at 60°C temperature in hot air oven for few days and then the material was grinded and sieved through 1.18μm, to obtain uniform sized material for experiments. After that, the biomass was stayed inside HCl (0.1M) solution for 30 minutes. Biomass was then filtered (Whatman Filter No.42) and washed with double distilled water till that the washing was neutral. The biomass was then dried in a hot air-oven at 80°C temperature till drying. The acid treatment also helped to remove any previously adsorbed metals. It was presumed that such a treatment will enhance the uptake capacity of the biomass. The biomass was stored in airtight plastic container till further use.

2.3 Chemicals

All chemicals used in this work were of analytical grade and obtained from Merck (India/Germany). All Solutions were prepared with double distilled water. All utensils and bottles utilized in the experiments were washed with 5% HCI solution and rinsed with distilled water. Manganese ions were prepared dissolving its corresponding sulphate salt in double distilled water. The pH of the solution was adjusted with 0.1M HCl and NaOH. All other solutions were prepared from the stock solution.

2.4 Adsorbate Solution

The tests of removal of Mn (II) ions were carried out using synthetic solution obtained starting from sulphate salt of manganese ($MnSO_4$. H_2O).

2.5 Instrumentation

An Atomic Absorption Spectrophotometer AAS4129D, ECIL India, was used for measurement of Mn (II) concentration. The Fourier Transform Infrared Spectroscopy (FT-IR) Thermo Nicolet, Avatar 370 Model FTIR spectrometer in the range 4000-400 cm^{-1} having resolution 4 cm^{-1} was used for FTIR analysis. High precision electrical balance TB-214 was used for weighing. A vacuum filtration pump was used for filtration and a high precision Mettler Toledo AL204 analytical top loading balance was used for weighing and a digital ELICO pH/mv meter model LI-617 equipped with combined electrode was used for the measurements of pH.

2.6 Batch adsorption study

Batch adsorption experiments were performed at a constant temperature ($27\pm2^{\circ}C$). In all sets of experiment using 50 ml of synthetic water sample containing Mn (II) concentration 200 mg L^{-1} was prepared. The pH adjustment of the solution by using 0.1M HCl and NaOH solution and added a calculated amount of adsorbent 1gm $50mL^{-1}$ was thoroughly mixed in 100mL shake flask. The adsorbent in solution was agitated in a rotary shaker at a speed of 150 rpm. Blank solution was treated similarly without the adsorbent under control conditions. After adsorption the mixture was filtered by vacuum filtration pump through 0.45 $\mu\boldsymbol{m}$ Millipore filter paper. The residual concentration of Mn (II) in the solution was determined by Atomic adsorption spectrophotometer. Before analysis, the instrument was initially calibrated using standards of Mn (II) solution. All experiments were performed in triplicate and results are reported as average. The removal percentage and adsorbent capacity of adsorbent were calculated as reported by this formula –

$$Removal\ Efficiency(\%) = [Ci - Ce/Ci]100 \qquad \text{Eq. (1)}$$

Where C_i and C_e are the metal concentration in the sample solution before and after treatment.

The adsorption capacity of an adsorbent which is obtained from the mass balance on the sorbate in a system with solution volume '*V*' is often used to acquire the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacity of the adsorbent for each concentration of Mn (II) calculated using by this formula –

$$qe(mg/g) = \frac{Ci-Ce}{M} \times V \quad \text{Eq. (2)}$$

3. RESULT AND DISCUSSION

3.1 Effect of pH on biosorption

The effect of pH study on the removal of Mn (II) are shown in (Fig. 1). The metal ion are in competition with the protons in the solution at low pH values, for the biosorption on active sites biomass surface [20]. In this batch performance the pH varying from (1-9). When the pH increases upto 1-4, the removal efficiency of Mn (II) increases. After pH 4 they were slightly decreases upto the 7 pH and at higher pH the removal efficiency decreases because of formation of anionic hydroxide complex. So, the removal efficiency was shows maximum 91.1% at pH 4.

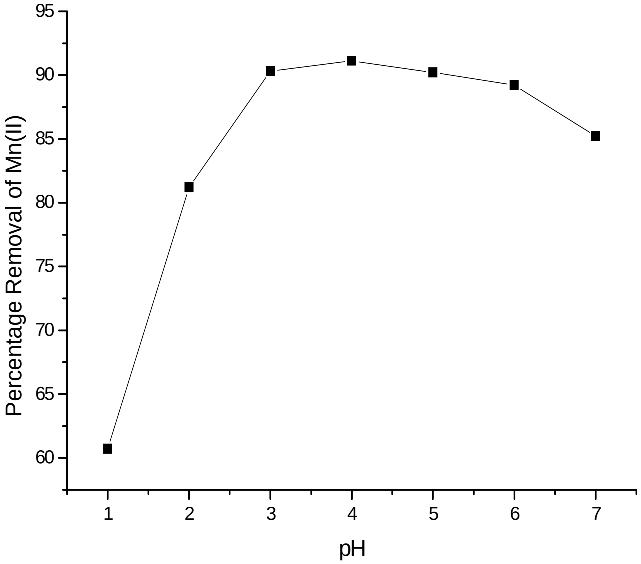

Fig. 1 Effect of pH on the percentage removal of Mn (II) for *T. cordifolia:* Biosorption conditions: C_0 = 200 mg L^{-1}; biosorbent dosage = 1.0 g; temperature = 25±2ºC; rotational speed = 150 rpm; contact time = 30 min

3.2 Effect of initial metal ion concentration on biosorption

The effect of concentration of metal ion on the biosorption was studied by varying the heavy metal concentration, from (50-500mg L^{-1}). In starting the adsorption was increases and then it was stable (Fig. 2). Further, the concentration increases the percentages biosorption was slightly decreases it may be caused by the lack of sufficient surface area to accommodate much more manganese ions available in the solution.

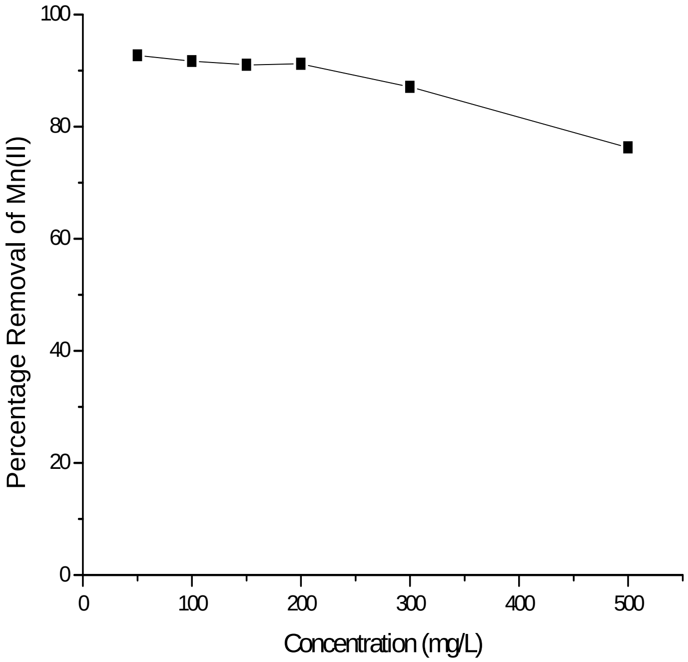

Fig. 2 Effect of concentration on the percentage removal of Mn (II) for *T. cordifolia*: Biosorption conditions: pH = 4.0; biosorbent dosage = 1.0 gm 50mL^{-1}; temperature = 25±ºC; rotational speed = 150 rpm; contact time = 30 min.

3.3 Effect of Adsorbent Dosage

The effect of variation of biomass dosage (0.5-7.0 gm 50mL^{-1}) on amount of metal adsorbed are trend of increment in adsorption capacity with increment in adsorbent dosages. Adsorbent recorded a maximum capacity of Mn (II) removal when using 1gm of the biomass. Further increment of adsorbent dose the adsorbent capacity was decline. The initial increment of adsorbent capacity with increase in adsorbent dosages was expected, since the number of adsorbent particles increase and thus more surface areas were available for metals attachment.

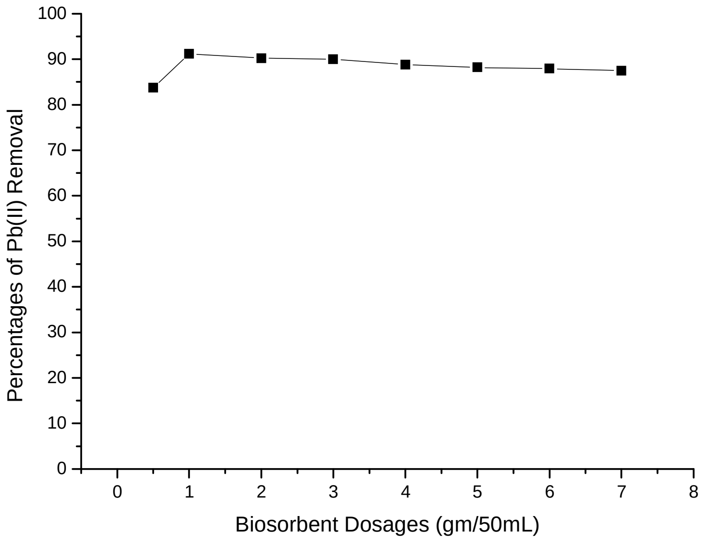

Fig. 3 Effect of adsorbent dosages on the percentage removal of Mn (II) for *T. cordifolia*: Biosorption conditions: pH = 4.0; concentration = 200 mg L^{-1}; temperature = 25±ºC; rotational speed = 150 rpm; contact time = 30 min.

3.4 Effect of Contact Time

The Effect of contact time for the biosorption of Manganese ions on the *T. cordifolia* showed that a contact time of 30 minutes is needed to achieve equilibrium. More than 80% of Mn (II) was removed of the starting 15-20 minutes they can remove 91% Mn (II) in the solution. The biosorption decreases significantly with further increase in contact time.

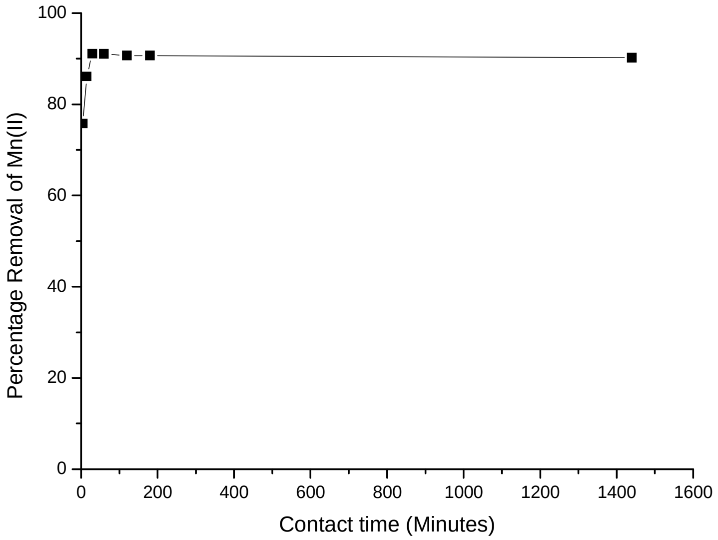

Fig. 4 Effect of contact time on the percentage removal of Mn (II) for *T. cordifolia*: Biosorption conditions: pH = 4.0; concentration = 200 mg L^{-1}; biosorbent dosages = 1 gm mL^{-1}; temperature = 25±ºC; rotational speed = 150 rpm.

4. ISOTHERM STUDY

An adsorption isotherm describes the equilibrium relationship between adsorbent and adsorbate, which is the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. It indicates how the adsorbed molecules get distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Isotherm data were obtained by increasing initial manganese concentration from (50-500 mg L^{-1}).

4.1 Langmuir isotherms

In the present work, Langmuir isotherm model was applied to study the process of biosorption. The Langmuir model is probably the best known and most widely applied adsorption isotherm. This model suggests a monolayer adsorption with a homogeneous distribution of adsorption sites and adsorption energies, without interactions between the adsorbed molecules.The Langmuir parameters were determined from a linearized form of equation represented by-

Langmuir model: $q_{eq} = Q_{max} \times K_L \times C_{eq}/(1 + K_L \times C_{eq})$ Eq. (B.1)

Langmuir model in linear form: $\frac{C_{eq}}{q_{eq}} = \frac{1}{(Q_{max} \times K_L)} + \frac{1}{Q_{max}} \times C_{eq}$ Eq.

(B.2)

Where q_{eq} is the metal amount adsorbed per unit mass of adsorbent (mg/g), C_{eq} is the equilibrium concentration of metal in the solution (mg L^{-1}), Q_{max} is the maximum adsorption capacity (mg/g), and K_L is the constant related to the free energy of adsorption.

The adsorption data used for Langmuir isotherms are given in (Table No. 1). Langmuir adsorption isotherm is plotted by taking C_{eq} versus C_{eq}/q_{eq}. C_{eq} and q_{eq} are the equilibrium adsorbate concentrations in the aqueous and solid phases, respectively and b is the equilibrium constant related to the energy of adsorption.

The Langmuir isotherms for manganese are shown in (Fig. 5). The values of correlation coefficient R^2 were 0.997 which were high and indicated a monolayer adsorption for Mn (II) onto the biosorbent. The important characteristics of the Langmuir isotherm can be described by a separation factor also called as dimensionless equilibrium parameter, the magnitude of R^2 obtained for *T. cordifolia* was 0.977 as the values lie between the 0 to 1, and the adsorption process for manganese seems to be favorable.

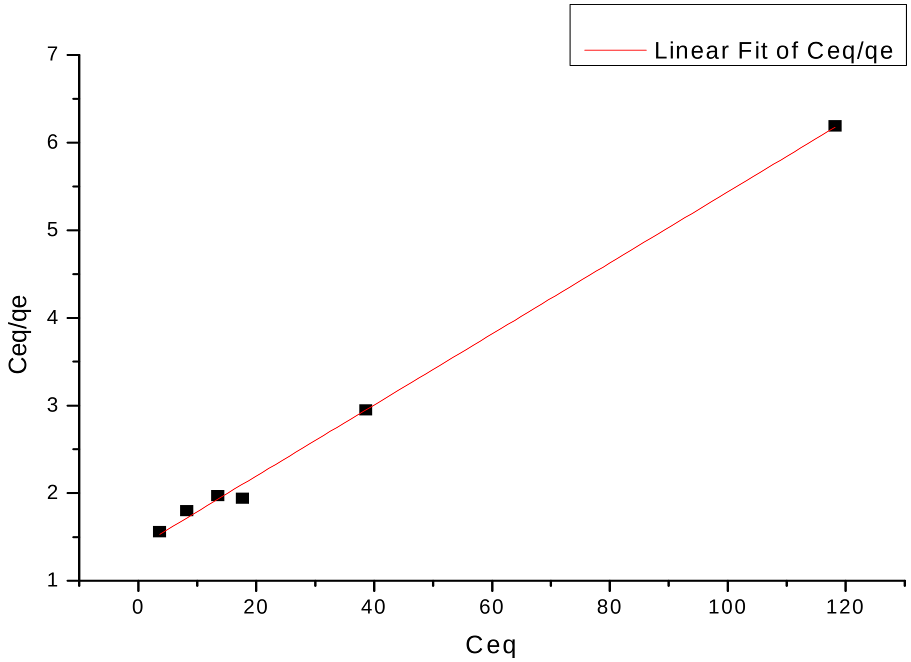

Fig. 5 Langmuir adsorption Isotherm for Batch study

Where - C_{eq} = Equilibrium constant of metal in the solution (mg L^{-1})

q_{eq} = The Metal amount adsorbed per unit mass of adsorbent (mg g^{-1})

4.2 Freundlich isotherms

A Freundlich isotherm is a popular model for a single solute system based on the solute between the solid phase and aqueous phase at equilibrium. It states that the uptake of metal ion occurs on a heterogeneous surface by multilayer adsorption and the amount of adsorbate increases infinitely with an increase in concentration.

The Freundlich equation also has been employed for the adsorption of Mn (II) on the adsorbent. The Freundlich isotherm has been represented as –

$$Log\ S = \left(\frac{1}{n}\right) \log Ce\ + \log K \qquad \text{Eq. (B.3)}$$

Where log S is the metal ion sorbed (mg/g), C_e is the equilibrium concentration of metal ion solution in mg L^{-1}, and K and n were constant. A plot of log C vs log S represents the isotherm and straight line with a slope of 1/n and intercept of log K_f (Fig. 6). K_f and n are the Freundlich constants and represent the adsorption capacity and adsorption intensity respectively. Higher K_f values indicate a greater adsorption capacity. The value of the correlation coefficient, R^2 was 0.941, obtained for *T. cordifolia*. The calculated and experimental values correlate more correctly with the Langmuir values. On the basis of comparison it is concluded that Freundlich model was found suitable to fit the experimental data in the present study.

The values of Q_{max} (mg/g), b (1/mg) K_f, n and R^2 (regression correlate ion coefficient) are evaluated from the Langmuir and Freundlich plot are presented in the (Table No. 1).

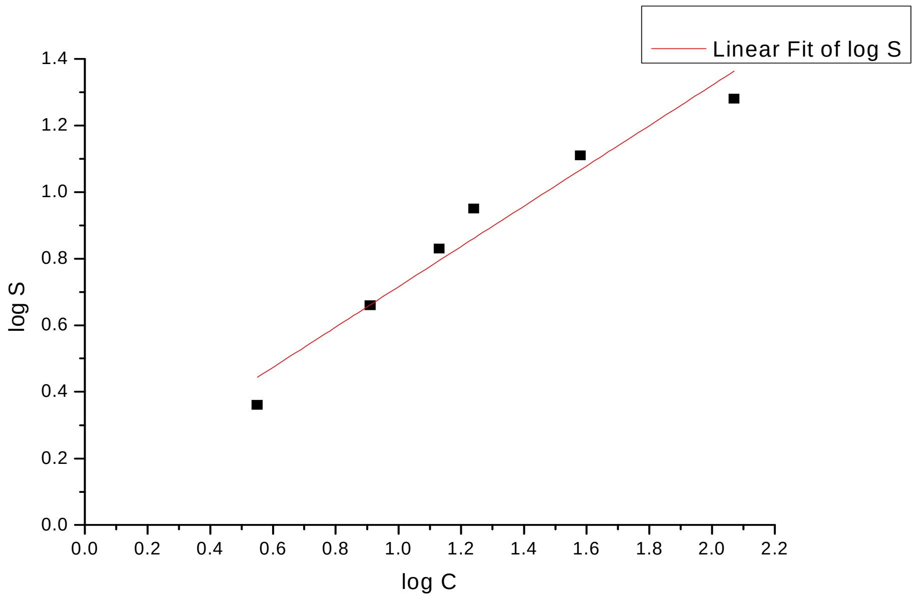

Fig. 6 Freundlich adsorption Isotherm for Batch study

Where - log C = Equilibrium concentration of metal ion solution (mg L^{-1})

log S = Metal ion sorbed (mg g^{-1})

Table No. 1: Langmuir and Freundlich constants and correlation coefficients of isotherm models

	Langmuir Isotherm			**Freundlich Isotherm**		
Temperature (°C)	Q_{max}(mg/g)	K_L(Lmg^{-1})	R^2	1/n	K_F (mg/g)	R^2
27	24.69	0.029	0.997	1.65	1.29	0.941

5. FT-IR (FOURIER TRANSFORM INFRARED SPECTROSCOPY) METHOD

The FTIR spectra of the prepared adsorbents before and after treatment were presented in (Fig. 7). FTIR spectrum of prepared bioadsorbent coming from *T. cordifolia* (constituted by carbohydrates, proteins, lipids, and fibers) was recorded to identify functional groups responsible for the metal ion coordination. The FTIR spectra of the biosorbent and metal ion loaded biosorbent were compared to determine which functional groups (Table No. 2) are responsible for the manganese biosorption. When compare, the two spectra before and after adsorption, spectra from before metal adsorption, the spectra display a number of absorption peaks, indicating the nature of the biomass of *T. cordifolia*. The bands observed at 3419.73 cm^{-1} and 2922 cm^{-1} bonded –OH group and aliphatic -C-H group. The peak around 1637.15 cm^{-1} corresponds to the –C=O group. The peak observed at 1515.53 cm^{-1}, 1431.56 cm^{-1}could be assigned to aromatic -C=C- weak bands, the another peak 1235.23 cm^{-1} and 1074.93 cm^{-1}shows the strong peak of presence of acid and alcohol group.

But after metal adsorption, there were clear band shift and intensity decrease of the band 3420.27 cm^{-1}, 2936.18 cm^{-1} and 1628.77 cm^{-1} etc. According to this observation mainly hydroxyl –OH, aliphatic -C-H and carbonyl –C=O groups are responsible for metal binding to the biomass.

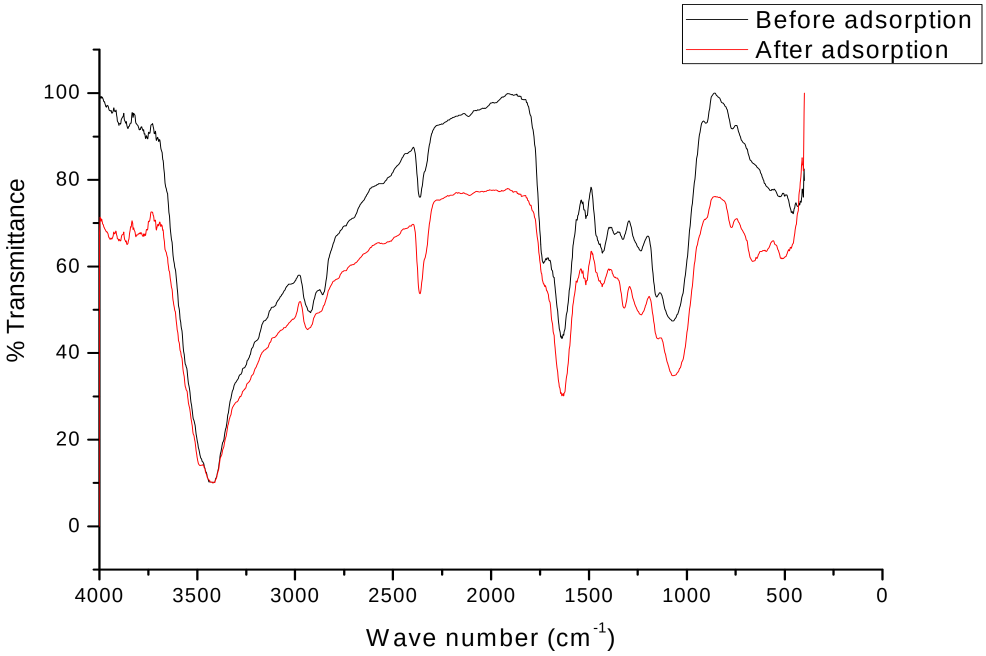

Fig. 7 FTIR spectra of biomass *Tinospora cordifolia* before and after adsorption of Mn (II)

Table No. 2: **IR absorbtion band and corresponding functional groups**

S. No.	Native biomass (cm^{-1})	Metal loaded biomass (cm^{-1})	Change in peak behavior on loaded biomass	IR Peak range (cm^{-1})	Functional group reported corresponding to the observed peak behavior
1	3419.73	3420.27	Shift	3200-3600	O-H alcohol and phenols groups, stretching vibration
2	2922.73	2936.18	Shift	3000-2800	C-H (sp^3 carbon) strong, broad and multi-banded
3	1637.15	1628.77	Shift	1760-1665	Carbonyl C=O group (ketone, aldehyde, amide, ester) stretching
4	1515.53	1515.93	Shift	1550-	Nitro N-O compounds,

				1475	asymmetric stretching
5	1235.23	1233.6	Shift	1210-1320	Acid group, stretching
6	1074.93	1073.65	Shift	1050-1150	Alcohol group, stretching

6. COMPARATIVE STUDY OF *TINOSPORA CORDIFOLIA* WITH OTHER ADSORBENTS

The capacity of *T. cordifolia* to remove manganese ions was compared with other natural bioadsorbent discussed in this paper. The results of this study showed that the biomass demonstrate good uptake capacity for removal of Mn (II) (24.69 mgg^{-1}) when compared with results reported for other bioadsorbent. The values of adsorption capacities of different biomass are presented in (Table No. 3), but it is observed that *T. cordifolia* has the highest adsorption capacity of Mn (II) ion when compared with other bioasorbents.

Table No. 3: Comparative study of different bioadsorbent for removal of Mn (II)

Adsorbent	pH	Qmax (mg g^{-1})	References
T. cordifolia	**4**	**24.69**	**This paper**
Immobilized *Trichoderma asperellume BHU216*	6	18.88	[21]
Prosopis cinararia leaf	3	10.06	[2]
Banana peel	4	11.8	[18]
Moringa oleifera seeds	4	3.09	[22]
Rhodo coccusopacus		6.91	[23]
Militia ferruginea	4	3.41	[7]

5. APPLICATION OF BIOMASS *TINOSPORA CORDIFOLIA* FOR REMOVAL OF MANGANESE FROM WASTEWATER

The suitability of the bio-adsorbent material for the removal of Mn (II) was tested with a coal mine wastewater sample, the sample was collected in SECL plant district Korba, Chhattisgarh (India). The characteristics of the discharge water are given in (Table No. 4). The pH of the wastewater sample was maintained at 4.0. The adsorbent dose was 1gm 50 mL^{1}, agitate for 30 minutes. It was found in this experiment that the treatment of Mn (II) ion in coal mine wastewater was satisfactory: almost 90% of the Mn (II) remove from the wastewater are possible.

Table No. 4: Characteristics of water discharge from Coal-mine

Parameters	[Concentration (mg l^{-1}) Before adsorption]	[Concentration (mg l^{-1}) After adsorption]	Results

pH	6.4 (adjusted 4 pH)	6.8	-
Cond.(µs)	245	-	-
TSS	13	-	-
Mn (II)	1.156	0.11	90%
Zn(II)	0.068	0.03	55%
F	0.10	0.02	80%

6. CONCLUSION

It can be concluded from above study that biomass *Tinospora cordifolia* can effectively use as adsorbent for removal of Mn (II) from water under our experimental conditions and for the studied metal, pH plays an important role in the adsorption process, particularly on the adsorption capacity. The pH selected for an optimal rate of adsorption for all ions investigated is 4.0. Adsorption was seen to take place in 30 minutes for the concentration levels of the metal studied and the equilibrium concentration of Mn (II) solution was 200 mg L^{-1}. The *T. cordifolia* has good adsorption capacity for Mn (II) removal was 24.69 mgg^{-1} for the batch study accordance to Langmuir adsorption isotherm. The correlation coefficient value of adsorption isotherm model Langmuir and Freundlich was 0.997 and 0.941. The high values of R^2 in Langmuir model give an indication of favorable adsorption.

The bioadsorbent was characterized by FTIR analysis. On the basis of FTIR, the characterization of adsorbent indicates that mainly the hydroxyl, alkane and carboxyl functional groups were responsible for manganese binding.

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