

ORIGINAL ARTICLE

Equilibrium Studies on Biosorption of Manganese on *Ficus religiosa* Leaves Powder

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ABSTRACT

Biosorption process has been proposed as an efficient, potential, cost effective way of removing toxic metals from industrial effluents at low concentrations. In the present study a new biosorbent material, agro waste *Ficus religiosa* leaf powder was used as an adsorbent. This research paper reports the performance of low cost biosorbent, *Ficus religiosa* (peepul) leaf powder for batch biosorption of manganese from aqueous solutions. The variables investigated were: agitation time, biosorbent size, and dosage, initial concentration of manganese in the aqueous solution, pH and temperature of the aqueous solution. The equilibrium agitation time was found to be 180 min. The optimum biosorption was observed at a dosage of 40 g/L. The extent of biosorption was decreased from 99.7% (0.58 mg/g) to 61.34 % (5.7 mg/g) with an increase in initial concentration of manganese from 22.4 mg/L to 285.31 mg/L. The % biosorption was decreased with an increase in temperature. The equilibrium data were well fitted by Reddlich-Peterson ($R=0.99$), Freundlich ($R=0.98$), Langmuir ($R=0.91$) and Temkin ($R=0.88$) isotherm models in that order. The data were well represented by second order kinetics with a rate constant value of 1.02 g/ (mg-min). The maximum uptake capacity was 2.17 mg/g at pH = 7.45, in 50 mL of the aqueous solution for 40 g/L of 38 μ m diameter adsorbent. From the thermodynamic parameters, sorption was found to be exothermic and spontaneous. The reversible biosorption was tending towards irreversibility.

Key words: Biosorption, Manganese, *Ficus Religiosa* Leaf Powder, Thermodynamics, Sigma plot

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INTRODUCTION

Pollution by heavy metals is a serious threat to aquatic ecosystems because some of these metals are potentially toxic, even at very low concentrations. Additionally, heavy metals are not biodegradable and tend to accumulate in living organisms, and they can cause severe problems to both human health and wildlife. [3]

Natural processes and human activities have polluted and reduced the quality of water resources in Nicaragua. Groundwater and superficial water have been contaminated in various ways; e.g. by mining wastes including cyanide and toxic heavy metals, by agricultural chemicals, by industrial and domestic sewage that is sometimes discharged without treatment into waterways and by natural trace elements (e.g. arsenic).

Since it is important to eliminate or reduce the concentration of heavy metals in the aquatic ecosystems, various methods and technologies are commonly applied in the treatment of mining and refining industry effluents before they are discharged to receiving water. These methods include precipitation, ion exchange, and membrane processes. However, the application of some of these methods may be impractical due to economic constraints or may be insufficient to meet strict regulatory requirements. Furthermore, they may generate hazardous products or products which are difficult to treat [13, 14].

The traditional coagulation and flocculation processes use inorganic coagulants such as aluminum hydroxides in drinking water treatment. Metal coagulants can be used to partially remove heavy metal from wastewater[15], but, the use of metal coagulants is not 100% effective for removing metal cations from water at pH 7 [2].

The high cost of adsorbents such as activated carbon and some ion-exchange resins used for the treatment of water and wastewater have conducted to new more effective and cheaper adsorbents. [1]

Mentioned that natural materials that are available in large quantities or industrial waste products can also be used as adsorbents. The sorption process also depends on the physicochemical characteristics of the aqueous solutions, such as pH, pE, temperature, metallic ion concentration and Biosrbent dosage and size.

THREATS TO AQUATIC ECOSYSTEMS

Increasingly, aquatic ecosystems are under increasing stress due to the rapidly growing population, technological development, urbanisation and economic growth. Human activities are causing aquatic species to disappear at an alarming rate. It has been estimated that between 1975 and 2015, species extinction will occur at a rate of 1 to 11 percent per decade. Aquatic species are at a higher risk of extinction than mammals and birds. Losses of this magnitude impact the entire ecosystem, depriving valuable resources used to provide food, medicines, and industrial materials to human beings [16]. Runoff from agricultural and urban areas, the invasion of exotic species, and the creation of dams and water diversion have been identified as the greatest challenges to freshwater environments. Some of the threats and causes to aquatic ecosystem are presented in Table-1.

Table.1: Causes and Type of Threats to Aquatic Ecosystem

S.No.	Type of Threat	Causes
1.	Water Regime	Flooding; reclamation; water diversion; erosion/siltation; roads; irrigation; water works (floods)
2.	Water pollution	Solid waste refuse; siltation; sewage/fecal; mining; pesticides; fertilizers; salinization of soils
3.	Physical Modification	Erosion; flooding; clearance and fire; sedimentation; infrastructure/housing; quarrying and sand winning; hunting; recreation; agriculture
4.	Over-exploitation	Fishing; fuel wood; hunting of birds and mammals; grazing

During the 1970's increasing environmental awareness and concern led to a search for new techniques capable of inexpensive treatment of polluted wastewaters with metals. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on binding capacities of various biological materials.

Till date, research in the area of biosorption suggests it to be an ideal alternative for decontamination of metal/dye containing effluents. Biosorbents are attractive since naturally occurring biomass/adsorbents or spent biomass can be effectively used. Biosorption is a rapid phenomenon of passive metal/dye sequestration by the non-growing biomass/adsorbents. Results are convincing and binding capacities of certain biomass/adsorbents are comparable with the commercial synthetic cation exchange resins.

The biosorption process involves a solid phase (sorber or biosorber; adsorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (adsorbate, metal/dyes). Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases.

There are many types of adsorbents [24]; Earth's forests and plants, ocean and freshwater plankton, algae and fish, all living creatures, that including animals are all "biomass/ adsorbents". The renewable character of biomass that grows, fuelled directly or indirectly by sunshine, makes it an inexhaustible pool of chemicals of all kinds.

The objective of the present work has been to study the removal of Manganese Mn (II) from aqueous solution using *Ficus religiosa* leaf powder. Equilibrium and kinetic experiments at different metallic ion concentrations and with different particle sizes have been performed. The experimental data have been tested with the Langmuir equation, and simplified kinetic models have been applied to determine the rate-controlling mechanisms for the adsorption process. In addition, desorption studies and the studies of application of *Ficus religiosa* leaf powder for the removal of heavy metals from natural water and mining effluents have been carried out. To accomplish this, the biosorbent has been produced on a laboratory scale from agricultural waste, *Ficus religiosa* leaf powder.

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

MATERIALS AND METHODS

Materials and Reagents

All the chemicals used in this investigation were of analytical grade and used without further purification. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (99%) was used as the source of Mn(II) and all solutions were made with distilled water. The different concentrations of Mn (II) were prepared from a stock solution contains 1000mg of Mn (II) in 1 L.

Preparation of Biosorbent

Fresh matured *Ficus religiosa* [8] leaves were collected from tall peepul trees in Andhra University and washed with water to remove dust and soluble impurities. They were dried at room temperature in a shade. The crisp leaves are obtained by sun-drying. The dried leaves are finely powdered and sized by passing the powder through a set of sieves ranging from 350 to 100 mesh sizes. The powders of 38, 63 and 125 μm fractions are collected separately and preserved in glass bottles for use as biosorbent.

Preparation of stock solution

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$ is used as the source of manganese stock solution. All the required solutions are prepared with analytical reagents and double-distilled water. 3.104 g of 99% $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ is dissolved in distilled water in 1 L volumetric flask up to the mark to obtain 1000 ppm (mg/L) of manganese stock solution. Synthetic samples of different concentrations of manganese were prepared from this stock solution by appropriate dilutions. 100 mg/L manganese stock solution was prepared by diluting 100 mL of 1000 ppm manganese stock solution with distilled water in 1000 mL volumetric flask up to the mark. Similarly solutions with different metal concentrations such as (22.4, 44.3, 69.2, 91.25, 118.42, 139.25, 164.7 and 187.24 mg/L) were prepared. The pH of aqueous solution is adjusted to the desired value by addition of 0.1 N H_2SO_4 or 0.1N NaOH solution. **Experimental Procedure:**

The biosorption was carried out in a batch system by adding a specific amount of ficus religiosa leaf powder with 50 mL of aqueous solution of $\text{Co} = 91.25 \text{ mg/L}$ at constant temperature (30°C). The mixture was agitated for a predetermined time interval in an orbital shaker at 160 rpm. The mixture is filtered and the filtrate was analyzed in an atomic absorption spectrophotometer (AAS, Perkin Elmer-3100 model, wave length is 279.9 nm) to obtain the residual manganese present in it. Similarly more samples are prepared in conical flasks and the above procedure is followed varying the agitation time, biosorbent size, and dosage, initial concentration of manganese and volume of the aqueous solution, pH and temperature of the aqueous solution. In order to determine the order of biosorption reaction, the above procedure is repeated for varying agitation times of 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 60, 120, 180, 240, 300 and 360 min for various biosorbent dosages of 0.5, 1, 1.5, 2 and 2.5 g of 38 μm size. The thermodynamic parameters are determined by adopting the same procedure at different temperatures for different volumes of the solutions. The extent of biosorption is found from the relation (% removal) = $[(C_0 - C_t) \times 100 / C_0]$. The amount of Mn (II) adsorbed per unit mass of the adsorbent, q in mg/gm = $(C_0 - C_t) / m$. The values of parameters investigated are shown in Table 2.

Table.2: Experimental conditions investigated

S.No.	Parameter	Values Investigated
1	Agitation time, t, min	1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 120, 180, 240 and 300
2	Biosorbent size, d_p , μm	38, 63 and 125
3	Biosorbent dosage, w, g/L	1, 2, 5, 10, 20 and 30
4	Initial concentration of Cd, C_0 , mg/L	22.4, 44.3, 69.2, 91.25, 118.42, 139.25, 164.7, 187.24, 238.2 and 285.31
5	pH of the aqueous solution	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12
6	Temperature, K	283, 293, 303, 313, 323 and 333

RESULTS AND DISCUSSION

In the present investigation, the potential of dry *Ficus religiosa* leaf powder as a biosorbent for removal of manganese metal present in an aqueous solution is investigated. The effects of various parameters on biosorption of manganese were studied. The measured data consist of initial and final concentration of manganese in the aqueous solution, agitation time, biosorbent dosage, biosorbent size, pH of the aqueous solution and temperature of the aqueous solution.

Effect of agitation time:

Duration of biosorption equilibrium is defined, as the time required for heavy metal concentration to reach a constant value during biosorption. The equilibrium agitation time is determined by plotting the % removal of manganese against agitation time in figs.2-4 for various 'w' and ' d_p ' values in the interaction time intervals of 1 min to 360 min. For 38 μm size of 40 g/L biosorbent, 84.88 % (1.93 mg/g) of manganese is adsorbed in the first 5 min. The % biosorption is increased briskly up to 60 min reaching 90.58 % (2.06 mg/g). From 60 to 180 min. the biosorption is marginally and gradually increased to 92.11 % (2.10 mg/g) from 90.58 % (2.06mg/g). Beyond 180 min, the % biosorption is constant indicating the

attainment of equilibrium conditions. The maximum biosorption of 92.11% (2.10 mg/g) is attained for 180 min of agitation time with 40 g/L of 38 μ m size biosorbent mixed in 50 mL of aqueous solution ($C_0 = 91.25$ mg/L). The rate of biosorption is fast in the initial stages because adequate surface area of the biosorbent is available for the biosorption of manganese. As time increases, more amount of manganese gets adsorbed onto the surface of the biosorbent due to Vanderwaal's forces of attraction and results in decreased of available surface area. The adsorbate, normally, forms a thin one molecule thick layer over the surface.

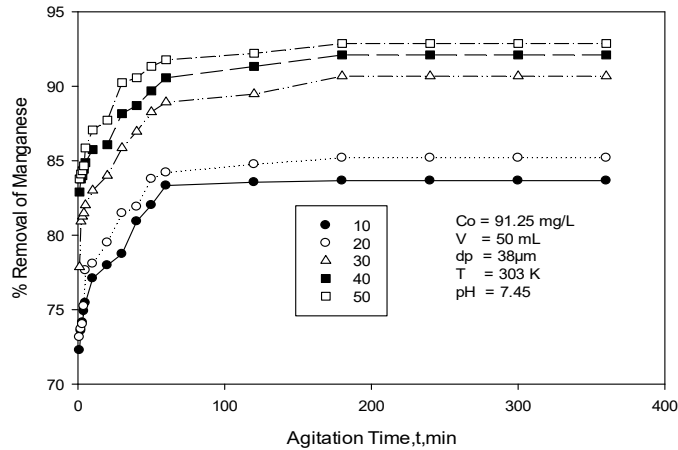


Fig.2:Effect of Agitation time on % removal of Manganse

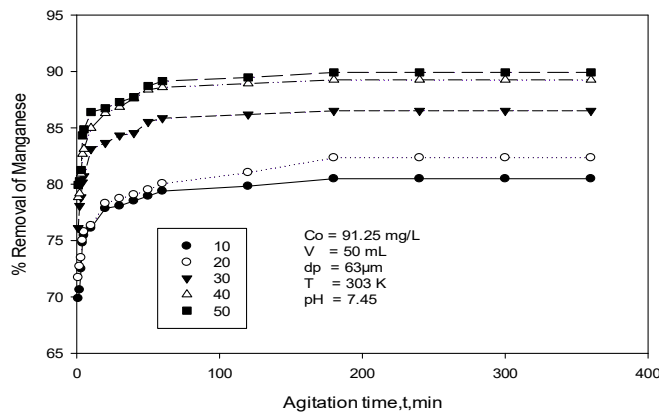


Fig.3:Effect of Agitation time on % removal of Manganse

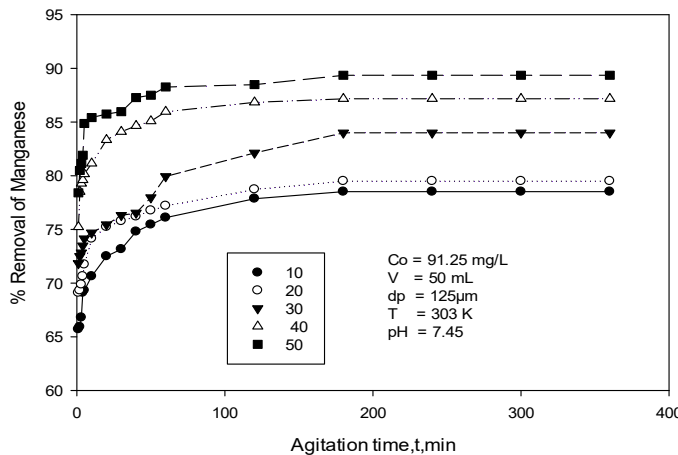


Fig.4:Effect of Agitation time on % removal of Manganse

Effect of biosorbent dosage and size:

The percentage removal of manganese is drawn against adsorbent dosage for 38 μm size biosorbent in fig.5. The removal of manganese increases from 83.68% (7.63 mg/g) to 93.32 % (1.41 mg/g) with an increase in biosorbent dosage from 10 to 60 g/L. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for manganese removal would be more. The change in percentage removal of manganese is marginal from 92.11% (2.10 mg/g) to 93.32% (1.41 mg/g) when 'w' is increased from 40 to 60 g/L. Hence all other experiments are conducted at 40 g/L dosage. The variations in % removal of manganese from the aqueous solution with biosorbent size (38 μm , 63 μm and 125 μm) are obtained at different dosages at the equilibrium agitation time of 180 min. The results are drawn in fig.6 with % removal of manganese as a function of biosorbent size. The percentage removal of manganese is increased from 87.17% (1.98 mg/g) to 92.11% (2.10 mg/g) as the biosorbent size decreases from 125 to 38 μm for $w = 40$ g/L. With an increase in biosorbent sizes, surface area of the biosorbent increases, there by the numbers of active sites available on the biosorbent are better exposed to the adsorbate.

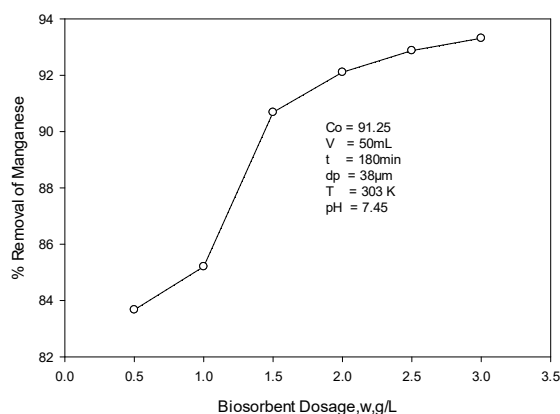


Fig.5: % Removal of Manganese as Function of Biosorption

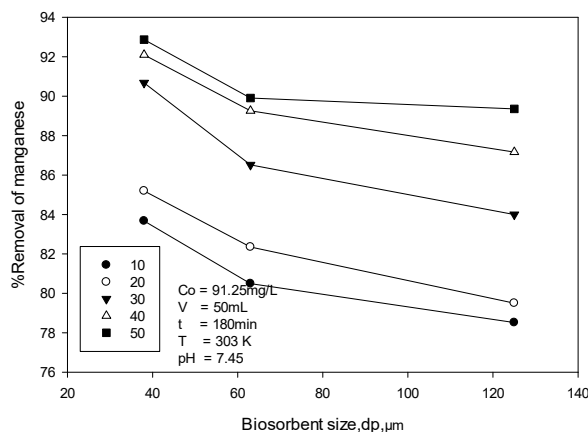


Fig.6: Removal of manganese as a function of biosorbent size

Effect of pH of the aqueous solution:

pH controls biosorption by influencing the surface change of the biosorbent, the degree of ionization and the species of adsorbate. In the present investigation, manganese biosorption data are obtained in the pH range of 1 to 12 of the aqueous solution ($C_0 = 91.25$ mg/L) using 40 g/L of 38 μm size biosorbent. The effect of pH of aqueous solution on % removal of manganese is drawn in fig.7. The % removal of metal is increased from 56.49 % (1.28 mg/g) to 95.50 % (2.17 mg/g) as pH is increased from 1 to 7 and decreased beyond pH value of 8. % biosorption is increased steeply from pH = 1 to 2 reaching 85.53 % (1.95 mg/g) from 56.49 % (1.28 mg/g). % biosorption is marginally increased from 85.53% (1.95 mg/g) to 95.50% (2.17 mg/g) as pH increases for 2 to 7. Low pH depresses biosorption of manganese, due to competition with H^+ ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and $\text{Mn}(\text{II})$ ions replace H^+ ions bound to the biosorbent (or forming part of the surface functional groups such as OH, SO_4 , etc).

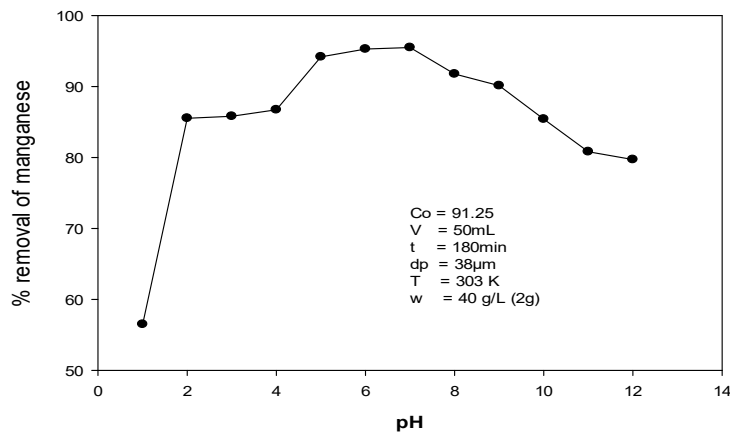


Fig.7:Effect of Aqueous solution on % removal of manganese

Effect of initial concentration of manganese in the aqueous solution:

The effect of initial concentration of manganese in the aqueous solution on the percentage removal of manganese is shown in fig.8. The percentage removal of manganese is decreased from 99.70 % to 61.34 % with an increase in C_0 from 22.4 mg/L to 285.31 mg/L in the temperature range of 283 to 323 K while the uptake capacity is increased from 0.55 to 4.37 mg/g. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the biosorbent. These plots also confirm that the % removal decreases with an increase in temperature.

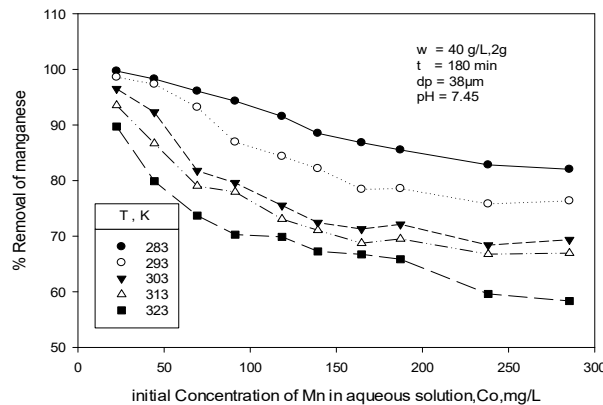


Fig.8: Effect of initial concentration of Manganese on % Removal of Mn

Isotherms

An isotherm is the equilibrium relationship between the concentration of metal in the fluid phase and the concentration on the adsorbent at a given temperature. Freundlich isotherm [4] is $q_e = K_f C_e^n$ or $\log q_e = \log K_f + n \log C_e$. Freundlich isotherm was drawn between $\log C_e$ and $\log q_e$ shown in Fig. 6. The following equation was obtained at $d_p = 38 \mu m$ varying the initial concentration of Mn (II): $\log q_e = 0.444 \log C_e - 0.259$ $R=0.98$. The slopes (n) of the above equation 0.444 satisfying the condition of $0 < n < 1$ for favourable biosorption. Freundlich isotherm describes the biosorption with rice husk [17] and lignite [18]. Langmuir isotherm [6] is the most widely used two- parameter equation. The relationship of a hyperbolic type form: $(C_e/q_e) = 1/bq_m + C_e/q_m$. Fig.7 is drawn between (C_e/q_e) and C_e for $d_p = 38 \mu m$ varying the initial concentration of Mn (II). The slope ($1/q_m$) and the intercept ($1/bq_m$) are calculated from the graph. The equation obtained from the graph was: $C_e/q_e = 0.0634 C_e + 3.355$ $R = 0.91$. The slope ($1/q_m$) is 0.0634 and the intercept ($1/bq_m$) is 3.355. The separation factor (RL) value of $0.222 < 1$ indicates favorable biosorption. The correlation coefficient obtained for Langmuir isotherm was less than that obtained for Freundlich isotherm. [19] Suggested Langmuir isotherm for biosorption with sargassum biomass ($q_m = 0.629$ mg/g and $b = 0.567$). Biosorption with pseudomonas aerations [20] were explained by Langmuir isotherm.

Redlich and Peterson [7] proposed a three parameter isotherm to incorporate features of both Langmuir

and Freundlich equations. It can be described as follows: $q_e = \frac{AC_e}{1 + BC_e^g}$ where A (L/g) and B (L/ mg)

were the Redlich-Peterson isotherm constants and 'g' was the Redlich - Peterson isotherm exponent that lies between 0 and 1. The linear form of the equation is $\ln\left(\frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln B$, although a

linear analysis is not possible for a three parameter isotherm, the three isotherm constants (A, B and g) can be evaluated from the pseudo linear plot using trial and error optimization method. Fig.8 shows the Redlich - Peterson plot drawn between $\ln [A(C_e/q_e)-1]$ and $\ln C_e$. For the present experimental data the equation obtained from the plots drawn in fig.11 for A = 1L/mg (assumed), V = 50 mL, T = 303 K and $d_p = 38 \mu\text{m}$ is $\ln [(C_e/q_e)-1] = 1.406 \ln C_e - 1.879$. Redlich- Peterson^[7] isotherm constants A (L/mg), B (L/mg) and Redlich- Peterson isotherm exponent (g) for w = 40 g/L, C₀ = 91.25 mg/L and $d_p = 38 \mu\text{m}$ are 1L/mg, 0.1527 L/mg and 1.406 respectively. Tempkin isotherm equation describes the behavior of many adsorption systems on the heterogeneous surface and it is based on the following equation $q_e = RT \ln(A_T C_e) / b_T$. The linear form of Tempkin isotherm can be expressed as $q_e = (RT/ b_T) \ln(A_T) + (RT/b_T) \ln(C_e)$

where $A_T = \exp [b(0) \times b(1) / RT]$, $b(1) = RT/ b_T$ is the slope, $b(0) = (RT/ b_T) \ln (A_T)$ was the intercept and $b = RT/b(1)$. The present data were analysed according to the linear form of Tempkin isotherm and the linear plot is shown in fig.11. The equation obtained for manganese biosorption was: $q_e = 0.953 \ln C_e + 0.633$ with a correlation coefficient 0.88. The isotherm constants obtained for various isotherm models were shown in Table-3. The best fit model is determined based on the linear regression correlation coefficient (R). From the table, it was found that biosorption data were well represented by Redlich-Peterson isotherm with higher correlation coefficient of 0.99, followed by Freundlich, Langmuir and Tempkin isotherms with correlation coefficients of 0.98, 0.91 and 0.88 respectively.

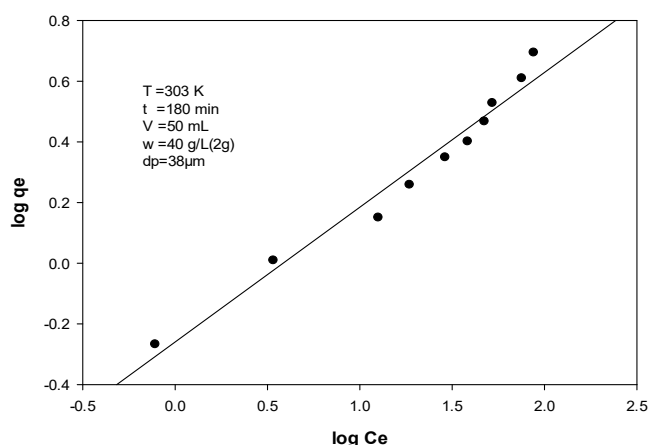


Fig.9: Freundlich isotherm for biosorption of manganese w.r.t. Concentration

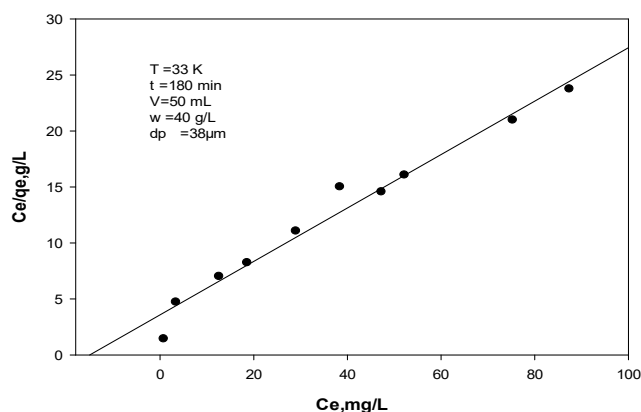


Fig.10: Longmuir isotherm for Biosorption of Manganese w.r.t. Concentration

Fig.11:Tempkin isotherm for biosorption of manganese w.r.t. concentration

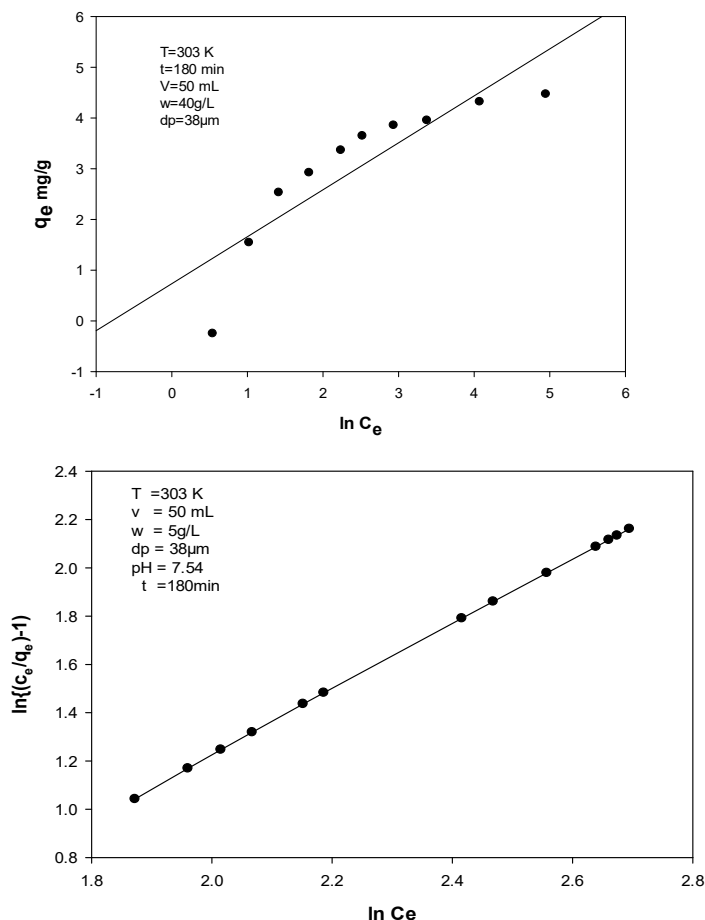


Fig.12: Redlich-Peterson isotherm for biosorption of Manganese w.r.t. Concentration

Table-3: Isotherm constants

Freundlich isotherm	Langmuir isotherm	Redlich-Peterson isotherm	Tempkin isotherm
$K_f = 0.7716, L/g$	$q_m = 15.772, mg/g$	$A = 1, L/g$	$A_T = 1.828, L/mg$
$n = 0.444, g/L$	$b = 0.0188, L/mg$	$g = 1.406$	$b_T = 2643.38$
$R = 0.98$	$R = 0.91$	$R = 0.99$	$R = 0.88$

Kinetics of biosorption:

The data regarding biosorption kinetics is necessary for the design of industrial columns. The order of adsorbate – biosorbent interactions has been described traditionally by the pseudo first order model of Lagergren (1898) or by pseudo second order kinetics [10, 11, 12] in certain cases. In the case of biosorption preceded by diffusion through a boundary, the kinetics in most cases follows pseudo first order rate of equation of Lagergren: $(dq_t/dt) = K_{ad} (q_e - q_t)$. Plot of $\log (q_e - q_t)$ versus 't' gives a straight line for first order kinetics. In case of pseudo second order kinetics, $(dq_t/dt) = K (q_e - q_t)^2$ is applicable. This equation can be written as $(t/q_t) = (1/Kq_e^2) + (t/q_e)$. If the pseudo-second order kinetics is applicable, the plot of (t/q_t) versus t gives a linear relationship that allows computation of q_e and K. Lagergren plot of $\log (q_e - q_t)$ versus agitation time (t) for the present investigation was drawn in Fig.10 and the resulting equations are: $\log (q_e - q_t) = - 0.0094 t - 0.728, R = 0.98$ for $d_p = 38 \mu m$, $\log(q_e - q_t) = - 0.0134 t - 0.747, R = 0.94$ for $d_p = 63 \mu m$, $\log (q_e - q_t) = - 0.0127 t - 0.715, R = 0.98$ for $d_p = 125 \mu m$. The pseudo-second-order model was applied to assess the suitability of the rate equation for the present data. The plots (t/q_t) versus (t) for the present data are shown in Fig. 11 for $d_p = 38 \mu m$. The plots for $d_p = 63$ and $125 \mu m$ are not shown. The second order rate equations obtained are compiled in Table 4. The results show that the correlation coefficients for second order rate equations (1.000) are higher than those for the first order rate

equations. Hence, the pseudo second order rate equation is more suitable to explain the biosorption. The second order rate constant (K) values are varied from 1.1772 to 0.1150 g/(mg-min).

Table-4: Second order kinetics

For $d_p = 38 \mu\text{m}$

W, g/L	Equation	K, (g/mg-min)	R
10	$(t/q_t) = 0.131 t + 0.1025$	0.1674	1.00
20	$(t/q_t) = 0.256 t + 0.211$	0.3105	1.00
30	$(t/q_t) = 0.361 t + 0.354$	0.3681	1.00
40	$(t/q_t) = 0.474 t + 0.389$	0.5775	1.00
50	$(t/q_t) = 0.588 t + 0.376$	0.9195	1.00

For $d_p = 63 \mu\text{m}$

W, g/L	Equation	K, (g/mg-min)	R
10	$(t/q_t) = 0.135 t + 0.083$	0.2195	1.00
20	$(t/q_t) = 0.265 t + 0.255$	0.2570	1.00
30	$(t/q_t) = 0.379 t + 0.183$	0.7849	1.00
40	$(t/q_t) = 0.490 t + 0.235$	1.0217	1.00
50	$(t/q_t) = 0.608 t + 0.314$	1.1772	1.00

For $d_p = 125 \mu\text{m}$

W, g/L	Equation	K, (g/mg-min)	R
10	$(t/q_t) = 0.139 t + 0.168$	0.1150	1.00
20	$(t/q_t) = 0.274 t + 0.267$	0.2811	1.00
30	$(t/q_t) = 0.389 t + 0.707$	0.214	0.999
40	$(t/q_t) = 0.501 t + 0.343$	0.7317	1.00
50	$(t/q_t) = 0.612 t + 0.388$	0.9653	1.00

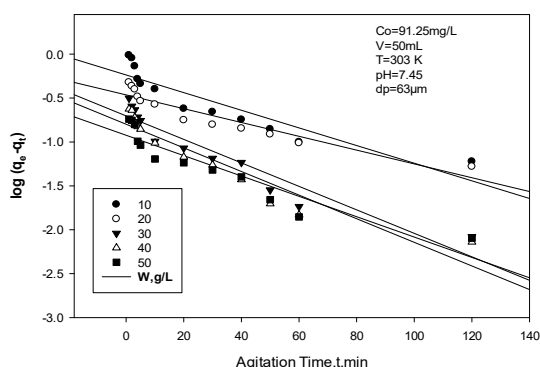


Fig.13(b): First Order kinetics for biosorption of manganese

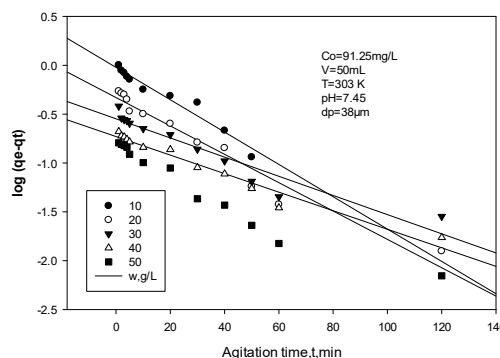


Fig.13(a): First Order kinetics for biosorption of manganese

Thermodynamics

Biosorption was usually exothermic and the amount adsorbed at a given concentration decreases as the temperature increases, in accordance with Le-Chateliers principle. The thermodynamic criterion for biosorption was well explained by evaluation of the three important thermodynamic parameters. They are change in enthalpy (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS). Net enthalpy change (ΔH) is related to ΔG and ΔS as $\Delta G = \Delta H - T(\Delta S)$. The Van't Hoff's equation is $\log(q_e/C_e) = -(\Delta H/2.303R)(1/T) + (\Delta S/2.303R)$ Where (q_e/C_e) is called the biosorption affinity. ΔH and ΔS values are calculated from slope = $-\Delta H/(2.303R)$ and intercept = $\Delta S/(2.303R)$ Experiments were conducted to understand the biosorption behavior of manganese with respect to temperature for $w = 40 \text{ g/L}$ and $d_p = 38 \mu\text{m}$ and the data are shown in Figure 12 with $\log(q_e/C_e)$ as a function of $(1/T)$. The equation obtained was $\log(q_e/C_e) = 2023 (1/T) - 7.608$ for $V = 50\text{mL}$ Thermodynamic parameters calculated for biosorption of Mn (II) on to *Ficus Riligiosa* powder are shown in Table 5.

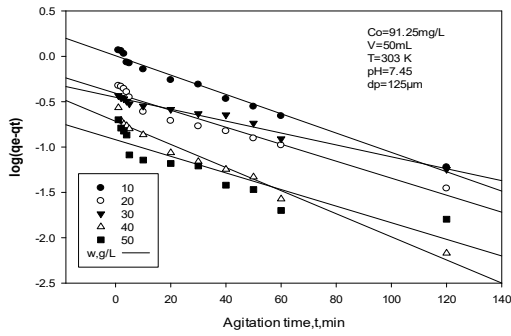


Fig.13(c): First order Kinetics for biosorption of manganese

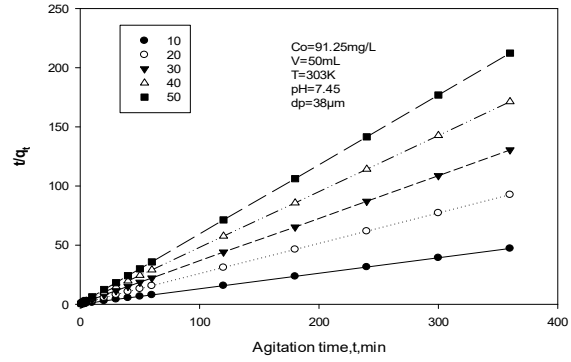


Fig.14(a): Second order kinetics for biosorption of manganese

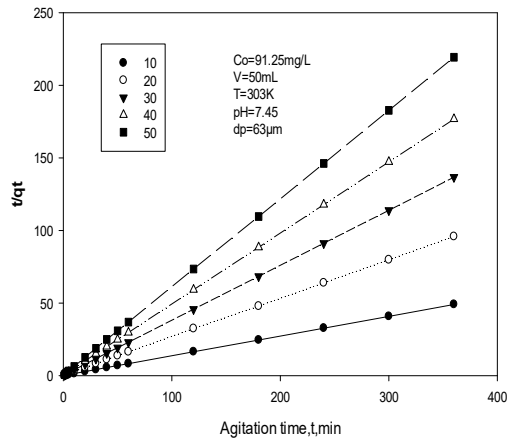


Fig.14(b): Second order Kinetics for biosorption of manganese

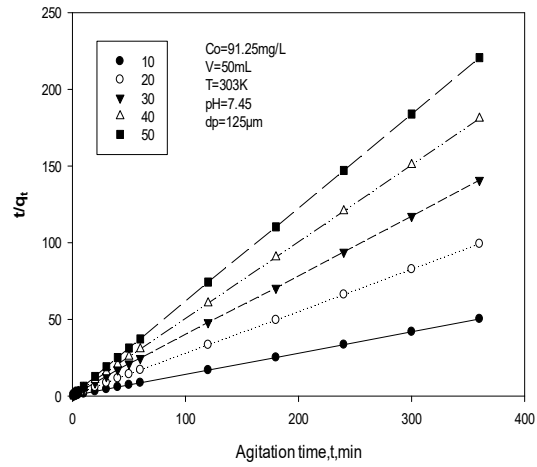


Fig.14(c): Second order Kinetics for biosorption of manganese

Table-5: Thermodynamic parameters for biosorption of manganese for various C₀ values

S.No.	C ₀ , mg/L	- S kJ/(mol-K)	- H kJ/mol	G, kJ/mol				
				at different temperatures, K				
				283	293	303	313	323
1	22.4	0.2267	60.83	3.3261	5.5931	7.8601	10.1271	12.394
2	44.3	0.1862	53.765	-1.0704	0.7916	2.6536	4.5156	6.3776
3	69.2	0.1574	43.195	1.3492	2.9232	4.4972	6.0712	7.6452
4	91.25	0.1457	38.734	2.4906	3.9473	5.4040	6.8607	8.3174
5	118.42	0.1264	32.377	3.3942	4.6582	5.9222	7.1862	8.4502
6	139.25	0.1037	25.159	4.1767	5.2133	6.2499	7.2865	8.3231
7	164.7	0.0962	22.21	5.0230	5.9853	6.9476	7.9099	8.8722
8	187.24	0.0854	20.889	3.4178	4.2767	5.1356	5.9945	6.8534
9	238.2	0.0942	21.502	5.1566	6.098	7.0406	7.9826	8.9246
10	285.31	0.0882	19.74	5.2121	6.0938	6.9755	7.8572	8.7389

CONCLUSIONS

Investigations were carried out to find out the equilibrium kinetics and Thermodynamic parameters for biosorption of manganese from an aqueous solution using *Ficus religiosa* leaf powder. The analysis of the experimental data results in the following conclusions. The equilibrium agitation time for manganese

biosorption was 180 minutes. The percentage removal of manganese from an aqueous solution increases with a decrease in the particle size of the biosorbent. The percentage removal of manganese was increased significantly with increase in biosorbent dosage. Increase in the volume of the aqueous solution results in gradual decrease in the percentage removal of manganese. With an increase in the initial concentration of manganese in the aqueous solution, the percentage removal of manganese from the aqueous solution was decreased. Percentage removal of manganese from the aqueous solution increases significantly with increase in pH from 1 to 7. Thereafter percentage removal decreases for further increase in pH. In the range of variables studied, percentage removal was increased from 60.62% (4.23mg/g) to 99.7% (0.58mg/g). The kinetic studies show that the biosorption of manganese was better described by pseudo second order kinetics. The thermodynamic data show that percentage biosorption decreases with increase in temperature. The investigation also reveals that: The exothermic nature of biosorption as ΔH was negative, the reversibility of biosorption initially as ΔS was negative and biosorption tending towards irreversibility as ΔS was increasing, The spontaneity of the biosorption as ΔG was negative, and increase in ΔG value with an increase in temperature indicates that the biosorption of manganese was less favorable.

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