Evaluation of *Saccharum bengalense* as a Non-Conventional Biomaterial for Biosorption of Mn (II) Ions from Aqueous Solutions

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ABSTRACT: *In this study, Saccharum bengalense (SB) was used as biosorbent for the removal of Mn (II) ions from aqueous solution. The influence of biosorbent dose, time, pH and temperature was investigated in the biosorption process. Studies showed that by increasing pH of the solution, metal removing efficiency of Saccharum bengalense from the aqueous environment was enhanced but to a specific extent, pH 5.0, at time 50minutes and dose 0.1g/50mL. Langmuir, Freundlich, Harkin Jura and Halsey adsorption isotherm were used to studying adsorption efficiency of Saccharum bengalense. Langmuir and Harkin Jura adsorption isotherms well explained the adsorption process as compared to other isotherms with correlation coefficient 0.943 and 0.968 respectively. At 313K temperature, adsorption capacity (q_e) of Saccharum bengalense for removal of Mn (II) ions from aqueous solution was 21.72mg/g. Kinetic study showed that pseudo second order was best followed by the adsorption process with correlation coefficient 0.997.*

KEYWORDS: *Saccharum bengalense; Isotherm; Manganese; Kinetics; Thermodynamics.*

INTRODUCTION

Heavy metals are added in water through electroplating, fertilizers, mining, metallurgical, electronic and nuclear processes [1] and contaminate it. They contaminate surface as well as underground water. Although, metals in appropriate quantities are essential for humans and animals their excess affects the living cell by denaturing the protein [2]. Toxic metals can be accumulated in the human body and its surrounding environment and can be retained there for a long period of time [3]. Persistence of toxic metals in the environment adversely affects human metabolism and can cause serious health issues.

Metals have a wide range of applications in many fields of life. Among them, Mn (II) is used in ceramic

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manufacture glass, matches, electronic objects, alloys production, in agrochemicals and batteries. Manganese present in drinking water damages the nervous and respiratory system [4]. It is accumulated in the brain and disrupts it [5]. When humans are exposed to manganese polluted environment, they undergo neurotoxicity [6, 7]. Parkinson disorder is enhanced in the exposure of manganese polluted environment [8]. 0.1mg/L and 1.5mg/L amount of manganese in drinking water was set as maximum limit by World health organization and Mexican legislation respectively [9]. Thus, an excess quantity of manganese should be removed from drinking water.

Various methods have been used for the purification of metal contaminated water. These methods are chemical precipitation, coagulation [10], solvent extraction, ion exchange, adsorption [11], membrane filtration [12] and electrolysis [13]. These methods are efficient for the removal of toxic metals from polluted water but these are of the high cost. There is a need to find such methods that are less costly and much effective to remove toxic metals from contaminated samples. Many researchers are trying their best in this regard [14]. Among different methods used for the removal of toxic metals, biosorption by using non-living biomass [15], agriculture wastes [16] and seaweeds [17] is economically favorable and environmental friendly [18]. Dead biomass used in biosorption can be regenerated for further application [5]. Metal ions are adsorbed on the surface of biosorbent due to the presence of some specific group like carboxyl, carbonyl, hydroxyl, sulfate, amino, thio ether, phenol, amide, hydroxyl and phosphate groups [19]. Biosorption is useful than other methods because it is less costly; can be regenerated, has high ability to remove metals and the minimum waste product is formed [20]. Therefore, many researchers have made significant contribution in the field of adsorption by using agriculture wastes like rice husk [21], sugar beet pulp [22], modified sunflower stalks [23], modified *Moringa oleifera* tree leaves and bark [5], pinus pin aster bark [24], activated carbon derived from baggase [25], petiole felt-sheath of palm [26], papaya wood [27] and black carrot residues [1], etc. Biosorbents can be modified in different ways to improve the removal efficiency of heavy metals from the aqueous environment. Manganese can be removed from contaminated water by using ultra filtration following by pre-chlorination process [28], bioreactors [29], agriculture residue [1] and biosorbents like green tomato husk [9].

Saccharum bengalense (SB) is called 'Kana'or 'Sarkanda' in Urdu in Pakistan. It was found from Sind, Punjab and Khyber Pakhtunkhwa in Pakistan, Afghanistan, North, and Northwest India. *Saccharum bengalense* is a very large tufted grass with Leaf-blades having a length up to 90cm long and width 3-10 mm. SB is effective biosorbent and produces large quantities of biomass to carry out adsorption process [30]. To the best of our knowledge, no research work has been reported to investigate the biosorption of Mn (II) ions from the aqueous medium on *Saccharum bengalense*. The objective of this research is to explore the effective adsorption of Mn (II) ions on *Saccharum bengalense*.

EXPERIMENTAL SECTION

Collection of biosorbent

Saccharum bengalense (SB) was obtained from the bank of the river Satluj, Bahawalpur, Pakistan. The plant was not certified and its stem pulp was used as an adsorbent for removal of Mn (II) from aqueous medium. It was washed with water to remove dust and then dried under shade. Dried SB was grinded into a fine powder. The dried powder was passed through the mesh sieve to obtain particles of 125μm size. Powdered SB was stored in plastic bottles. These bottles were air tight and labeled as SB [31].

Preparation of stock solution

All the solutions were prepared from the required chemicals. Manganese stock solution (1000mg/L) was prepared by dissolving the calculated amount of $KMnO_4$ in distilled water (2.87g/L). Using the dilution method, standard solutions of different concentrations were prepared from a stock solution of $KMnO_4$. All sample bottles and glassware were washed with deionized water and dried in an oven at 100°C.

Biosorption experiments

Factors affecting the biosorption process such as SB content, time of adsorption reaction, pH and temperature of solution were studied by varying the amount of SB (0.1, 0.2, 0.3, 0.5, 0.7, 1.0, 1.5 and 2.0g), contact time (10-80minutes with 10minutes interval), pH (1-11) and temperature (283-343K) respectively. Perkin-Elmer Atomic Absorptions Spectrophotometer with

flame of a mixture of air and acetylene was used to determine the concentration of Mn(II) in the sample solution. Maximum removal efficiency and biosorption capacity for each factor (amount of metals adsorbed per gram of the adsorbent) were found out by the Equations (1) and (2).

$$\text{Biosorption capacity } (q_e) = \frac{C_o - C_e}{m} \times V \quad (1)$$

$$\%\text{ removal efficiency} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

C_i and C_f in the above mentioned equations are the initial and final amount of Mn (II) in the sample solutions while V and m are the volume of solution in liters and amount of biosorbent in grams, respectively.

RESULTS AND DISCUSSION

Biosorbent characterizations

SB was characterized to evaluate the interaction between metal ions and adsorbent functional groups for the removal of metal ions from aqueous solution. Elemental analysis was performed by Perkin-Elmer 2400 Series II CHNS/O Elemental Analyzer with sulfanilamide as the standard. It showed SB contain 41.2%, 4.2%, 0.9% carbon, hydrogen and nitrogen, respectively [30-32].

Functional groups in SB were determined by FT-IR spectroscopy. FTIR spectra were recorded by using FT-IR spectrophotometer (Tensor 27, Bruker Germany) with KBr pellets. The FTIR spectra of SB determines the change in the vibrational frequency of functional groups within the range 4000–400cm^{-1} before and after adsorption of Mn (II) as shown in Fig. 1a. Peaks appeared in the FTIR spectrum of SB indicated the heterogeneity of adsorbent surface and the presence of different functional groups like OH, COOH. A peak appeared at 3356cm^{-1} indicated the presence of free and bonded hydroxyl groups in SB. A small peak appeared at 2909cm^{-1} determined stretching vibration of the C–H group in the lignin. Two peaks appeared at 1731cm^{-1} and 1601cm^{-1} due to carbonyl groups of ester and carboxylic acid and carbonyl groups of aldehydes and ketones respectively. A peak appeared at 1038cm^{-1} due to stretching of C–O bond of OCH_3 group. The appearance of small peaks at 662 and 898cm^{-1} due to bending modes of aromatic compounds indicated the presence of the lignin structure in BS [30, 32]. Manganese ions attach to the surface of adsorbent through these functional groups and were removed from the water. This characteristic of the adsorbent surface makes SB suitable for adsorption of Mn with enhanced metal removal efficiency [31].

The FT-IR spectrum of Mn (II) loaded SB is more or less similar to that obtained before adsorption, however, some changes are observed in the intensity and position of IR peaks which can be associated with metal bonded functional groups (Fig. 1b). The shift of the peaks 3356cm^{-1} and 1731cm^{-1} towards the lower wave number is suggestive of the decrease in the free hydroxyl group of SB due to their bonding with Mn(II) ions.

Similarly, the association of the C-O group in metal sorption is indicated by the minor shift of the concerned peaks towards lower wave number in the IR spectrum. Therefore, it can be suggested that oxygen containing functional groups *viz*, carboxy –COOH, methoxy –OCH_3 and phenolic –OH groups, are involved in the Mn(II) uptake process [31-32].

Effect of biosorbent content

Effect of biosorbent dose was observed by changing the sorbent amount from 0.1 to 2.0g while the concentration of metal ion solution was taken as 50mg/L. Removal of Mn(II) from aqueous solution increases with the increase of SB content up to 0.1g but a further increase of SB decrease metal removal efficiency of SB as shown in Fig. 2.

This might be due to the overlapping of adsorbent sites because of excess adsorbent [33, 34]. When adsorbent increases above a certain extent, it aggregates among themselves and effective surface required for metal ion binding decreases [35] and ultimately, metal ions do not find many sites for their adsorption [36]. This behavior was observed for the effect of adsorbent dose on its adsorption capacity q_e (mg/g). Amount of adsorbate (mg) per adsorbent (g) was decreased with the increase of adsorbent above 0.1g. The concentration of SB required for the maximum removal of Mn(II) was 0.1g/50mL of solution.

Effect of adsorption reaction time

Effect of adsorption reaction time on the biosorption process was also studied. Samples containing 0.1g/50mL of solution were stirred at 150rpm for 80minutes with intervals of 10minutes. The percentage removal efficiency of adsorbent was increased with the increase of adsorption process time because more metal ions were adsorbed on the adsorbent with the passage of time and attain

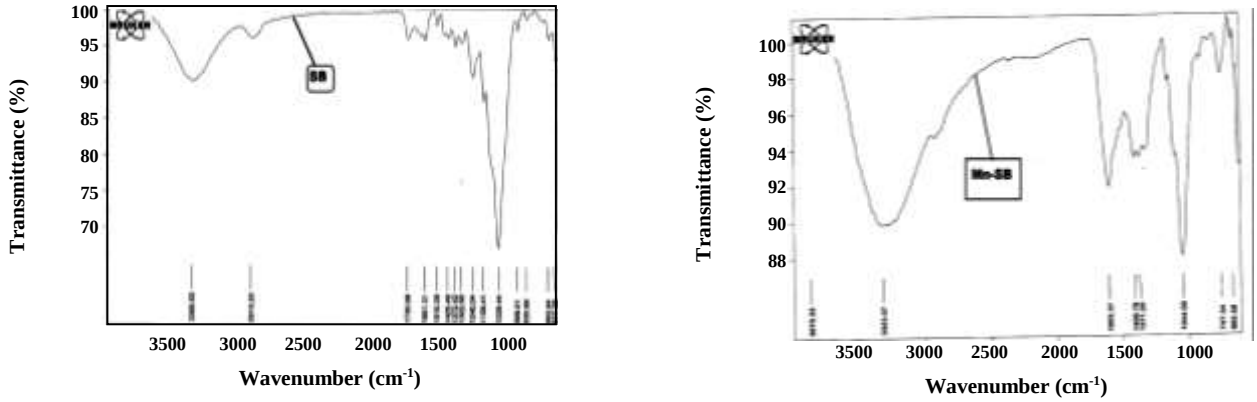

Fig. 1: (a) FT-IR of SB. (b) FT-IR of Mn (II) loaded on SB.

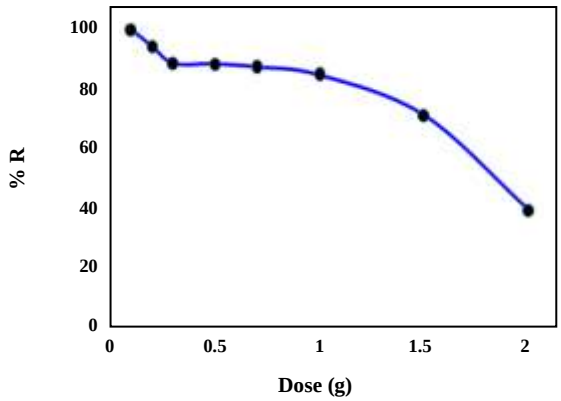

Fig. 2: Effect of biosorbent dose (SB) on the removal of Mn (II) ions from solution.

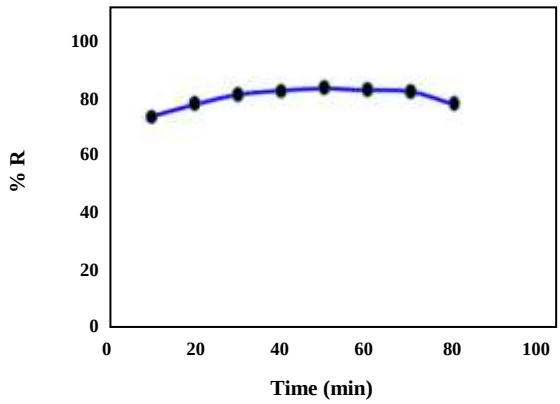

Fig. 3: Effect of contact time for adsorption of Mn (II) on SB.

equilibrium. At equilibrium active sites were not available for more adsorption of metal ions on SB surface [37] and a further increase in adsorption was not observed. However, adsorption started to decrease after equilibrium as shown in Fig. 3. Maximum Mn(II) removal efficiency of adsorbent and equilibrium was attained at 50 minutes.

Effect of pH

Another important factor that affects the adsorption of metal on SB is the pH or acidity of an aqueous solution. By changing the acidity of the solution, surface features (charge on the surface) of biosorbent are changed [11] and therefore, the rate of adsorption is altered. There is an optimum pH at which maximum metal ions are adsorbed on the surface of the adsorbent or removed from the aqueous environment.

At lower pH, carboxylate group present in SB is not ionized or deprotonated. That is why metal ions may not easily reach these functional groups and are not removed from the solution to a large extent. Hydrogen ion competes with Mn(II) ions [38] and preferably occupy active sites of SB due to their high concentration and mobility [39] thus lower the adsorption of metal ions due to their excess at low pH. When pH is increased, the carboxylate group becomes deprotonated or the surface of adsorbent becomes negatively charged [38]. More carboxylate ions group are available to bind with manganese ions and adsorption increases. Further increase of pH leads to the higher OH concentration that makes metal hydroxide $Mn(OH)_2$ (precipitate) [33] instead of removing metal ions from solution and slightly lowers the adsorption. This trend was studied in the present research by changing the pH of samples from 1 to 11 (Fig. 4) at 25 °C. At pH 1 and 2, less adsorption was observed to take place (Fig. 4). However on increasing the pH from 3-5,

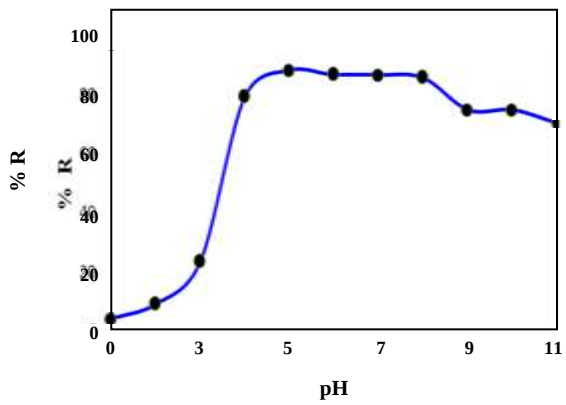

Fig. 4: Effect of pH on metal ion removal efficiency of SB (dose: 0.1g/50mL, time: 50min).

adsorption sharply increased. There is little difference in percentage removal efficiency of adsorbent at pH 5 and 6. The maximum amount of Mn(II) was removed from the solution at pH 5 as shown in Fig. 4. Further increase in pH decreases the manganese removing efficiency of SB.

Sorption isotherm models

Adsorption isotherms represent the adsorbents-adsorbates relationship and help in understanding the mechanism of adsorption process [40]. These isotherms are used to find the adsorption capacity of the adsorbent to remove heavy metals from contaminated water. In this work, SB was used to find its efficiency of removing Mn(II) from aqueous solution. Isothermal study was performed by using sample solutions with different manganese ion concentration like 10mg/L, 20mg/L, 30mg/L, 40mg/L and 50mg/L. Optimum pH value was maintained as 5 by using 0.1M HCl solution with contact time 50minutes. Different isotherms could be used to represent the adsorption data in a proper way. In this experiment, we used Langmuir, Freundlich, Harkin Jura and Halsey adsorption isotherms to represent the experimental data and to evaluate the adsorption process.

Langmuir adsorption isotherm

According to Langmuir, the adsorbent surface is homogeneous. Adsobate molecules form a single layer on the surface of adsorbent [41]. There is only one site for each molecule to be adsorbed on the surface of the adsorbate. Langmuir adsorption isotherm model in linear form can be represented as follow

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \tag{3}$$

In this equation C_e (mg/L), represents equilibrium concentration of manganese ions in the solution where q_e (mg/g) is the equilibrium concentration of manganese ion adsorbed on the surface of the adsorbent. K_L (L/mg) and q_m (mg/g) are Langmuir constant and biosorption capacity of the adsorbent respectively [39]. Greater the biosorption capacity, greater the metal removing efficiency of the adsorbent. Fig. 5(a) shows a linear plot between $1/q_e$ vs $1/C_e$ from which the value of R^2, q_m, and K_L can be calculated.

Value of q_m for removal of Mn(II) by SB is 21.74mg/g as shown in Table 1. R^2 (0.943) value indicates the validity of Langmuir isotherm for the adsorption process. K_L (0.28) of Langmuir adsorption isotherm represent the shape of isotherm, its value lies within the range of 0-1 represent favorable adsorption process [38]. From K_L another dimensionless parameter can be calculated which is given as

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{4}$$

The value of R_L provides information about the adsorption equilibrium [42]. The value of R_L can be 1, >1, <1 or zero indicates linear sorption, unfavorable sorption, favorable sorption or irreversible sorption respectively. In this experiment, $R_L < 1$ (0.98) indicates adsorption of Mn(II) on SB from aqueous solution is favorable.

Freundlich adsorption isotherm

It assumes the surface of adsorbent heterogeneous [11]. The general form of Freundlich adsorption isotherm is

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

This equation indicates the relationship between adsorbed manganese ions on the adsorbent q_e and unabsorbed manganese ions present in the solution C_e. The linear form of Freundlich adsorption isotherm is given below

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

The linear plot is drawn by using this equation as shown in Fig. 5(b) and K_F is obtained from intercept indicates adsorption capacity. Value of 1/n was found out from the slope

Table 1: Linear Adsorption Isotherm Parameters and correlation coefficients for adsorption of Mn(II) ions onto SB.

Langmuir $\frac{1}{q_e} = \left(\frac{1}{K_L . q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	q_m (mg/g)	21.74
	K_L (L/mg)	0.28
	R^2	0.943
Freundlich $\ln(q_e) = \ln(K_f) + \frac{1}{n}\ln(C_e)$	K_F (L/mg)	3.9
	n	1.3
	R^2	0.925
Harkin Jura $\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right)\log C_e$	A	18.18
	B	0.82
	R^2	0.968
Halsey $\ln q_e = \frac{1}{n}\ln K - \frac{1}{n}\ln C_e$	n	-1.276
	K	0.178
	R^2	0.925

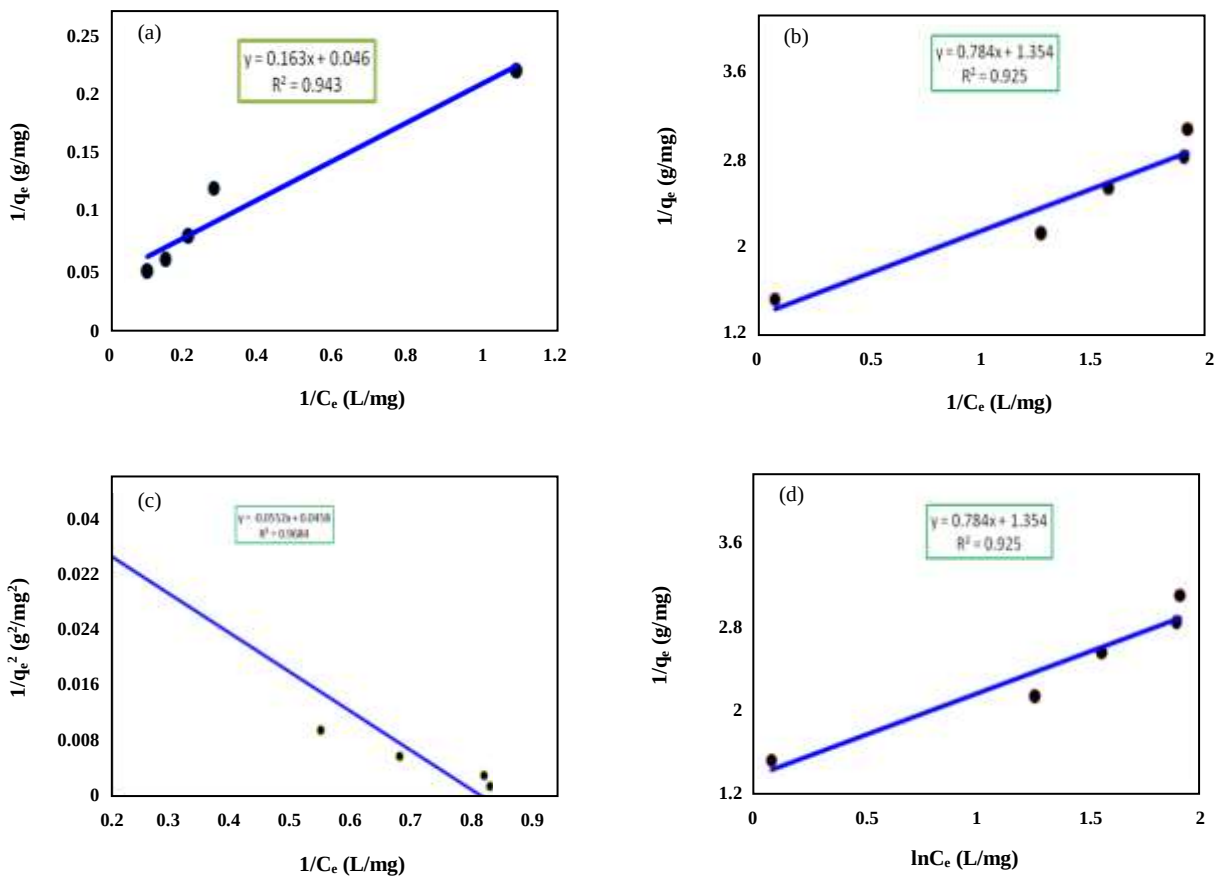

Fig. 5: (a) Langmuir adsorption isotherm for adsorption of Mn(II) onto SB at 50°C;size of SB 125µm;pH 5.0;SB dose 0.1g/50mL. (b) Freundlich adsorption isotherm for adsorption of Mn(II) onto SB at 50°C; size of SB 125µm; pH 5.0; SB dose 0.1g/50mL. (c) Harkin Jura adsorption isotherm for adsorption of Mn(II) onto SB at 50°C; size of SB 125µm; pH 5.0; SB dose 0.1g/50mL. (d) Halsey adsorption isotherm for adsorption of Mn(II) onto SB at 50°C; size of SB 125µm; pH 5.0; SB dose 0.1g/50mL.

that indicate the intensity of adsorption [37]. K_F, n and R^2 values for adsorption are shown in Table 1. Higher values of K_F and n indicate better adsorption capacity of free biomass over immobilized biomass. Previous research work showed that the value of n greater than unity for all biosorbent represents the favorable adsorption [43]. Its value can be in the range of 1-10 [44] for better adsorption. Thus in the following experiment, the adsorption process was favorable as the calculated value of n was 1.3. The value of correlation coefficient (0.925) indicated the adsorption process was complicated and multilayer's of manganese ions were formed on the surface of the adsorbent.

Harkin Jura adsorption isotherm

This isotherm assumes multilayer adsorption with heterogeneous pore distribution [37]. Harkin Jura adsorption equation is given as,

$$\frac{1}{q_e^{\,2}} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e \qquad (7)$$

In this equation, A and B are Harkin Jura constant. A plot of $1/qe^2$ vs $\log C_e$ was drawn as in Fig. 5(c).

Harkin Jura constants A, B and adsorption coefficient R^2 were calculated from slope and intercept of this plot as shown in Table 1. Value of R^2 (0.968) for this isotherm indicates that adsorption process can be best explained by Harkin Jura adsorption isotherm.

Halsey adsorption isotherms

It was used to study the sorption energy of multilayers of manganese ions adsorbed on the surface of the adsorbent [45]. The linear form of Halsey adsorption isotherm is

$$\ln q_e = \frac{1}{n}\ln k - \frac{1}{n}\ln C_e \qquad (8)$$

k is Halsey adsorption isotherm constant where *n* is an exponent of equation $\ln q_e$ vs $\ln C_e$ give a linear plot as shown in Fig. 5(d) and Halsey adsorption parameters are shown in Table 1.

Value of R^2 (0.925) indicates the applicability of Halsey adsorption isotherm but less applicable as compared to Langmuir and Harkin Jura adsorption isotherm. Experimental data showed among four adsorption isotherms (Langmuir, Freundlich, Harkin Jura, and Halsey) Langmuir and Harkin jura isa best fitted model to explain the adsorption process with high R^2 values.

Sorption kinetic model

The kinetic study is usually done to predict mechanisms of adsorption process [38]. Various kinetic models can be used to study kinetic of adsorption processes. Among them, the pseudo second order is well known to represent adsobate-adsorbent system [47]. First order and second order equation is given as follow

$$\ln C_e = \ln C_o - k_1 t \qquad (9)$$

$$d\frac{1}{C_e} = \frac{1}{C_o} + k_2 t \qquad (10)$$

C_e (mg/L) and C_o (mg/L) are metal ion concentration in solution at equilibrium and initial concentration in solution respectively. K_1 is the first order rate constant while k_2 is the second order rate constant. R_2 and rate constant value for the first order and second order are given in Table 2.

Pseudo second order equation in the linear form [48] is

$$\frac{t}{q_t} = \frac{1}{k_2' q_e^{\,2}} + \frac{t}{q_e} \qquad (11)$$

In the above equation q_e (mg/g) and q_t (mg/g) are the manganese ion concentration adsorbed by an adsorbent at equilibrium and at any time *t* (min) during the adsorption process respectively. While k'_2 (g/mg.min) is the rate constant of pseudo second order reaction. A plot was obtained by drawing t/q_t vs t as shown in Fig. 6. It represents adsorption of manganese on SB best follows pseudo second order reaction.

The calculated value of k'_2 and q_e from slope and intercept of this plot were (0.014) and (23.8mg/g) respectively.

In this experiment, first order, second order and pseudo second order were studied to evaluate the adsorption process. Value of R^2 given in Table 2, showed the best applicability of pseudo second order as compared to first and second order reaction to explain the kinetics of the adsorption of Mn(II) on SB.

Comparative study of biosorptive performance of SB with some other biosorbents

It is quite difficult to directly compare the efficiency of biosorbents to remove Mn (II) ions from aqueous solutions because the adsorption process depends upon different factors like adsorbent nature and environmental conditions.

Table 2: Kinetic parameters for adsorption of Mn(II) on SB.

First order model $\ln C_e = \ln C_o - K_1 t$	k_1 (min^{-1})	0.019
	R^2	0.646
Second order model $\frac{1}{C_e} = \frac{1}{C_o} + K_2 t$	k_2 (g/mg.min)	0.001
	R^2	0.579
Pseudo second order model $\frac{t}{q_t} = \frac{1}{K'_2 q_e^2} + \frac{t}{q_e}$	k^2 (g/mg.min)	0.014
	q_e (mg/g)	23.8
	R^2	0.997

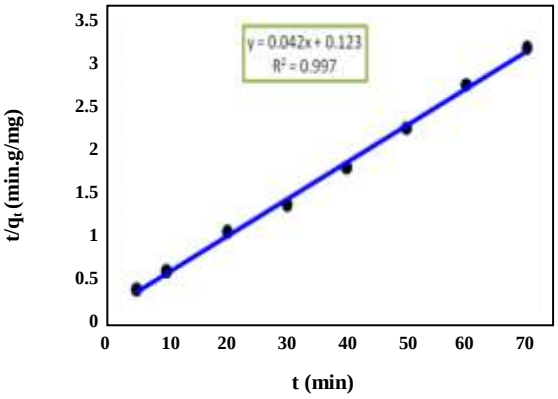

Fig. 6: Pseudo second order kinetic model for adsorption of Mn (II) onto SB at 50°C; the size of SB 125μm; pH 5.0; SB dose 0.1g/50mL.

Adsorption capacity q_m of the different adsorbent for removal of Mn(II) find out by other worker have been shown in Table 3. It can be easily observed that the biosorption capacity of SB is high as compared to a number of other reported materials.

CONCLUSIONS

In this research work, *Saccharum bengalense* (SB) has been investigated as a potential biosorbent for the removal of Mn (II) ions from aqueous solution. Experimental data was studied by using Langmuir, Freundlich, Harkin Jura and Halsey adsorption isotherm. Characteristic parameters and correlation coefficient of each isotherm were determined. Langmuir and Harkin Jura was found best fitted isotherm model for the adsorption process. First order, second order, and pseudo second order model were applied to discuss the kinetics of the adsorption process. Pseudo second order well explain the dynamic behavior of adsorption of Mn(II) on *Saccharum bengalense*. Experimental results indicate that *Saccharum bengalense* is an efficient and low cost adsorbent for the removal of Mn(II) from aqueous environment. It can be used for the removal of other heavy metals in contaminated water.

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Abbriviations

SB	*Saccharum bengalense*
AAS	Atomic Absorption Spectroscopy
FT-IR	Fourier Transforms InfraRed spectroscopy
C_e	Equilibrium concentration of Mn(II) in the solution, mg/L
C_o	Initial concentration of Mn(II) solution, mg/L
K_L	Langmuir constant, L/mg
q_m	Langmuir adsorption capacity, mg/g
q_e	Equilibrium concentration of metal on adsorbent, mg/g
R_L	Langmuir dimensionless parameter
K_F	Freundlich constant
N	Freundlich constant
A and B	Harkin Jura constant
K	Halsey constant
N	Halsey constant
R	General gas constant, 8.314J/mol.K
T	Temperature. K
t	Time, min
ΔG°	Gibes free energy, kJ/mol
ΔS°	Change in entropy, kJ/mol.K
ΔH°	Change in enthalpy, kJ/mol

Table 3: Comparison of biosorption performance of SB for removal of Mn (II) with some other biosorbents.

Biosorbents	q_m (mg/g)	pH	Isotherm model	Reference
Crab shell chitin	0.981	5.4	Langmuir	[49]
Demineralized Crab shell chitin	5.43	5.2	Langmuir	[49]
Aspergillus niger	14.58	2-7	Freundlich	[50]
Saccharomyces cerevisiae	11.25	2-7	Freundlich	[50]
Maize stalk	16.61	5	Langmuir	[51]
Gloeothece magna	0.906	------	Freundlich	[52]
Black carrot residue	5.170	5.25	Langmuir	[1]
Rice husk	7.7	5.5	Langmuir	[53]
Saccharum bengalense	21.74	5	Langmuir	Present work

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