

EQUILIBRIUM, KINETIC, AND THERMODYNAMIC STUDIES OF THE BIOSORPTION OF Mn(II) IONS FROM AQUEOUS SOLUTION BY RAW AND ACID-TREATED CORNCOB BIOMASS

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Biosorption was carried out in a batch process to test the suitability of corncob for the removal of manganese ion (Mn(II)) from aqueous solution. The amount of metal ions removed from solution depended on the metal ion-substrate contact time, ion concentration, temperature, and pH. The adsorption capacity of the biosorbent from corncob was also enhanced by treatment with acid. Kinetic modeling of the data obtained from the study showed that the biosorption of Mn(II) ions by the untreated and acid-treated corncob followed the Lagergren pseudo-first order model. The adsorption capacity of the raw biomass was found to be 6.54 mg/g, while acid-treated biomass showed an adsorption capacity of 7.87 mg/g. The data obtained from this study fitted well with the Freundlich and Langmuir adsorption isotherms.

Keywords: Biosorbent; Manganese; Kinetics; Pseudo-first order; Corncob

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INTRODUCTION

Cost is an important parameter when comparing sorbent materials. However, cost information is seldom reported. The expense of individual sorbents varies depending on the degree of processing required and local availability. Conventional methods of removing toxic metal ions from the aqueous solutions, such as coagulation, flocculation, filtration, ozonisation, and ion exchange, generally have high operating cost (Rao *et al.* 2002). Similarly, adsorption techniques, which have proved to be versatile and readily applicable for the removal of heavy metal ions, are disadvantaged by the high costs of activated charcoal – a desirable adsorbent (Gupta *et al.* 2003; Aravindhan *et al.* 2009). In general, an adsorbent can be termed “low-cost” if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Khan *et al.* 2004). Of course improved sorption capacity may compensate for the cost of additional processing (Bailey *et al.* 1999). Therefore, cheap bio-derivable materials of renewable sources are suitable alternatives. Thus, agricultural residues seem to be the most preferred (Saeed *et al.* 2005; Horsfall *et al.* 2006; Agarwal *et al.* 2006; Bello *et al.* 2008; Wang *et al.* 2009; Sousa *et al.* 2009; Adeogun *et al.* 2010), and as such, value can be added to the so-called agricultural wastes, which are in many cases also sources of pollution.

Biosorption has gained important credibility in recent years because of its eco-friendly nature, its excellent performance, and above all, the fact that it is a low cost domestic technique for the removal of heavy metal from wastewater (Ahalya *et al.* 2004). Recently, biosorption experiments have focused attention on waste materials, which can be by-products or from agricultural products and materials from large-scale industrial operations. Pagnanelli *et al.* (2002) had employed mycelia available from fermentation process of olive mill solid residue for removal of Cu(II) from aqueous solution. Their results revealed that copper was maximally adsorbed in the range of 5.0 to 13.5 mg/g under the different operating conditions.

Manganese is seldom found alone in a water supply; it is frequently found in iron-bearing waters. Manganese-polluted water is annoying in many respects, as it affects the appearance, taste, odour, and colour of the water. In low concentrations, it produces extremely objectionable stains on everything with which it comes in contact, including fabrics. The recommend limit of manganese is 0.05 mg/L for drinking water and 0.01 to 0.02 mg/L for many industrial purposes. It has been observed to cause neurological disorders in man when ingested or inhaled at high concentrations (>10 mg/day) (USEPA 1999); thus there is need for effective removal of Mn(II) from its aqueous solution.

Among the possible contaminants found in waste water, especially from mining sources, Mn has been found notoriously difficult to remove (Johnson *et al.* 2005; Sibrel *et al.* 2007). Over the last three decades many treatment technologies have been developed to address and correct the deleterious effects of contaminants on the quality of natural streams, especially those from mining sources. The most common approach for the removal of Mn is its oxidation followed by its precipitation as manganese oxide (MnO₂). However, this requires high pH, since abiotic and biological oxidation rates are slow for pH < 8.0, and can also be inhibited by the presence of iron (Fe) (Johnson *et al.* 2005). In addition, Benner *et al.* (1999) had reported partial removal of manganese under reducing conditions; this was attributed to its precipitation as rhodochrosite (MnCO₃).

To the best of our knowledge, adsorbent prepared from corn cob had not been used for the removal of Mn ions from aqueous solution. Therefore, this study examines the performance of biosorbent prepared from corncob for biosorption of Mn(II). The effects of initial metal concentration, temperature, contact time, pH, and treatment with mineral acid on biosorption capacity were also examined. Experimental data were fitted with Freundlich and Langmuir isotherms, whereas the Lagergren pseudo-first-order, and Ho's pseudo-second order models were used to analyse the kinetic data. Also the thermodynamic parameters of the process were determined and reported.

EXPERIMENTAL

Materials

All chemicals used in this study were Analar grade, purchased from British Drug House London, England. Corncobs were obtained from Eruku village in Ewekoro local government area of Ogun State in Nigeria and used for the preparation of the biosorbent.

The corncobs were washed with distilled water, cut into smaller pieces, and sun-dried for 10 days. The dried biomass was then pulverized using a mechanical grinding

machine and sieved through a 150 μm mesh copper sieve. To compare the effect of treatment on the performance of the biosorbent, treated biomass was prepared by mixing five grams of the raw biomass with 200 mL of 1M solution of oxalic acid, followed by agitation at 200 rpm for 24 hours (Park et al. 2005). The samples were kept in an air-tight container until the time of usage.

An aqueous solution of Mn(II) ion was prepared from MnCl_2 . The stock solution was prepared with deionized water at the initial concentration of 1000 mgL^{-1} of Mn (II). The solutions used for the study were obtained from the stock solution by dilution. The pH values of the solutions were adjusted by the addition of 0.1M HCl and/or 0.1M NaOH solution in drops.

Methods

Biosorption equilibrium studies

Equilibrium studies were carried out in a set of 43 Erlenmeyer flasks (100 mL) wherein the solutions of Mn(II) ions (50 mL) with different initial concentrations (50 to 300 mg/dm^3) were placed. Equal mass of the biosorbent (1 g of biosorbent with particle size $150 \mu\text{m}$) were added to the solutions of Mn(II) ion and kept on an isothermal shaker (orbital shaker) at $25 \pm 1 \text{ }^\circ\text{C}$ for 24 h to reach equilibrium of the solid-solution mixture. Similar procedures were followed for another set of Erlenmeyer flasks containing the same amount of Mn(II) ion concentration but without adsorbent (biomass); these sets were used as a control. The flasks were then removed from the shaker and filtered before the final concentrations of Mn(II) ions in the solutions were determined. Filtration prior to the analysis is in order to minimize interference effect of the biosorbent particles. Each experiment was duplicated under identical conditions. The amount biosorbed at equilibrium, Q_e (mg/g), was calculated using Equation 1,

$$Q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg/dm^3) are the liquid-phase concentrations of Mn(II) ion at initial and equilibrium stage, respectively, V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

Batch kinetic studies

The procedures for the kinetic experiments were basically identical to those of equilibrium studies. The aqueous samples were taken at preset time intervals, and the concentrations of Mn(II) ion were similarly measured. The amount of Mn(II) ion biosorbed, Q_t (mg/g), at time t , was calculated using Equation 2 below,

$$Q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where C_o and C_t (mg/dm^3) are the liquid-phase concentrations of Mn(II) ion at initial and any time t , respectively, V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

Effect of Agitation Time and Concentration of Mn(II) Ion on Biosorption

Eight contact time experiments for biosorption of Mn(II) ion were carried out at different initial concentrations (50 to 300 mg/dm³) and at temperature of 25 ± 1 °C. The contact time necessary for Mn(II) ions with initial concentrations between 50 and 300 mg/dm³ to reach equilibrium was about 30 minutes, and the amount of the Mn(II) ion biosorbed onto the biosorbent from the raw sample increases with time (Fig. 1).

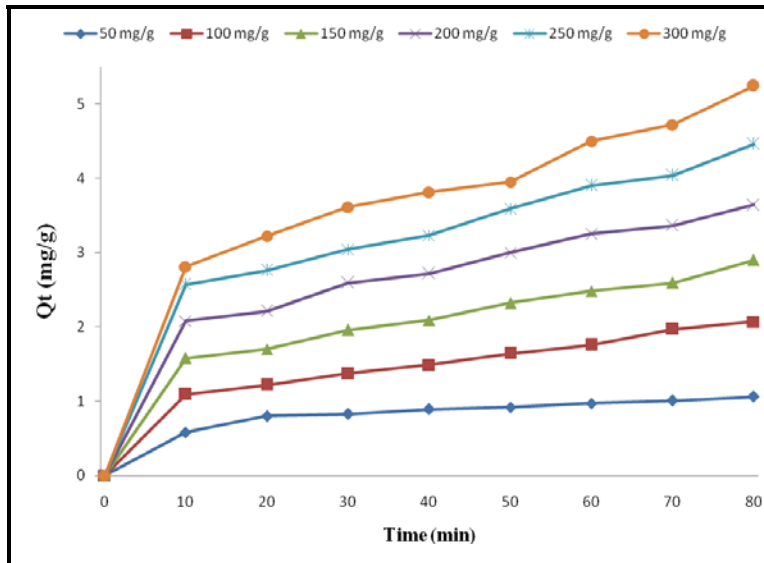


Fig. 1. The variation of amount of Mn(II) ion biosorbed with time at various concentrations of Mn(II) ions at 25 ± 1 °C (pH 3, W = 1 g raw biomass)

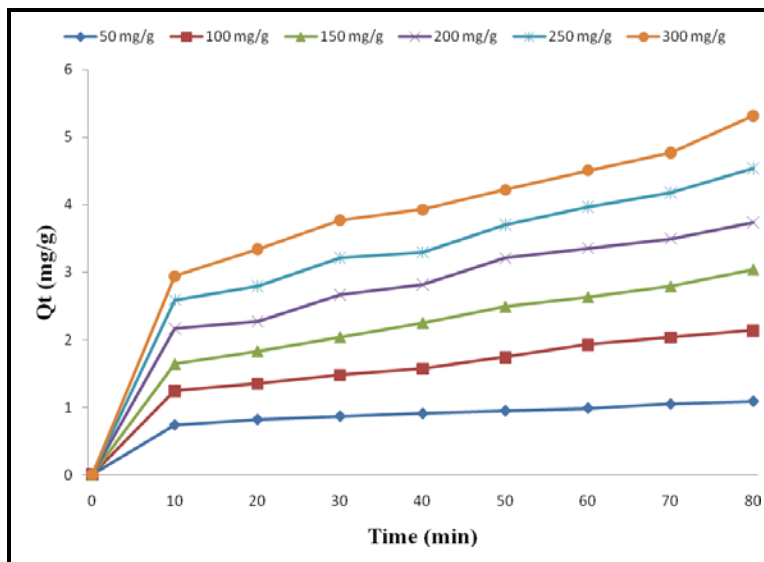


Fig. 2. The variation of amount of Mn(II) ion biosorbed with time at various concentrations of Mn(II) ions at 25 ± 1 °C (pH 3, W = 1 g acid-treated biomass)

When treated with oxalic acid, the Mn(II) ion removed from the solution by the biosorbent increased slightly (Figs. 1 and 2). The amount of Mn(II) ion biosorbed with time increased from 1.09 to 5.19 mg/g for the raw biomass and from 1.15 and to 5.42 mg/g for an acid-treated sample when the Mn(II) ion concentration increased from 50 to 300 mg/g initial concentrations. This shows that adsorption capacity is not seriously affected by acid treatment, especially at higher metal concentration.

Effect of Biosorbent Dose on Biosorption

The increase in the sorption of metal ion from aqueous solution depends on the number of available sites on the sorbent (Bello et al. 2008). Biosorbent quantity is therefore very essential because it determines the capacity of biosorbent for removal of a particular metal ion concentration.

The sorption percentage of Mn(II) ion increased with increase in the amount of biosorbent used. The optimum value was at a biosorbent quantity of 1g, above which the effect of biosorbent quantity became irrelevant (Fig. 3). This may be due to the saturation of sorption sites at higher biosorbent concentration.

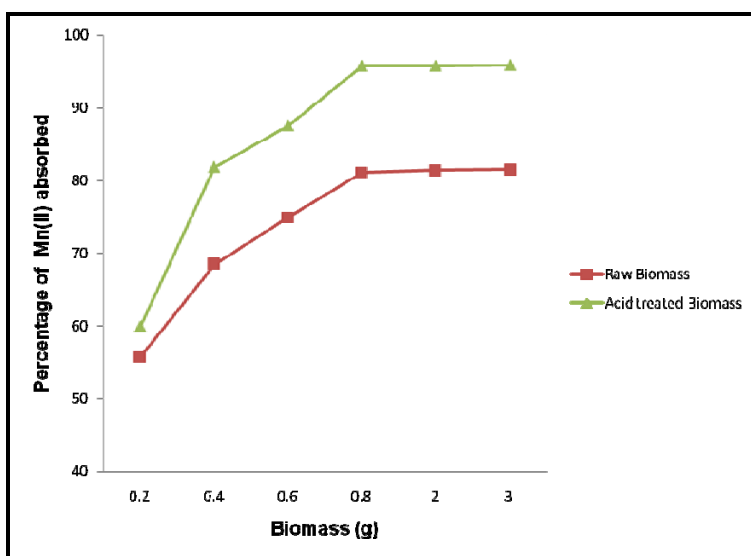


Fig. 3. Effect of initial biosorbent concentrations on the amount of Mn(II) ion biosorbed from solution by raw and acid-treated corncob at 25 ± 1 °C (pH 3, $[\text{Mn}^{2+}] = 50 \text{ mg/dm}^3$)

The initial metal concentration led to the reduction in biosorption capacity of both the raw and acid-treated corncob (Fig. 4). The percentage sorption of Mn(II) ion decreased from 87.2 to 69.1.6 % for the raw corncob and from 93.8 to 72.7 % for the acid-treated corncob as the initial metal concentration increased from 50 to 300 mg/L. This may be due to the fact that at lower concentration, competition for the available binding sites is low; thus, percentage biosorption was higher at lower concentration than at higher concentration, where saturation of the binding sites and competition between the ions for the binding sites were obvious.

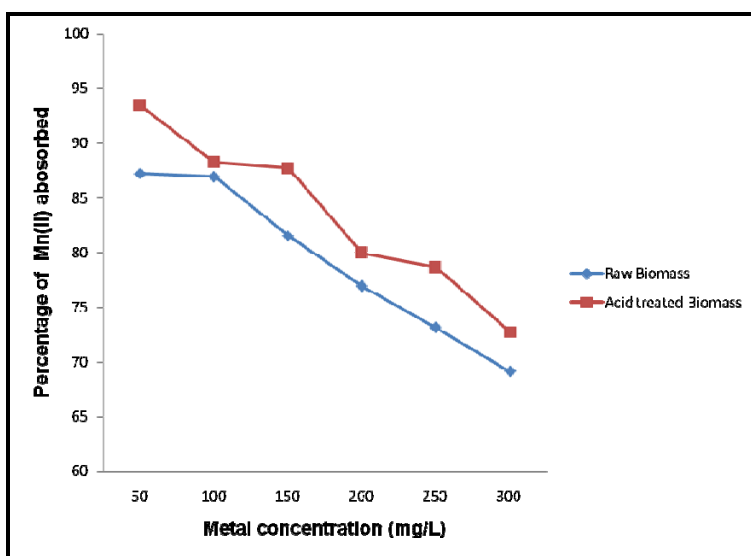


Fig. 4. The effect of initial metal concentration on the amount of Mn(II) ion biosorbed from solution by the raw and acid-treated biomass at at 25 ± 1 °C (pH 3, Biosorbent dose of 1g)

Effect of pH on Biosorption

The percentage removal of metal ion was pH-dependent, as shown in Fig. 5. The sorption of Mn(II) ions by both biosorbents was favoured in the acid range of 2.0 to 3.0. Maximum adsorption was observed at a pH of 2.0. For both biosorbents, sorption percentage was lower at a pH of 7.0. A similar trend had been observed earlier (Samdani *et al.* 2008).

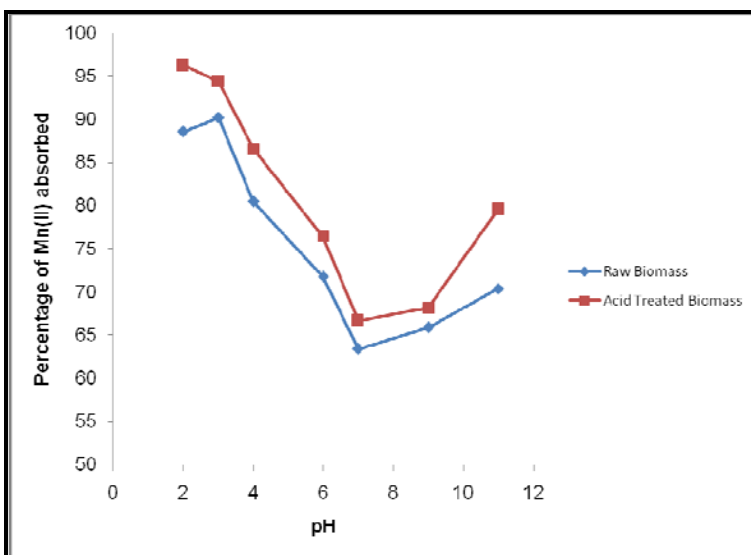


Fig. 5. The effect of pH on the amount of Mn (II) ion absorbed by raw and acid-treated biomass. ($[Mn^{2+}] = 50 \text{ mg/dm}^3$ acid treated biomass and Biosorbent dose of 1g)

The effect of pH on the adsorption capacity may be attributed to the combined effect of the nature of surface and the presence of acid and base used to adjust the pH of the solution. It is also believed that the mechanism for the adsorption of anion onto adsorbent surface involves a surface complexation mechanism. Maximum metal sorption at lower pH seems to be due to the presence of net positive charge on corncob surface. It is also well known that the pH of the medium affects the solubility of the metal ions and concentration of the counter ions on the functional groups of the biosorbent cell walls (Vijaya et al. 2010).

Kinetic Modeling of the Biosorption Processes

The kinetic data for the adsorption of Mn(II) ions were analyzed with the linear form of both the Lagergren-pseudo-first order model (Equation 3) and the Ho's pseudo-second order model (Equation 4) respectively,

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

where Q_e is the amount of adsorbate adsorbed at equilibrium, Q_t is the amount of adsorbate adsorbed at time t , and k_1 and k_2 are the rate constants for first and second order reactions respectively. For the first order model, the plot of $\log(Q_e - Q_t)$ versus t should give a straight line with a slope of $k_1/2.303$ and the intercept $\log Q_e$. For the second order model, the plot of t/Q_t versus t should produce a straight line with a slope of $1/Q_e$ and an intercept of $t/k_2 Q_e^2$.

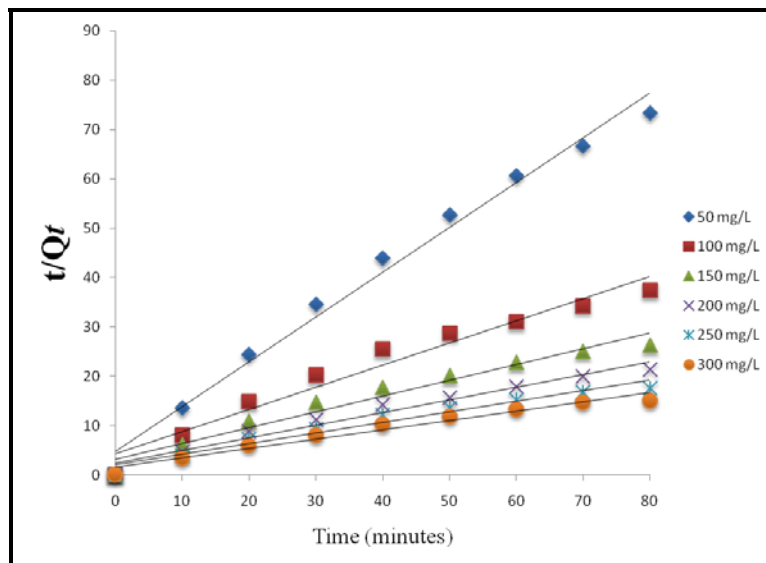


Fig. 6. Second order model of biosorption of Mn(ii) ion with untreated biomass

Table 1. Kinetic Parameters of the Sorption of Mn (II) by Raw Biomass

Concentration (mg/L)	$Q_{e(\text{exp})}$ (mg/g)	$Q_{e(\text{cal})}$ (mg/g)	k_1 (min^{-1})	R^2	% SSE	$Q_{e(\text{cal})}$ (mg/g)	k_2 (min g^{-1})	R^2	% SSE
50	1.06	0.78	0.038	0.96	0.095	1.09	0.20	0.99	0.005
100	2.07	1.88	0.034	0.96	0.099	2.16	0.23	0.95	0.033
150	2.9	2.27	0.028	0.9	0.202	2.95	0.35	0.96	0.034
200	3.64	2.91	0.032	0.96	0.24	3.76	0.48	0.96	0.053
250	4.46	3.44	0.029	0.95	0.339	4.55	0.58	0.96	0.039
300	5.24	4.08	0.028	0.94	0.484	5.29	0.65	0.95	0.01

The kinetic data obtained from the raw and acid-treated corncob fitted well with the first- and second-order kinetic models. The fitting parameters of the kinetic models for the raw and acid treated samples are shown in Tables 1 and 2, respectively. The Q_e values obtained from the second-order kinetic model agreed with the experimental values, and the values of the coefficients of determination (R^2) also confirmed that second order model was more preferred (Fig. 6).

Table 2. Kinetic Parameters of the Sorption of Mn (II) by Acid-Treated Biomass

Concentration (mg/L)	$Q_{e(\text{exp})}$ (mg/g)	$Q_{e(\text{cal})}$ (mg/g)	k_1 (min^{-1})	R^2	% SSE	$Q_{e(\text{cal})}$ (mg/g)	k_2 (min g^{-1})	R^2	% SSE
50	1.09	1.36	0.037	0.91	0.098	1.10	0.25	0.99	0.011
100	2.14	1.86	0.036	0.92	0.067	2.23	0.28	0.96	0.033
150	3.04	2.47	0.031	0.96	0.222	3.13	0.37	0.96	0.018
200	3.74	3.06	0.035	0.96	0.258	3.89	0.51	0.97	0.042
250	4.54	3.58	0.031	0.95	0.360	4.65	0.59	0.96	0.030
300	5.32	3.95	0.027	0.94	0.410	5.35	0.72	0.96	0.018

Test of Kinetic Models

Apart from the value of R^2 , the applicability of both kinetic models were also verifiable through the sum of error squares (SSE, %). The biosorption kinetics data of Mn(II) ion on adsorbent prepared from corncob were subjected to the sum of error squares test at different initial metal concentrations. The validity of each of the models was determined using Equation 5 below,

$$SSE(\%) = \sqrt{\frac{\sum (Q_{e(\text{exp})} - Q_{e(\text{cal})})^2}{N}} \quad (5)$$

where N is the number of data points.

The higher the value of R^2 and the lower the value of SSE, the better will be the goodness of fit. As shown in Tables 1 and 2, the calculated results confirmed the fact that the kinetic data from this study were best described by the second-order kinetic model.

Thermodynamic Studies

Effect of temperature on biosorption

The temperature dependence of the removal of Mn(II) ions from aqueous solution by the raw and acid-treated corncob is also reported. The sorption capacities of both the raw and acid treated biosorbents increased with increasing temperature. For raw biomass the value increased from 87.3 to 99.6%, while an increase from 90.2 to 99.8% was noted for the acid-treated biomass (Fig. 7). Such behavior usually is interpreted as an indication of endothermic nature of the biosorption process; however, it is also possible that this may be attributed to an increase in the number of active sites available for sorption at higher temperature due to bond ruptures and decrease in intracellular diffusion resistance leading to exposure of more active sites. The results also showed that the acid-treated corncob adsorbed Mn(II) ions more effectively than the raw corncob biomass.

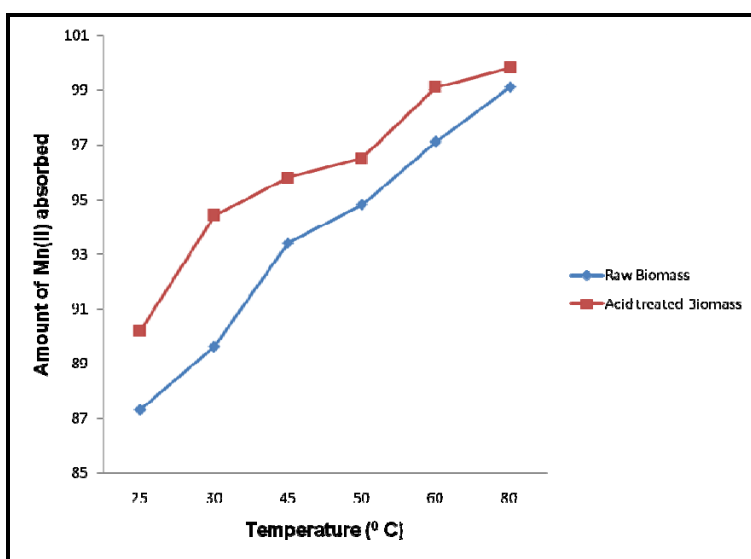


Fig. 7. The effect of temperature on the adsorption of Mn (II) ion by raw and acid-treated biomass (pH 3, $[Mn^{2+}] = 50 \text{ mg/dm}^3$ acid-treated biomass and Biosorbent dose of 1g)

Thermodynamic Parameters

Thermodynamic parameters of the biosorption process, i.e. free energy change (ΔG), entropy change (ΔS), as well as the enthalpy change (ΔH), were determined using the expression below:

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

where

$$\Delta G = -RT\ln Q_e \quad (6)$$

The values of ΔH and ΔS were determined from the plot of ΔG versus T ; the slope of straight line obtained is $-\Delta S$, while the intercept is ΔH (Ertugay et al. 2008). The plot of the free energy change versus temperature of the two biosorbents in the sorption of Mn

(II) ions are shown in Fig. 8, while the thermodynamic parameters are shown in Table 3. The negative value of the free energy change is an indication that sorption process is feasible and spontaneous.

Table 3. Physical Parameters of Thermodynamic of Corncob for the Sorption of Mn (II)

Temperature (K)	Raw Biomass				Acid Treated Biomass			
	Q_e (mg/g)	ΔG (kJ/mol)	ΔH (kJ/mol/l)	ΔS (J/mol/K)	Q_e	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
298	0.48	1.81	11.71	-34.07	0.89	0.30	4.15	-13.05
303	0.58	1.38			1.00	0.012		
318	0.75	0.78			1.09	-0.22		
323	0.82	0.52			1.12	-0.31		
333	0.96	0.11			1.15	-0.39		
353	1.02	-0.44			1.19	-0.50		

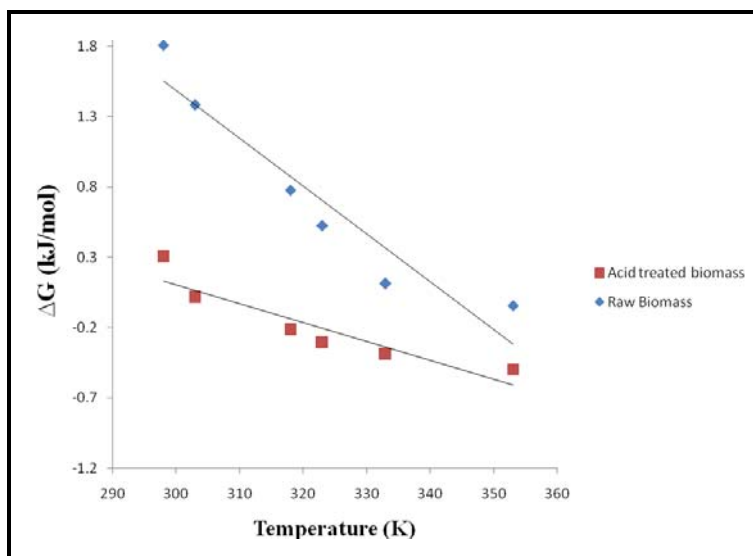


Fig. 8. The free energy change versus temperature for the sorption of Mn (II) ions

The values obtained for the enthalpy change were positive for both biosorbents, which indicates that the sorption process is endothermic in nature. The enthalpy change of the acid-treated corncob was, however, lower than that of the untreated corncob. This implies that higher temperature will be required for the sorption process in the raw samples to achieve comparable results with the acid-treated biomass.

Biosorption Isotherms

The isotherm indicates how the biosorbed molecules are distributed between the solid and liquid phases when the biosorption process reached the equilibrium state. The

analysis of equilibrium data, by means of different isotherm models, is an important step in finding a suitable model that can be used for design purposes (Haghseresht and Lu 1998). In this study, Langmuir, Freundlich, and Temkin isotherms were used to fit the equilibrium data. The Langmuir isotherm assumes the formation a monolayer of adsorption onto a surface containing a finite number of adsorption sites with uniform strategies of adsorption and no transmigration of adsorbate in the plane of surface (Fytianos *et al.* 2003). The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage (Fytianos *et al.* 2003), while the Temkin isotherm is based on the assumption that heat of adsorption would decrease linearly with increase of coverage of adsorbent due to sorbate/sorbent interaction (Liu and Liu 2008). The applicability of the isotherm equation was compared by judging the coefficients of determination, R^2 .

Langmuir isotherm

The linear form of Langmuir's isotherm model is given by the following equation,

$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o}\right)C_e \quad (7)$$

where C_e is the equilibrium concentration of the adsorbate (Mn(II) ion mg/L), Q_e is the amount of adsorbate adsorbed per unit mass of adsorbate (mg/g), and Q_o and b are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. When $\frac{C_e}{Q_e}$ was plotted against C_e , a straight line with slope $\frac{1}{Q_o}$ was obtained (Fig. 9), indicating that the biosorption of the Mn(II) ions onto biomass followed the Langmuir isotherm.

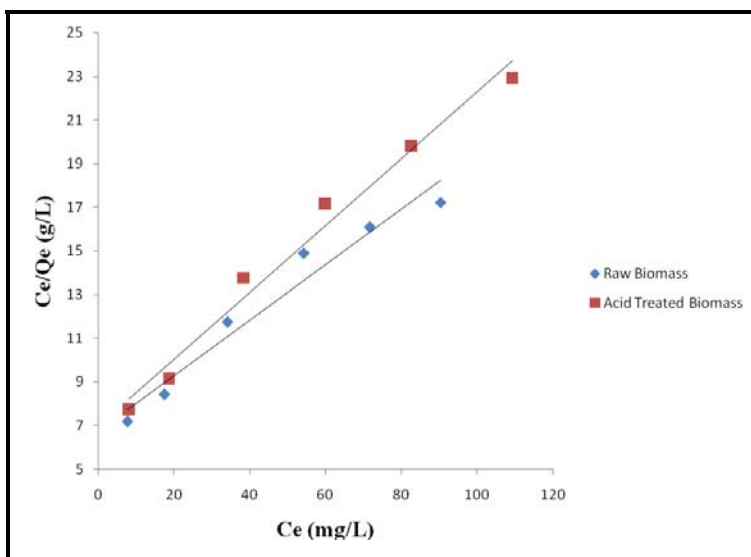


Fig. 9. Langmuir adsorption isotherms for the biosorption of Mn(II) ions on corncob biomass

The Langmuir constants b and Q_o were calculated from this isotherm, and their values are given in Table 4. Conformation of the experimental data to Langmuir isotherm model indicates the homogeneous nature of the biosorbent surface, i.e., each Mn(II) ion molecule/biomass biosorption has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of Mn(II) ion at the surface of the biosorbent. Similar observations were reported on the biosorption of chromium ion on tamarind (*Tamarindus indica*) fruit shell (Popuri *et al.* 2007).

Table 4. Langmuir and Freundlich Isotherm Constants for Mn(II) Ions at 25±1 °C

	Raw Biomass	Treated Biomass
Langmuir Isotherm parameters		
Q_o (mg/g)	6.54	7.87
b (L/mg)	1.07	1.23
R^2	0.98	0.96
R_L	0.003	0.003
Freundlich Isotherm parameters		
$1/n$	0.563	0.614
K_F (mg/g)(1/mg) ^{1/n}	0.352	0.335
R^2	0.99	0.99
Temkin isotherm parameters		
a_T	0.22	0.87
b_T (kJ/mole)	1.518	1.754
R^2	0.96	0.98

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) (Webi and Chakarvort 1974), which is defined by,

$$R_L = \frac{1}{(1 + bC_o)} \quad (8)$$

where b is the Langmuir constant and C_o the highest metal ion concentration (mg/L).

The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values of 0.003 found for raw and treated biomass confirmed that the biosorbent prepared from the corncob biomass is favourable for biosorption of Mn(II) ion under conditions used in this study.

Freundlich isotherm

The well-known logarithmic form of Freundlich model is given by the following equation,

$$\log Q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (9)$$

where Q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (Mn(II) ion), and K_F and n are Freundlich constants, n giving an indication of how favourable is the adsorption process. The parameter K_F [(mg/g)(1/mg)ⁿ] is the adsorption capacity of the adsorbent.

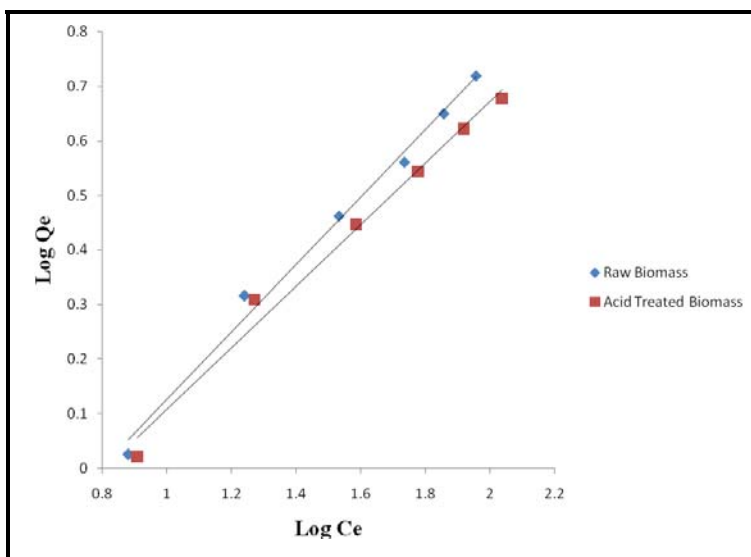


Fig. 10, Freundlich Adsorption Isotherms for the biosorption of Mn(II) ions on corncob biomass

K_F can be defined as the adsorption or distribution coefficient and represents the quantity of Mn(II) ion adsorbed onto biosorbent for a unit equilibrium concentration. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghseresht and Lu 1998). A value of $1/n < 1$ indicates a normal Langmuir isotherm, while above one is indicative of cooperative adsorption (Fytianos *et al.* 2003). The plot of $\log Q_e$ versus $\log C_e$ gives straight lines with slope ' $1/n$ ' (Fig. 10), which shows that the biosorption of Mn(II) ions also followed the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated and recorded. Table 4 shows the values of the parameters of the two isotherms and the related correlation coefficients. From the table, the Freundlich model yielded a relatively better fit ($R^2 = 0.99$) than the Langmuir model ($R^2 = 0.95$). The value $1/n$ of 0.61 (Table 4) is an indication of favourable adsorption (Adamson 2001).

Temkin isotherm

The Temkin isotherm is given by the expression

$$Q_e = \frac{RT}{b_T} \ln(a_T C_e) \quad (10)$$

The linear form of this isotherm model is given by the following equation,

$$Q_e = B \ln a_T + B \ln C_e \quad (11)$$

where C_e is the equilibrium concentration of the adsorbate (Mn(II) ion mg/L), Q_e is the amount of adsorbate adsorbed per unit mass of adsorbate (mg/g), a_T (L/g) is the equilibrium binding constant, corresponding to the maximum binding energy, b_T is a constant related to the heat of adsorption, T is the temperature (K), and R is the ideal gas constant ($8.315 \text{ J mol}^{-1} \text{ K}^{-1}$).

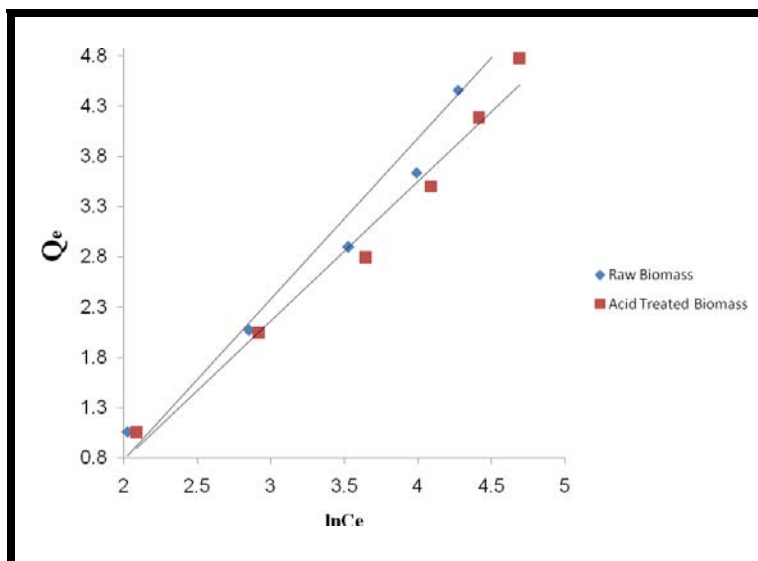


Fig. 11. Temkin Adsorption Isotherms for the biosorption of Mn(II) ions on corncob biomass

Table 5. Comparison of Mn(II) Ion Biosorption Capacity of Corn Cob with Different Biosorbents

Biosorbent	Absorption Capacity Q_o (mg/g)	Reference
<i>Riccia xuitans</i>	0.254	Chojnacka (2007)
<i>Bombax malabaricum</i>	0.2838	Emmanuel and Veerabhadrha (2009)
<i>Ipomea batatas</i>	0.3627	Emmanuel and Veerabhadrha (2009)
<i>Pithecelobium dulce</i>	0.4156	Emmanuel and Veerabhadrha (2009)
<i>Peltaforum ferruginium</i>	0.4433	Emmanuel and Veerabhadrha (2009)
Peanut shell	1.78	Vaggetti <i>et al.</i> (2008)
Natural Clay	10.0	Eba <i>et al.</i> (2010)
<i>Pseudomonas aeruginosa</i> AT18	20.32	Silva <i>et al.</i> (2009)
Biomass waste derived activated carbon	23.4	Budinova <i>et al.</i> (2008)
Corn cob biomass (untreated)	6.54	Present study
Corn cob biomass (acid treated)	7.87	Present study

Biosorption of Mn(II) ion on the corn cob also followed Temkin isotherm with suitable accuracy, indicating change in interaction between adsorbate and biosorbent. The constant b_T reflects bonding energy, which in turn dictates the type of interaction. The typical bonding energy range for ion exchange mechanism is reported to be 8 to 16 kJ/mol (Munir *et al.* 2010). It is observed that up to -20 kJ/mol is indicative of a physisorption process due to electrostatic interaction between charged molecules, whereas more negative than -40 kJ/mol involves chemisorption (Zafar *et al.* 2007). In this study, low values in the of b_T for raw and treated corn cob biomass (1.518 and 1.754 kJ/mol respectively) indicate that interactions between the sorbate and sorbent are neither purely through ion-exchange nor purely through physisorption (Kiran and Kaushik 2008).

CONCLUSIONS

1. The present investigation showed that biomass prepared from maize cob (corn cob) can be effectively used for the removal of Mn(II) ions from aqueous solutions over a wide range of concentrations.
2. Biosorption behaviour is well described by Freundlich and Langmuir adsorption isotherms.
3. Kinetic data follow a pseudo-second-order kinetic model. The value of the maximum adsorption capacity, Q_o (6.54 and 7.87 mg/g for raw and acid treated biomass, respectively) are comparable with the values observed for other biosorbents reported in the earlier studies (Table 5).
4. The Freundlich adsorption isotherm provides the best fit for the systems involving corn cob with Mn(II).
5. This study also shows that is possible to enhance the capacity of the biomass by modification with other reagents, and that increase temperature also favours the biosorption process.

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