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Equilibrium, Kinetics and Thermodynamic Studies of the Biosorption of Mn (II) Ions from Aqueous Solution by Raw and Acid-Treated Corncob Biomass

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Abstract: 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 Largergren pseudo-first order model. The adsorption capacity of the raw biomass is 6.54 mg g^{-1} while acid treated biomass has adsorption capacity of 7.87 mg g^{-1}. The data obtained from this study fitted well with the Freundlich and Langmuir adsorption isotherms.

Key words: Biosorbent, manganese, kinetics, pseudo-first order and corncob, biomass, Nigeria

INTRODUCTION

Manganese is seldom found alone in a water supply, it is frequently found in iron-bearing waters. Manganese polluted water is in every bit of it annoying as it affect 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 with including fabrics. The recommend limit of manganese is 0.05 mg L^{-1} for drinking water and 0.01-0.02 mg L^{-1} for many industrial purposes. It has been observed to cause neurological disorders in man, when ingested or inhaled at high concentrations (>10 mg day^{-1}) (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 source, Mn has been found notoriously difficult to remove (Johnson and Younger, 2005; Sibrell *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 (MnO_2). 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 and Younger, 2005). In addition, Benner *et al*. (1999) had reported partial removal of manganese under reducing conditions this is attributed to its precipitation as rhodochrosite ($MnCO_3$). Other conventional methods of removal of toxic metal ions from the aqueous solutions such as: Coagulation, flocculation, filtration, ozonisation and ion exchange are of high operating cost (Rao *et al*., 2002). Similarly, adsorption technique which proved to be versatile and readily applicable for the removal of heavy metal ions is incapacitated by high costs of activated charcoal-a desirable adsorbent (Gupta *et al*., 2003; Aravindhan *et al*., 2009). 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; Bello *et al*., 2008; Wang *et al*., 2009; Sousa *et al*., 2009; Adeogun *et al*., 2010).

Biosorption has gained important credibility in recent years because of its eco-friendly and excellent performance, above all, it is a low cost domestic technique for the removal of heavy metal form wastewater (Ahalya *et al*., 2003). Recently, biosorption experiments have focused attention on waste materials which are by products or waste materials 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

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removal of Cu (II) from aqueous solution. Their results revealed that copper was maximally adsorbed in the range of 5.0-13.5 mg g^{-1} under the different operating conditions.

This study examines the performance of biosorbent prepared from corncob for biosorption of Mn (II) from aqueous solutions. The effect of initial metal concentration, temperature, contact time, pH and treatment with mineral acid were on biosorption capacity were also examined. Experimental data were fitted with Freundlich and Langmuir isotherms, Lergergren 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.

MATERIALS AND METHODS

Materials: All chemicals used in this study were of reagent grade or higher quality. 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 were then, pulverized using 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 5 g of the raw biomass with 200 mL solution of oxalic acid and agitated (200 rpm) for 24 h (Park *et al*., 2005). The samples were kept in an air tight container till the time of usage.

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 mg L^{-1} of Mn (II). The solutions used for the study were obtained from the stock solution by dilution. The pH of the solutions were adjusted by the addition of 0.1M HCl and/or 0.1M NaOH solution in drops.

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 (50-300 mg dm^{-3}) were placed. Equal mass of the biosorbent (1 g of biosorbent with particle size 150 μm) were added to the solutions of Mn (II) ion and kept on an isothermal shaker (orbital shaker) at 25±1°C for 24 h to reach equilibrium of the solid-solution mixture. Similar procedures were followed for another set of Erlenmeyer flask 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^{-1}) was calculated using Eq. 1:

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

Where:

C_o (mg dm^{-3}) = The liquid-phase concentrations of Mn (II) ion at initial stage
C_e (mg dm^{-3}) = The liquid-phase concentrations of Mn (II) ion at equilibrium stage
V = The volume of the solution (L)
W = 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^{-1}) at time t was calculated using Eq. 2:

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

Where:

C_o (mg dm^{-3}) = The liquid-phase concentrations of lead ion at initial time t
C_t (mg dm^{-3}) = The liquid-phase concentrations of lead ion at any time t
V = The volume of the solution (L)
W = 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 (50-300 mg dm^{-3}) and at temperature of 25°C. The contact time necessary for Mn (II) ions with initial concentrations between 50 and 300 mg dm^{-3} to reach equilibrium was about 30 min and the amount of the Mn (II) ion biosorbed onto the biosorbent from the raw sample increases with time (Fig. 1).

When treated with oxalic acid, the Mn (II) ion removed from the solution by the biosorbent increased slightly and become constant sometimes above 80 min (Fig. 1 and 2). The sorption capacity increases from 1.09-5.19 mg g^{-1} for the raw biomass and from 1.15 and to 5.42 mg g^{-1} for acid treated sample when the Mn(II) ion concentration increases from 50-300 mg g^{-1} initial concentrations.

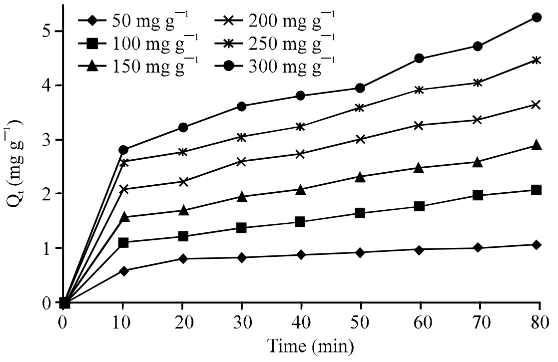

Fig. 1: The variation of adsorption capacity with biosorption time at various concentrations of Mn (II) ions at 25°C (pH 3, W = 1 g raw biomass)

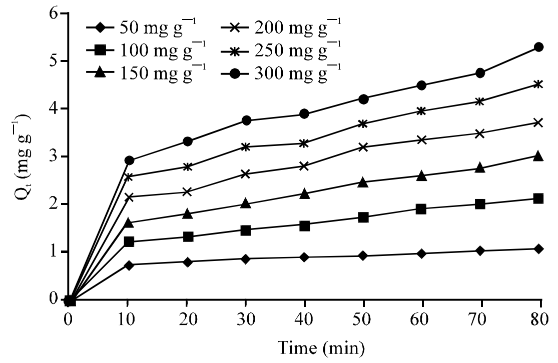

Fig. 2: The variation of adsorption capacity with biosorption time at various concentrations of Mn (II) ions at 25°C (pH 3, W = 1 g acid treated biomass)

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 increases with increase in the amount of biosorbent used, the optimum value was at biosorbent quantity of 1 g, above which the effect of biosorbent quantity becomes irrelevant (Fig. 3). This may be due to the saturation of sorption sites at higher biosorbent concentration.

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 decreases from 87.2-69.16% for the raw corncob and from 93.8-72.7% for the acid-treated corncob as the initial metal concentration increases from 50-300 mg L^{-1}. This may be due to the fact that at lower concentration, competition for the available binding site is low thus, percentage biosorption was higher at lower concentration than at higher concentration when saturation of the binding site and competition of the ions for the binding site is obvious.

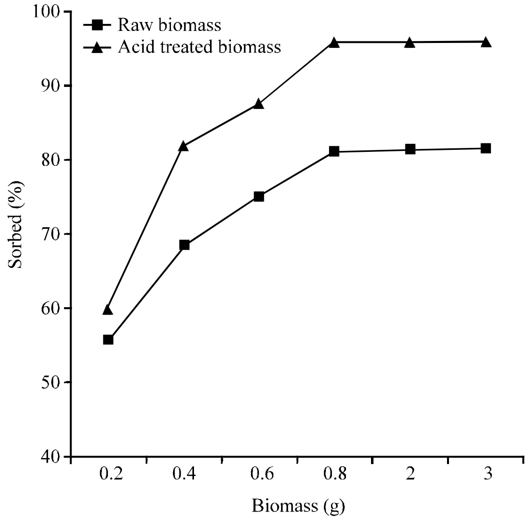

Fig. 3: Effect of initial biosorbent concentrations on the adsorption of Mn (II) ion by raw and acid-treated corncob

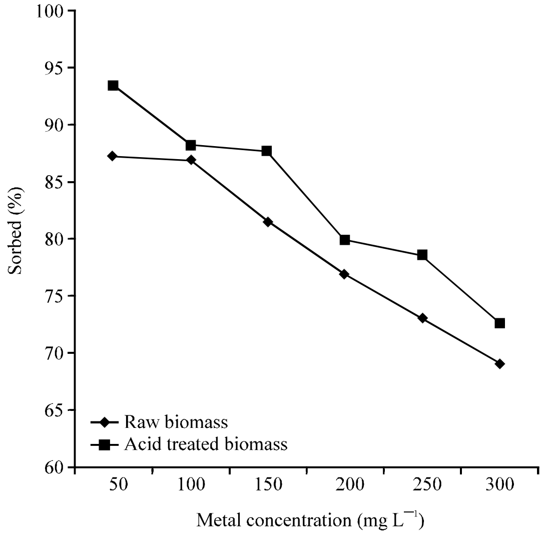

Fig. 4: The effect of initial metal concentration on the biosorption capacity of the raw and acid-treated biomass

Effect of temperature on biosorption: The temperature dependent of the removal of Mn (II) ion from aqueous solution by the raw and acid-treated corncob is also reported. The sorption capacities of both the raw and acid treated biosorbents increases with increase temperature.

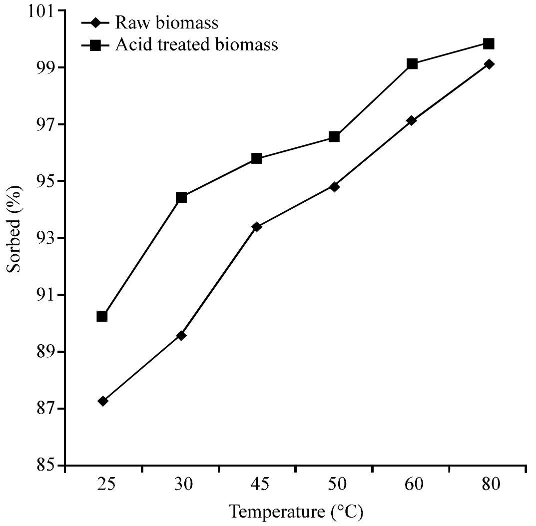

Fig. 5: The effect of temperature on the adsorption of Mn (II) ion by raw and acid-treated biomass

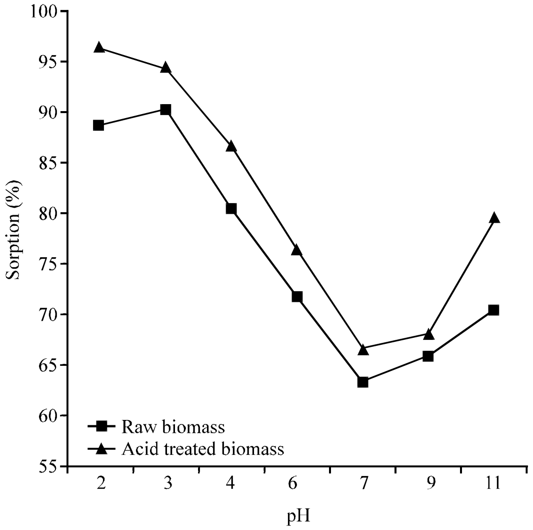

Fig. 6: The effect of pH on the adsorption of Mn (II) ion by raw and acid-treated biomass

For raw biomass the value increased from 87.3-99.6% while an increase from 90.2-99.8% was noted for the acid-treated biomass (Fig. 5). This is an indication of endothermic nature of the biosorption process and this may be attributed to the 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 better than the raw corncob biomass.

Effect of pH on biosorption: The percentage removal of metal ion is pH dependent as shown in Fig. 6. The sorption of Mn (II) ions by both biosorbents were favoured in the acid range of 2.0-3.0, maximum adsorption was observed at a pH of 2.0. For both biosorbents, sorption percentage was lower at a pH of 7.0. Maximum metal sorption at pH of 2.0 seems to be due to the presence of net positive charge on corncob surface at a lower pH. 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 (Saradhi *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 (Eq. 3) and the HO's pseudo-second order model (Eq. 4), respectively:

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

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

Where:

Q_e = The amount of adsorbate adsorbed at equilibrium
Q_t = The amount of adsorbate adsorbed at time t
k_1 and k_2 = 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 logQ_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/$k_2Q_e^2$.

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 kinetics models for the raw and acid treated samples are shown in Table 1 and 2, respectively. The Q_e values obtained from the second order kinetic model agree with the experimental values, the values of correlation coefficients (R^2) also confirmed that second order model is more preferred (Fig. 7).

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 Eq. 5.

Table 1: Kinetic parameters of the sorption of Mn (II) by raw biomass

Concentration (mg L^{-1})	$Q_{e(exp)}$ (mg g^{-1})	$Q_{e(cal)}$ (mg g^{-1})	k_1 (min^{-1})	R^2	SSE (%)	$Q_{e(cal)}$ (mg g^{-1})	k_2 (min g mg^{-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	2.90	2.27	0.028	0.90	0.202	2.95	0.35	0.96	0.034
200	3.64	2.91	0.032	0.96	0.240	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	0.010

Table 2: Kinetic parameters of the sorption of Mn (II) by acid treated biomass

Concentration (mg L^{-1})	$Q_{e(exp)}$ (mg g^{-1})	$Q_{e(cal)}$ (mg g^{-1})	k_1 (min^{-1})	R^2	SSE (%)	$Q_{e(cal)}$ (mg g^{-1})	k_2 (min g mg^{-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

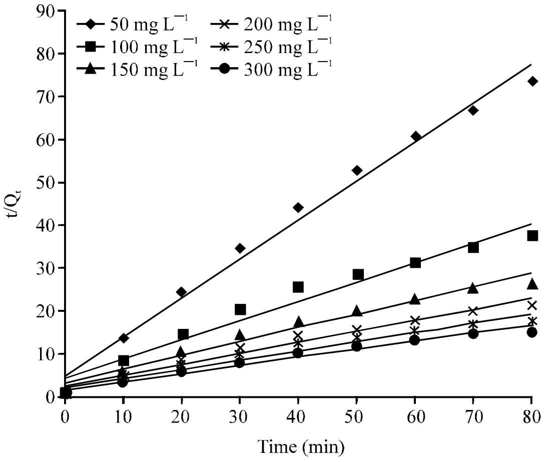

Fig. 7: Second order model of biosorption of Mn (II) ion with untreated biomass

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

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 Table 1 and 2, the calculated results confirmed the fact that the kinetic data from this study are best described by the second-order kinetic model.

Thermodynamic studies: 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:

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

Where:

$$\Delta G = -RT\ln Q_e \quad (7)$$

The values of ΔH and ΔS were determined from the plot of ΔG versus T; the slope of straight line obtained is -ΔS while the intercept is ΔH (Ertugay and Bayhan, 2008). The plot of the free energy change versus temperature of the two biosorbents in the sorption of Mn (II) ions were shown in Fig. 8 while the thermodynamic parameters were shown in Table 3. The negative value of the free energy change is an indication that sorption process is feasible and spontaneous.

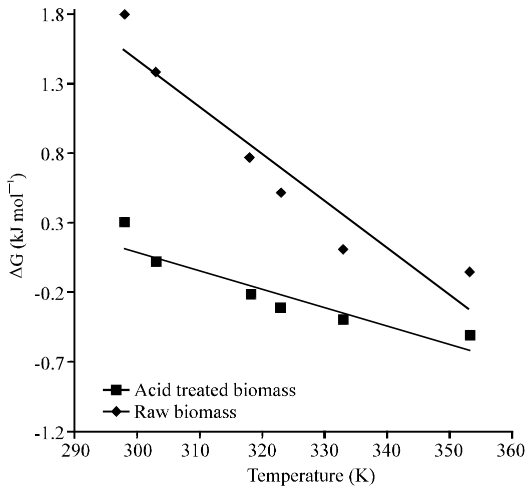

Fig. 8: The free energy change versus temperature for the sorption of Mn (II) ions

The values obtained for the enthalpy change were positive for both biosorbents which indicate that the sorption process is exothermic in nature. The enthalpy change of the acid-treated corncob is however, lower than that of the untreated corncob this implies that higher temperature will be required for sorption process in the raw samples compare with that of 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

Table 3: Physical parameters of thermodynamic of corncob for the sorption of Mn (II)

	Raw biomass				Acid treated biomass			
Temperature (K)	Q_e (mg g^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J/mol/K)	Q_e	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J/mol/K)
298	0.48	1.81	-	-	0.89	0.300	-	-
303	0.58	1.38	-	-	1.00	0.012	-	-
318	0.75	0.78	11.71	-34.07	1.09	-0.220	4.15	-13.05
323	0.82	0.52	-	-	1.12	-0.310	-	-
333	0.96	0.11	-	-	1.15	-0.390	-	-
353	1.02	-0.44	-	-	1.19	-0.500	-	-

equilibrium state. The analysis of equilibrium data with a different isotherm models is an important step to find the suitable model that can be used for design purpose (Haghseresht and Lu, 1998). In this study, Langmuir and Freundlich were used to fit the equilibrium data. Langmuir isotherm assumed the formation a monolayer 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) while Freundlich isotherm model assumed heterogeneous surface energies in which the energy term in Langmuir equation varies as a function of the surface coverage (Fytianos *et al*., 2003). The applicability of the isotherm equation was compared by judging the correlation coefficients, R^2.

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

$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o}\right) C_e \qquad (8)$$

Where:

C_e = The equilibrium concentration of the adsorbate (Mn (II) ion mg L^{-1})

q_e = The amount of adsorbate adsorbed per unit mass of adsorbate (mg g^{-1})

Q_o and b = Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively

When C_e/Q_e was plotted against C_e, straight line with slope $1/Q_e$ was obtained (Fig. 9) indicating that the biosorption of the Mn (II) ions onto biomass follows the Langmuir isotherm.

The Langmuir constants b and Q_0 were calculated from this isotherm and their values are shown 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.

Table 4: Langmuir and Freundlich isotherm constants for lead ions at 25°C

Isotherm parameters	Raw biomass	Treated biomass
Langmuir isotherm parameters		
Q_o (mg g^{-1})	6.540	7.870
b (L mg^{-1})	1.070	1.230
R^2	0.980	0.960
R_L	0.003	0.003
Freundlich isotherm parameters		
1/n	0.563	0.614
K_F (mg g^{-1}) (1 $mg^{-1})^{1/n}$	0.352	0.335
R^2	0.990	0.990

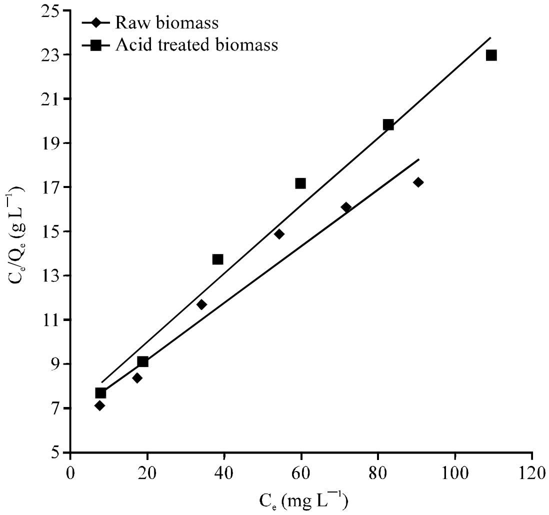

Fig. 9: Langmuir adsorption isotherms for the biosorption of Mn (II) ions on corncob biomass

Similar observations were reported on the biosorption of chromium ion on tamarind (*Tamarindus indica*) fruit shell (Popuri *at al*., 2007).

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

$$R_L = \frac{1}{(1 + bC_o)} \qquad (9)$$

where, b is the Langmuir constant and C_o the highest metal ion concentration (mg L^{-1}). 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 (RL = 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 Eq. 10:

$$\log Q_e = \log K_F + (1/n) \log C_e \quad (10)$$

where, Q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e 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 and K_F [(mg g^{-1}) (1 mg^{-1})^{n}] is the adsorption capacity of the adsorbent.

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). 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 logQ_e versus log C_e gives straight lines with slope 1/n (Fig. 10) which shows that the biosorption of Mn (II) ions also follows 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 yields 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 favourable adsorption (Adamson, 1990).

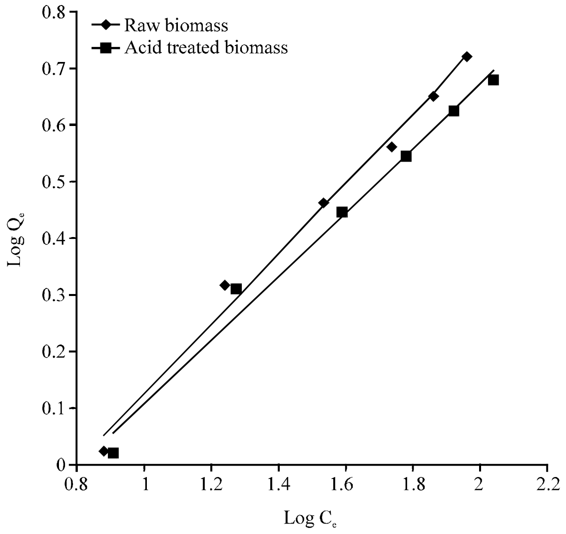

Fig. 10: Freundlich Adsorption isotherms for the biosorption of Mn (II) ions on corncob biomass

CONCLUSION

The present investigation showed that biomass prepared from maize cob (corncob) can be effectively used for the removal of Mn (II) ions from aqueous solutions over a wide range of concentrations. Biosorption behaviour is well described by Freundlich and Langmuir adsorption isotherms. Kinetic data follow pseudo second-order kinetic model. The value of the maximum adsorption capacity, Q_0 (6.54 and 7.87 mg g^{-1} for raw and acid treated biomass, respectively) are comparable with the values observed for other biosorbents reported in the earlier studies. The Freundlich adsorption isotherm provides the best fit for the systems corncob/Mn (II). 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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