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Research Article

REMOVAL OF MANGANESE FROM GROUND/ DRINKING WATER AT SOUTH MADRAS USING NATURAL ADSORBENTS

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ABSTRACT

In the present study the adsorption of manganese ions from aqueous solution with natural adsorbents such as *Moringa oleifera* leaf, *Borassus flabellifer* and *Mangifera indica* is experimentally investigated. The experiments were conducted to evaluate the effect of various experimental parameters such as effect of pH, adsorbent dosage and contact time on the removal efficiency. The results showed that optimum conditions for manganese removal were found to be pH of 6, adsorbent dosages of 0.2 g/l and equilibrium contact time of 120 min. The kinetic of adsorption system have been studied based on the assumption of pseudo-first, pseudo-second order reaction. The Experimental results have been analyzed using a Langmuir and Freundlich adsorption isotherm models. The Freundlich adsorption isotherm model was found to represent the equilibrium adsorption isotherm better than Langmuir adsorption isotherm. Surface morphology structure of before and after adsorbed activated carbons were recorded by using SEM analysis. Surface morphology structure various adsorbents were changed after adsorption of manganese metal ion. FT-IR spectra binding sites were recorded before and after adsorption. The spectral was measured within the range 400-4000 cm. The spectral frequencies were shifted to different wave number. This is a evident that manganese metal ion adsorbed into adsorbents.

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INTRODUCTION

The heavy metals in the environment represent a significant and long-term environment hazard. Even at low concentration of metals can be toxic to organisms, including humans [Ramrakhiani.L *et al*, 2011]. Heavy metals removal by activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment application throughout the world. Activated carbon remains an expensive materials since higher the quality of activated carbon the greater its cost [Babel.S and Kurniawan.T.A, 2003]. The discharge of industrial effluents into water bodies is a major environment problem worldwide, because it contains toxic heavy metals and other organic and inorganic pollutants. Industrial wastewater often contains heavy metal ions which are non-biodegradable and many of them are soluble in aqueous media and easily available to living organisms [Ashraf Ali]. Groundwater moves through rock and subsurface soil, it has a lot of opportunity to dissolve substances as it moves [Jusoh.A.B *et al*, 2005]. Most groundwater contains some metal such as manganese which naturally leaches from rocks and soil [Sampat.P, 2000]. Exposure to heavy water contamination has been found to cause kidney damage, liver

damage and anemia in low dose [Abdulkadir.A *et al*, ISSN; 2180-3242]. Manganese are common metallic elements found in the earth's crusts [Kenari.S.L.D and Benoit.B, 2014]. Manganese in finished water may cause organoleptic and operational problems including discoloration of water, unpleasant metallic taste and odor, increased turbidity and biofouling of pipelines as well. [Khaled.Z *et al*, 2015]. Manganese is one of the important heavy metals found in groundwater, wastewater, etc. Manganese can impair the quality of water from dual sources, natural and manufacture [El Wakeel K.Z *et al*, 2015]. According to the world health organization, the maximum acceptable drinking water concentration in drinking water is 0.05 mg /l for manganese [WHO, 2011]. Manganese is also toxic to the brain and abnormal concentration in the brain, especially in the basal ganglia, resulting in neurological disorders which is similar to Parkinson's disease [Okoniewska. E *et al*,].

For manganese purification, natural adsorbents, oxidation and precipitation of manganese and biological treatments are commonly used. However, these methods are costly and complicated and cannot simultaneously remove manganese; some of them can produce secondary pollution [Emmanuel. E.A, *et al*.2009]. This discharge of this volume of metal ion

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polluted effluent into waterways may cause serious problem for public health hazard and food chain [El Nemr.A, et al.2008]. Surveyed the design of treatment plants used in manganese removal. His survey indicates that the use of sand filters as a manganese removal reactor effectively restricts filter loading rate to about 4m h^{-1} . It is evident from this information that if the economic benefits of high rate filtration are to be achieved for high manganese removal must be achieved at stage preceding filtration [Green.L.A. 1970].

Indeed activated carbon production from agricultural waste has two advantages. First, waste material is converted to useful and value-added adsorbents. The disposal of agricultural by-products has become a major costly waste disposal problem. Second, produced activated carbons are used for removing organic chemicals and metals from wastewater [Ormi.A and Benzina.M 2014]. In this regard, the utilization of residues as precursors for obtaining of low-cost high-value carbon adsorbents is an interesting strategy that enables dealing with the problem of waste disposal, and in the same time, assess the potential possibilities for waste recycling by its application in the removal of toxic pollutants from water [Budinova.T et al, 2009]. Manganese has to be removed from some water and wastewater for various reasons; first of all, this heavy metal causes corrosion and pipe blockages [directly by precipitation or indirectly by creating favorable growth conditions]. Secondly, manganese affects the appearance of the water and imparts metallic taste to this water [Hallaji.M et al, 2014].

Adsorption is one of the more popular methods for the removal of heavy metals from the wastewater [Yavcez.O]. Adsorption is common of heavy metal removal from water. Several physicochemical properties such as specific surface area, pore structure, and surface chemistry of adsorbents regulate the adsorption efficiency, selectivity, equilibrium time of adsorption, regeneration capacity, and their stability in aqueous solutions [Shahidul Islam.Md,et al, 2015]. Activated carbon is prepared from a char form material such as almond, walnut hulls, woods and coal, zeolites, kaolinites, citrus peel, egg shell, coconut shell, fly ask, clay, pine bark, red mud will be used in activated carbon, In the present study Moringa oleifera leaf, Borassus flabellifer, Mangifera indica were used to removal manganese from wastewater samples [Dalai.C et al, 2015]. Several methods for removing manganese have been investigated. The existing methods for treating in precipitation, ion exchange, membrane technologies, adsorption, electrochemical processes, and recently also biological methods are commonly used [Jiancheng Shu et al, 2016].

The influences of the experimental parameters such as effect of pH, contact time, initial concentration, stirring speed, adsorbent dosage, temperature on adsorption were studied. The kinetic models used to describe rate data were discussed. Both Langmuir and Freundlich isotherm models were discussed [Estandior.N et al].

Surface characteristics of the adsorbents were studied using Scanning Electron Microscope [SEM], while Fourier Transform Infrared [FTIR] analysis were also done to understand the involvement of different functional group present on the surface of the adsorbent [Lin.Z et al, 2016].

MATERIALS AND METHODS

Reagents

All reagents were analytical pure grade and used as received without further purification. The chemicals used were Hydrochloric acid, Hydroxylamine hydrochloride, 1, 10 Phenanthroline, Ammonium acetate and Ferrous Ammonium Sulphate were analytical grade and purchased from E. Merck in India. NaOH and pH buffer solution [E. MERCK] were used to adjusted pH values of samples. The water samples including: Groundwater [GW] and Drinking Tap Water [DTW] were collected from South madras Mylapore, Chennai. Doubly Distilled Water [DDW] is obtained from our lab.

Instruments

UV-Vis spectra of before and after manganese adsorptions were obtained using ELICO SLI 159 UV-Vis spectrophotometer. An ELICO pH meter model LI 120 calibrated against two buffer solution at pH 4.0 and 9.2 was used for all pH-Measurements. Magnetic stirrer [REMI I MLH] was used for stirring experiments. Surface morphology structure of Moringa oleifera leaf, Borassus flabellifer and Mangifera indica examined and measured spectroscopically using a SEM [S-3500 N, Hikach] at 20 kV voltages. The FT-IR Spectra's were measured within the range of 400-4000 cm in a shimadzu spectrophotometer.

Preparation of MO, BF and MI

Moringa oleifera leaf (Drum stick leaf), Borassus flabellifer (Pacmyra pacm flower) and Mangifera indica (Mango seeds) were first washed thoroughly and with distilled water to remove the dust particles. After that known weight of Moringa oleifera leaf, Borassus flabellifer and Mangifera indica were cut into small sizes and washed then dried for 24 hours in sunlight. Then they were carbonized in muffle furnace at about 400-500°C for about two hours and allowed to cool at room temperature, the materials were powdered using mortar and sieved.



Fig 1 Structure of adsorbents

Preparation of Synthetic Manganese [MN (II)] Solution

The standard manganese solution 1000 mg/L was prepared by adding calculated amount of manganese sulphate in double distilled water. Then 5mg/L to 25mg/L synthetic solution was prepared from the stock solution. A calibration curve of concentration versus absorbance was first plotted for standard metal ion solution ranging from then the unknown samples were analyzed.

Adsorption Experiments

The adsorption of manganese by the Moringa oleifera leaf, Borassus flabellifer and Mangifera indica activated carbon were studied by the batch technique. The batch mode adsorption was selected due to its simplicity. Manganese synthetic solution [5 mg L^{-1}] was mixed with various dosages

of adsorbents. The pH of the solution was adjusted to 6.0 using [natural] a 0.01 N H₂SO₄. The shaking time was 120 minutes and experiments were done at room temperature. After the time solution were filtered with a whatmann filter paper. Then the supernatant was collected and analyzed for total manganese concentration by UV-Vis spectrophotometer. The effects of several parameters, such as contact time, pH, adsorbent dosage, temperature and initial concentration were also studied. The results of these studies were used to obtain the optimum conditions for adsorption capacity measurements. The percentage removal of manganese was calculated using below of formula

$$\% \text{ Removal of metal ion (E)} = \frac{C - C'}{C} \times 100$$

Where, C and C' are the initial and final [equilibrium] concentration of metal ion [mg L⁻¹], respectively,

Where, E is manganese ion removal, C -initial manganese concentration and C' -final equilibrium manganese concentration.

Adsorption isotherms were obtained by mixing with adsorbents in a flask containing 50ml of different initial metal ion concentrations for 1h in different dosage adsorbents. The amount of manganese metal ion filtrate solution was determined after adsorption using Moring Oleifera leaf, Borassus flabellifer and Mangifera indica.

RESULTS AND DISCUSSION

Effect of Initial Concentration

The effect of initial concentrations [5 to 25 mg L⁻¹]of the removal of total manganese [in terms of percentage removal] on Moringa oleifera leaf, Borassus flabellifer and Mangifera indica adsorbents were studied as shown in Fig.2. At lower concentration of manganese ions in the solution would interact with the binding sites and thus facilitated Moringa oleifera leaf [99%], Borassus flabellifer [86%] and Mangifera indica [85%] of adsorption takes places. However, at 25 mg/l initial concentration the metal adsorption decreased. Decreased percentage of adsorption at higher concentration may be due to competition among metal ion smaller number of available binding sites and also saturation of most of the binding sites. The similar results research coincides with other researchs.

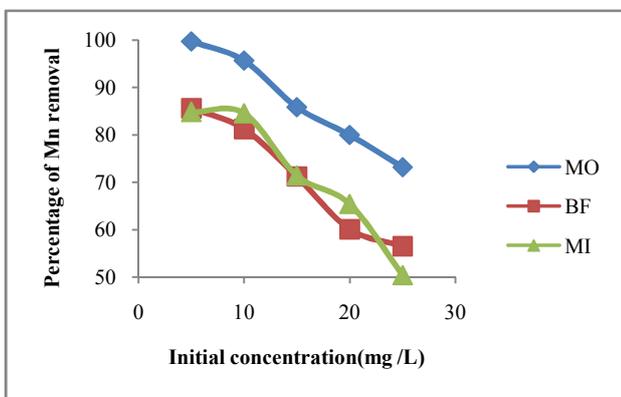


Fig 2 Effect of initial manganese concentration in mg L⁻¹ of remove manganese onto 0.2 g for Moringaoleifera leaf, 0.2g Borassus flabellifer and 0.2g Mangifera indica of adsorbent at pH 6 for 120mins contact time. mg L⁻¹

From these graphs it is observed that overall removal efficiency at constant time interval of all these activated carbon it is observed that maximum manganese removal efficiency obtained Moringa oleifera leaf. Decreases with the increase in initial concentration. At lower metal ion initial concentration, sufficient adsorption sites are available for adsorption of the heavy metal ions. However, at high concentration the available sites of adsorption become fewer and since the percentage removal of heavy metal is dependent upon the initial concentration. Further studies were carried out at initial concentration of 5 mg/L [Funes.A et al, 2014].

Effect of pH

The charge of the adsorbate and adsorbent depends on the pH. The effect of pH on the removal of manganese by Moringa oleifera leaf, Borassus flabellifer and Mangifera indica adsorbents were studied as shown in Fig.3. It has been established that the pH value of the solution is an important parameter which influences the performance of the coagulations. To examine its effect the sample was adjusted to the desired pH using sodium hydroxide or hydrochloric acid or sulphuric acid solution [Rao.M et al, 2002]. The pH of the aqueous solutions is an important operational parameter in the adsorption process because it affects the solubility of the metal ions, concentrations of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [Fadel.M et al, 2015]. The pH of synthetic manganese solution were varied from 2 to 10, initial concentration 5 mg /l, dosage of adsorbent 0.2 g /l, shaking time to minutes, temperature 30°C and agitation speed was kept at 600 rpm, respectively. At low pH values [pH<2] MO,BF and MI showed very low tendency for removal manganese due to protonation of its functional groups or competition between protons and positively charged metal ions. The pH above 6.0 was reported for adsorption of manganese. the maximum percentage removals of both adsorbents at pH 5. Above pH>6 the removal efficiency gradually decreased [Zhenzeli et al, 2010].

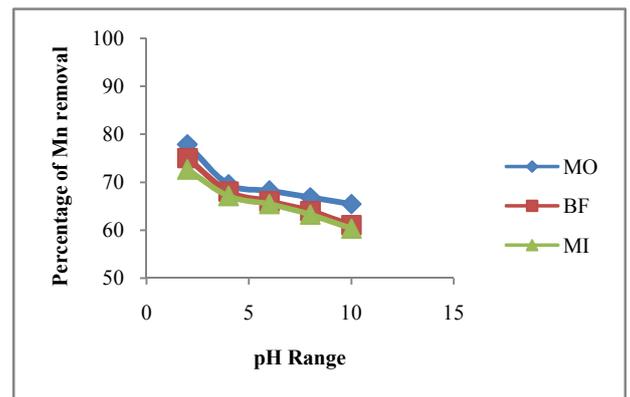


Fig 3 Effect of pH (experimental condition) initial concentration - 50mg/L. adsorbent dose 0.2g for Moringa oleifera leaf, 0.2g Borassus flabellifer and 0.2g Mangifera indica, time 120mins.

Effect of Adsorbent Dosage

Fig.4.shown the effect of adsorbent dosage on manganese adsorption. The weight of Moringa oleifera leaf, Borassus flabellifer and Mangifera indica was varied from 0.1 to 0.6 g/l, keeping all the other experimental variable, via pH 6, initial concentration 5 mg/l, and contact time 60min. this positive

correlation between adsorbent and removal was expected and could be due to the infraction of more binding sites and surface [Inui.T et al, 2010]. However, further increases in the dosage of adsorbent results in percentage of remaining almost constant, which could be attributed to saturation of the binding sites [Erdem.E et al, 2004]. The highest manganese removal efficiency for the Moringa oleifera leaf 98%, Borassus flabellifer 96% and Mangifera indica 96% respectively. Further studies were carried out of 0.2 mg/l is adsorbent dosage.

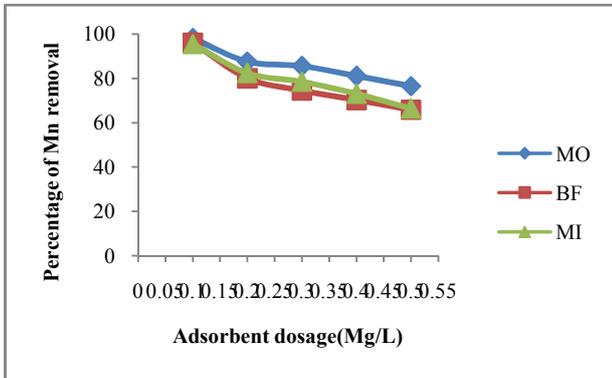


Fig 4 Effect of adsorbent dose on the removal of 5 mg L⁻¹ of manganese (0.2-1) g adsorbent at pH 6 for 120mins contact time.

Effect of Equilibrium Time

In this part, the effect of contact time on adsorption rate was investigated to find equilibrium time for adsorption. Figure.5. Shown amount of manganese adsorption in various time onto Moringa oleifera leaf, Borassus flabellifer and Mangifera indica adsorbents. The experiments were carried out at different contact time 5 to 120 min using magnetic stirrer at 600 rpm with adsorbent dosage 0.2g, initial concentration 5mg/l at a pH 6 and 50.0 ml contact solution. The equilibrium is reached within the first 60 min of shaking time and reached a saturation level. The highest percentage of manganese removal in Moringa oleifera leaf [MO] 98%, Borassus flabellifer [BF] 96% and Mangifera indica [MI] 95% of manganese reduction take places. As the contact time increased the active sites on the sorbent were filled. Further studied were carried out at contact time 120 mines. Contact time increased and percentage of manganese removal increased shown in figure.5.

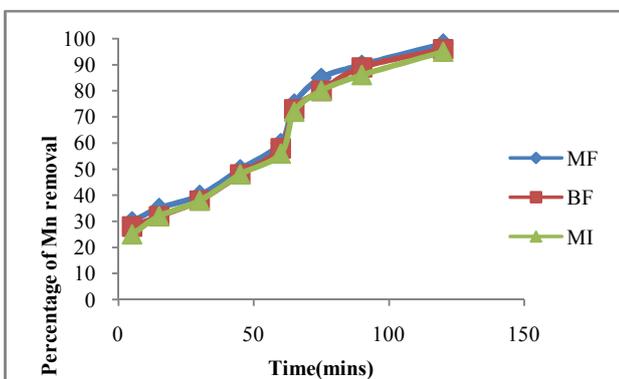


Fig 5 Effect of contact time on the removal of manganese on 0.2g for Moringa oleifera leaf, 0.2g Borassus flabellifer and 0.2g Mangifera indica of adsorbent at pH 6 for 5mins to 120mins contact time.

Effect of Temperature

The effect of temperature on the removal of manganese by Moringa oleifera leaf and Borassus flabellifer, Mangifera

indica increased with temperature from 20 to 50°C shown in fig.6. When increased the temperature the adsorption efficiency of adsorbents is increased due to the attractive forces between the adsorbents surface and manganese metal force increases. The increase in adsorption efficiency with temperature indicated that the reaction follows the endothermic pathway [I.L.Chia et al, 2004].

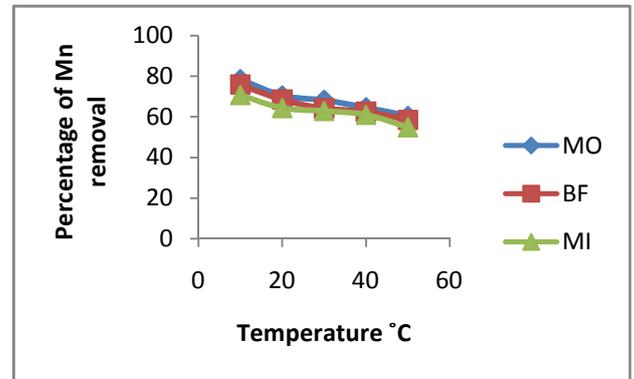


Fig 6 Effect of temperature on the removal of manganese on 0.2g for Moringa oleifera leaf and 0.2g Borassus flabellifer, 0.2g Mangifera indica of adsorbent at pH 6 for 120mins contact time.

Adsorption Isotherm

The method of an adsorption system was optimized to remove the manganese with the most appropriate correlations from the equilibrium data for each system. Three isotherm models that have been considered in the present study are Freundlich, Langmuir and Tempkin models. The applicability of the isotherm equations is evaluated by comparing the correlation coefficient R².

Freundlich Model

Freundlich isotherm is based on the multilayer adsorption with heterogeneous surface energies [Shavandi.M.A et al, 2012]. The Freundlich adsorption model is the most widely used isotherm for the explanation of adsorption of heavy metals on a wide variety of biosorbent. It is an empirical equation that can be used for non-ideal sorption that involves heterogeneous sorption. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surface. The amount of solute adsorbed, Q_e is related to the equilibrium concentration of solute in solution, C_e as following,

$$Q_e = K_F C_e^{\frac{1}{n}} \dots\dots\dots (1)$$

This expression can be linearized to give the following equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \dots\dots\dots (2)$$

Where, K_F is a constant for the system, related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and respects the quantity of metal ion adsorbed onto adsorbent for a unit equilibrium concentration [a measure of adsorption capacity, mg g⁻¹]. The slope 1/n, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneous [becoming more heterogeneous as its value gets closer to zero]. A value for 1/n below one indicates a normal Freundlich isotherm while 1/n above one is an indicative of

cooperative adsorption. A plot of $\log [Q_e]$ vs. $\log [C_e]$ was shown in Fig.7, where the values of K_F and $1/n$ are determined from the intercept and slope of the linear regressions.

Table 1 Freundlich isotherm parameters

Adsorbent	1/n	K_F ($\mu\text{g g}^{-1}$)	R^2
MF	0.261	3.8314	0.994
BF	0.382	2.6178	0.959
MI	0.371	2.6954	0.970

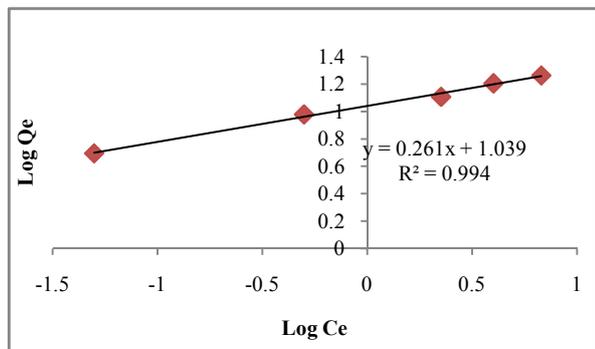


Fig 7 Freundlich isotherm for the adsorption of removal manganese on MO adsorbent.

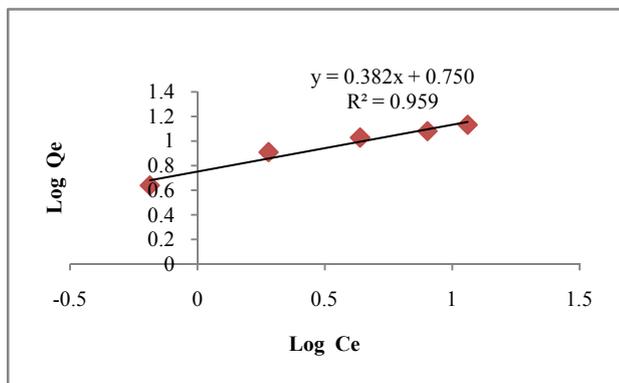


Fig 8 Freundlich isotherm for the adsorption of removal manganese on BF adsorbent.

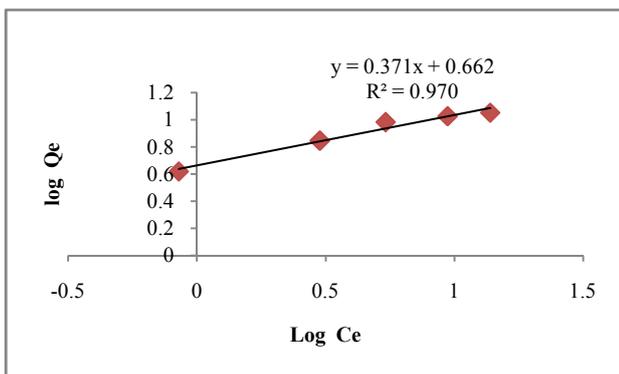


Fig 9 Freundlich isotherm for the adsorption of removal manganese on MI adsorbent.

Langmuir Model

Langmuir isotherm model mainly based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface. The Langmuir adsorption isotherm has been greatly used to many ground water effluent treatment processes and it has also been used to explain the adsorption of heavy metals by various adsorbents. Langmuir theory tells that adsorption takes place at specific

homogeneous sites within the adsorbent. It is then assumed that once a metal ion molecule occupies a site after that no adsorption takes place adsorbent sites and adsorbed layer was unimolecular. The theory can be represented by the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{3}$$

Where C_e is the equilibrium concentration [mg L^{-1}], Q_e is the amount adsorbed at equilibrium [mg g^{-1}], Q_m [mg g^{-1}] and K_L [L mg^{-1}] are Langmuir constants related to adsorption capacity and energy of adsorption respectively. Figure.10.shown the linear plot of C_e/Q_e vs. C_e for Moringa oleifera leaf, Borassus flabellifer and Mangifera indica powder. The values of Q_m and K_L were determined from slop and intercept of the linear plot of C_e/Q_e vs. C_e [Table 2]. The experimental data and the correlation coefficients [R^2] values of was Moringa oleifera leaf, Borassus flabelifer and Mangifera indica were 0.981, 0.996 and 0.996 indicates the applicability of the Langmuir isotherm model. The essential feature of Langmuir isotherm can be expressed by means of dimensionless constant referred to as the separation factor or equilibrium parameter, R_L which is defined by the following equation

$$R_L = \frac{1}{1 + K_L C_i} \tag{4}$$

Where C_i is the initial metal ion concentration [mg L^{-1}]. The value of separation factor R_L , indicates the nature of the adsorption process as given below:

R_L value	Nature of adsorption process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 3 Calculated R_L values

Mn concentration (mgL^{-1})	The R_L value		
	MF	BF	MI
5	0.0699	0.1419	0.1347
10	0.0349	0.070	0.0673
15	0.0233	0.0473	0.0449
20	0.0174	0.0354	0.0336
25	0.0139	0.0283	0.0269

Table 4 Langumuir isotherm parameters

Adsorbent	Q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
MF	19.230	1.8587	0.981
BF	15.384	0.4088	0.996
MI	12.987	0.4842	0.996

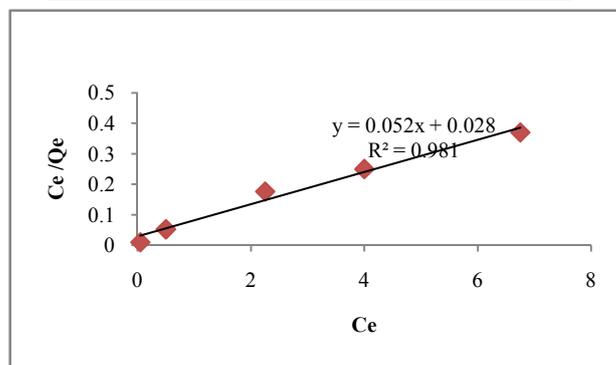


Fig 10 Langmuir isotherm for the adsorption of removal manganese on MO adsorbent.

The values of R_L values calculated for this study is given in Table .3. The adsorption process will be favorable if the R_L values lie between 0 and 1. The R_L values given in table.3.

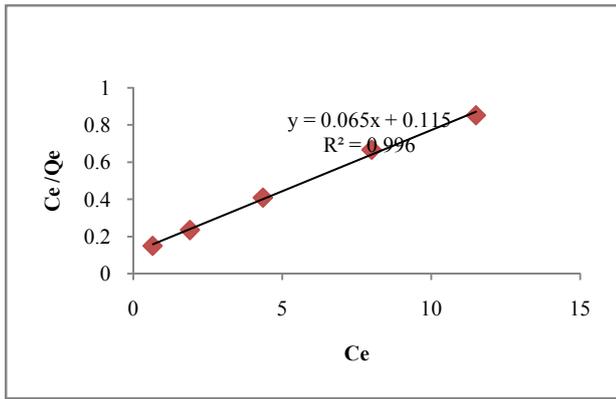


Fig11 Langmuir isotherm for the adsorption of removal manganese on BF adsorbent.

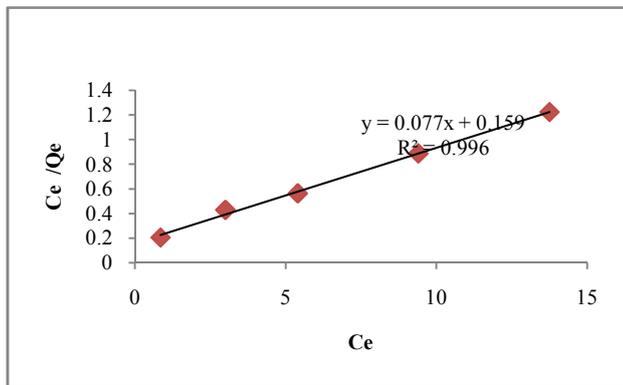


Fig12 Langmuir isotherm for the adsorption of removal manganese on MI adsorbent.

Tempkin Isotherm Model

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that the heat of adsorption of all molecular in the layer decreased linking with coverage due to adsorbate-adsorbate interaction and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. Tempkin isotherm has generally been used in the linearized and rearranged form as following;

$$Q_e = \beta \ln K_T + \beta \ln C_e \dots\dots\dots (5)$$

where, K_T is an equilibrium constant of binding corresponding to the maximum energy of binding [mg L^{-1}] and the β is related to the heat of adsorption. Figure.13. shows a plot of Q_e versus $\ln C_e$, which enables the determination of the isotherm constants K_T and β . The values of K_T , β and correlation coefficient, R^2 for Tempkin isotherm model are given in Tables.5.

Table-5 Tempkin isotherm Parameters

Adsorbent	B	K_T ($\mu\text{g L}^{-1}$)	R^2
MF	2.609	10.653	0.958
BF	3.104	4.3542	0.995
MI	2.660	3.9279	0.981

Adsorption Kinetics

In order to investigate the mechanism of total manganese adsorption onto adsorbents three kinetic models were studied; Lagergren’s first-order, Pseudo- second order and Elovich.

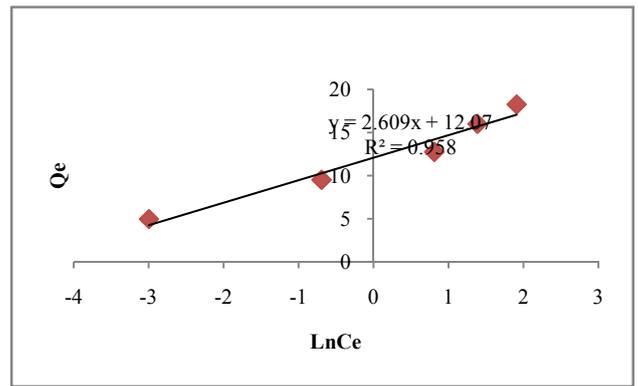


Fig13 Tempkin isotherm for the adsorption of removal manganese on MO adsorbent.

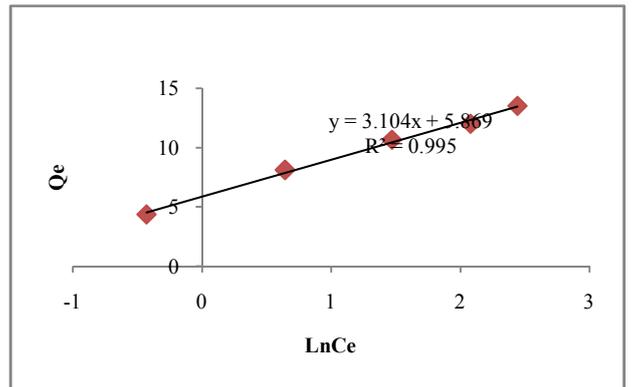


Fig 14 Tempkin isotherm for the adsorption of removal manganese on BF adsorbent.

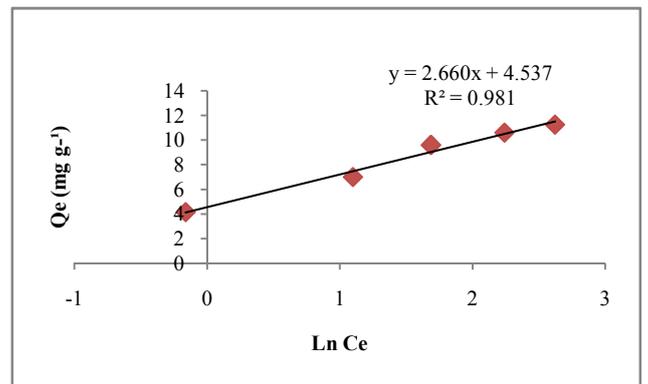


Fig 15 Tempkin isotherm for the adsorption of removal manganese on MI adsorbent.

Lagergren’S First-Order Kinetic Model

The pseudo-first-order kinetic model of lagergren is more suitable for lower concentration of solute and its linear form is

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \dots\dots\dots (6)$$

Where, Q_t (mg g^{-1}) is the amount of adsorbate adsorbed at time t [min]; Q_e [mg g^{-1}] is the adsorption capacity in the equilibrium; k_1 [min^{-1}] is the rate constant of pseudo-first-order model.

The values of k_1 and Q_e for Moringa oleifera leaf, Borassus flabellifer and Mangifera indica adsorbents was determined from the plot of $\log [Q_e - Q_t]$ vs. time which is shown in Fig.16.

The correlation coefficient, R^2 for Moringa oleifera leaf, Borassus flabellifer and Mangifera indica powder was presented in Table.5.

Table 6 Lagergren's first order kinetic model Parameters

Adsorbent	Q _e (cal)	Q _e (exp)	K ₁ × 10 ⁻³	R ²
MF	4.95	3.647	5.803	0.790
BF	4.35	4.102	2.349	0.850
MI	4.15	8.241	4.283	0.951

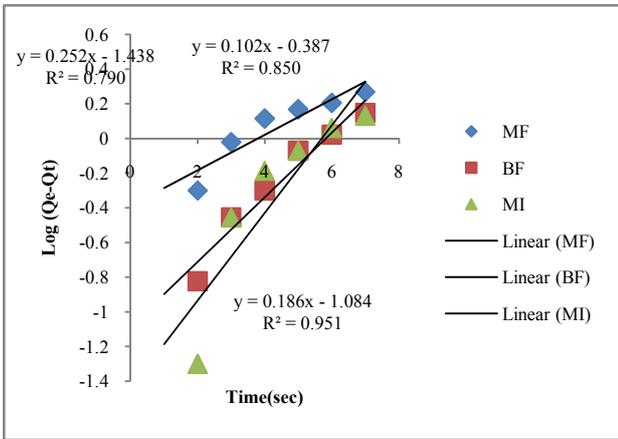


Fig16 Lagergren first-order kinetic model of remove manganese adsorption onto 0.2g L⁻¹ adsorbent, initial manganese concentration 5 mg L⁻¹, at pH 6.

Pseudo-Second-Order Kinetic Model

Adsorption kinetic was explained by the pseudo-second-order model expressed as following linear equation

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \dots\dots\dots (7)$$

Where, k₂ is the second order rate constant [g mg⁻¹ min⁻¹]. The values of k₂ for removal of manganese by Moringa oleifera leaf, Borassus flabellifer and Mangifera indica adsorbents was calculated from the slopes of the respective linear plots of t/Q_t vs. t [Figure.17]. The correlation coefficients, R² values for Moringa oleifera leaf, Brasuus flabellifer and Mangifera indica respectively suggest a strong relationship between the parameters and also explain that the process follows pseudo second order kinetics [Table 6].

Table 7 Pseudo-second-order kinetic model

Adsorbent	Q _e (cal)	Q _e (exp)	K ₂ × 10 ⁻²	R ²
MF	4.95	2.065	7.910	0.994
BF	4.35	2.051	6.970	0.990
MI	4.15	2.649	8.625	0.996

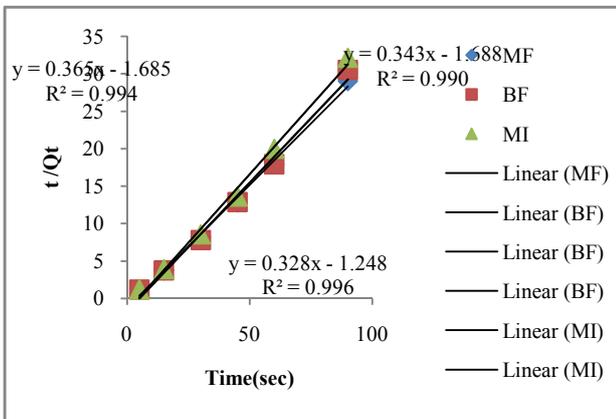


Fig 17 pseudo-second-order-kinetic model for the adsorption of remove manganese adsorption onto 0.2g L⁻¹ adsorbent with initial manganese concentration of 5 mg L⁻¹, at pH 6.

Elovich Kinetic Model

Elovich model suggests that the chemisorptions, i.e. a chemical reaction, is probably the mechanism that controls the rate of adsorption. This model can be applied with success in liquid solution and the linear form of the Elovich equation is:

$$Q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \dots\dots\dots (8)$$

Where, α [mg g⁻¹] is the initial sorption rate and β [g mg⁻¹] is the desorption constant. The values of α and β can be calculated from the slope and intercept of the plot of Q_t versus ln t show in Figure.18.

As can be seen from the figure.18, the values of R² are closer to unity for pseudo second order model than pseudo first order model and Elovich model is shown in table.7. Thus, adsorption of total iron onto adsorbent follows the pseudo second order model. Furthermore, values of Q_e (cal) calculated from pseudo second order model were in good agreement with experimental values, Q_e (exp) than those calculated from pseudo first order. The values of R² for pseudo first order and Elovich model are lower than the pseudo second order model and thus indicate that pseudo first order and Elovich model cannot be adequate to describe the kinetic of adsorption of manganese metal onto Moringa oleifera leaf, Borassus flabellifer and Mangi fera indica seed powder.

Table 8 Elovich kinetic model parameters

Adsorbent	A	β	R ²
MF	8.203	2.212	0.954
BF	1.984	2.439	0.872
MI	5.336	2.178	0.995

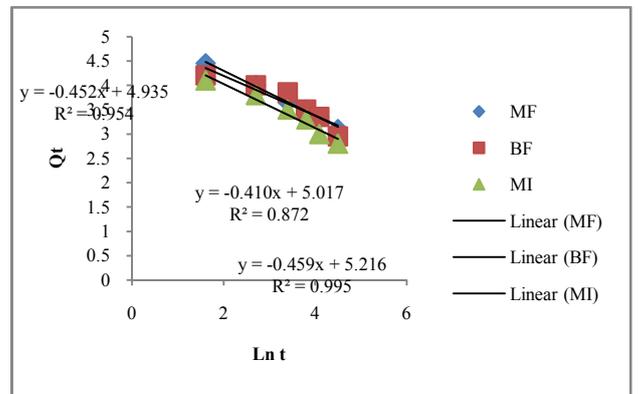


Fig 18 Elovich kinetic model for the adsorption of removal manganese adsorption onto 0.2g L⁻¹ adsorbent with initial manganese concentration of 5 mg L⁻¹, at pH 6.

Analysis of Sem and FT-IR Spectra

Sem Analysis

The surface morphology of the activated carbon was examined by Scanning Electron Micrography [SEM], the corresponding micrographs being obtained an accelerating voltage of 30Kv at 1000 X magnification Fig.19. As shown that rough surface area and wide variety of the pores present in the adsorbents, which is one of the factor for increasing adsorption capacity. By comparing the SEM image [a] Moringa oleifera leaf activated carbon [b] Manganese metal ion onto Moringa oleifera leaf after adsorbent manganese particles adsorbed on the adsorbent its conforms the colloidal like structure,[c], Borassus flabelifer activated carbon [d] Manganese metal ion onto Borassus

flabelifer after adsorption shows colloidal structure and particles present in the surface [e] Mangifera indica activated carbon [f] Manganese metal ion onto Mangifera indica shown the different flatted with sheet like structure and cavity presence of manganese particles adsorbed on the surface clearly shown in Fig.19. It is evident that manganese metal ion can easily be absorbed by Moringa oleifera leaf, Borassus flabelifer and Mangifera indica adsorbents.

Analy Sis for FT-IR Spectra

Fourier transform infrared spectroscopy [FTIR] was used to determine the functional groups on the carbon surface. The spectra was measured within the range 400-4000 cm^{-1} in a shimadzu spectrophotometer. Some fundamental FTIR frequencies of the Moringa oleifera leaf (MO), Borassus flabelifer (BF) and Mangifera indica (MI) adsorbents, before

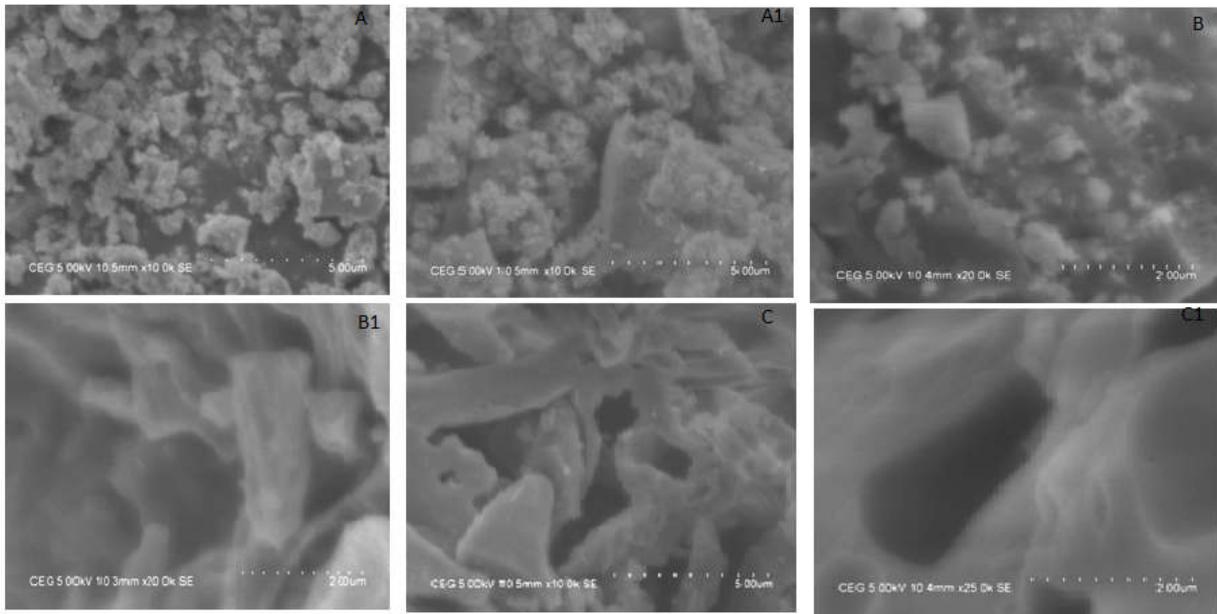


Fig 19 SEM Micrography of activated carbons [a] MO before adsorption [b] MO after adsorption [c] BF before adsorption [d] BF after adsorption [e] MI before adsorption [f] MI after adsorption.

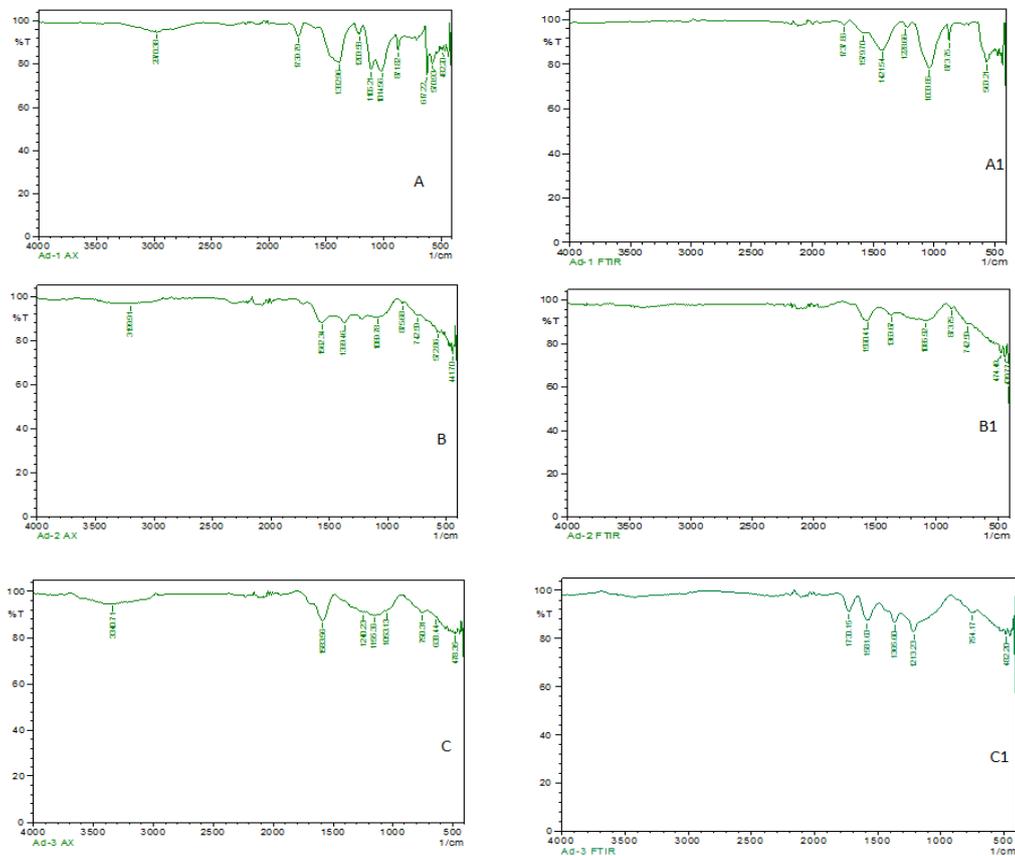


Fig 20 FT-IR Spectrum of activated carbon [a] MO before and after adsorption [b] BF before and after adsorption [c] MI before and after adsorption.

and after adsorption are presented and shown in Fig.20. And many other frequencies were shifted to different wave number with adsorption of manganese. From these predictions manganese metal ion was adsorbed onto the Moringa oleifera leaf, Borassus flabellifer and Mangifera indica adsorbents through interaction with the active functional groups. Moringa oleifera leaf adsorption the band appearing 2970 cm^{-1} which could be attributed to the overlapping of various C-H stretching vibration. MO before adsorption the band appearing before in 1739 cm^{-1} after adsorption the band shifted to 1737 cm^{-1} assigned to C=O stretching aldehyde, ketones and ester functional group vibration. 1382 cm^{-1} assigned to CH stretching vibration. The C-O-C deformation was observed at 1203 cm^{-1} . The broad and intense adsorption of Borassus flabellifer 3199 cm^{-1} corresponds to OH⁻ groups. Borassus flabellifer before adsorption the bands appearing 1562 cm^{-1} after adsorption the bond shifted 1560 cm^{-1} indicates C=O group. 1369 cm^{-1} assigned to CH stretching vibration. The broad and intense adsorption of Mangifera indica 3340 cm^{-1} corresponding to OH groups. The adsorption band at 1730 cm^{-1} was assigned to C=O stretching vibration of aldehydes, ketones, lactones and carboxylic groups. 1213 cm^{-1} assigned to C-O-C stretching vibration. The position of the peak is same as the manganese molecule vibration bond. This indicates that the Moringa oleifera leaf, Borassus flabellifer and Mangifera indica 1739 , 1560 , 1730 cm^{-1} vibrational is obtained. C=O group conformer the Mn (II) adsorption.

CONCLUSION

The present study deals that activated carbon prepared from Moringa oleifera leaf, Borassus flabellifer and Mangifera indica can be used very well for removal manganese from [5mg/l], ground water samples. The percentage of removal efficiency of Mn decreased when increases adsorbent dosage where as it was reverse when decreased dosage. When comparing both natural adsorbents the manganese removals from Moringa oleifera leaf, Borassus flabellifer are higher than Mangifera indica activated carbon. The percentage removals [99%, 96%, 93%] of Moringa oleifera leaf, Borassus flabellifer and Mangifera indica were optimum conditions for the removal of manganese is at pH 6, contact time 120min and adsorbent dosage of 0.2g/l for Moringa oleifera leaf, 0.2g/l Borassus flabellifer, 0.2g/l Mangifera indica were studied. Langmuir, freundlich and tempkin isotherm shows good correlation for manganese adsorption by Moringa oleifera leaf, Borassus flabellifer and Mangifera indica activated carbon. The adsorption process is good agreement with lagergren first order model and pseudo second order kinetic model yielded three linear regions which suggest that the adsorption process was followed by multiple sorption rates. The Moringa oleifera leaf activated carbon was highest removal of manganese compared to Borassus flabellifer, Mangifera indica activated carbon.

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