Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(18):87-94
(http://derpharmachemica.com/archive.html)

Adsorption of manganese (II) by nitric acid treated granular activated charcoal prepared from *Cordia Macleodii* tree bark

Atul K. Wanjari

Department of Chemistry, Mahatma Fule Art`s, Commerce and Sitaramji Chaudhari Science Mahavidyalaya Warud, Amravati University, Republic of INDIA.

ABSTRACT

Manganese is toxic to living systems and therefore it is essential to remove it from wastewater. The resent paper deals with the study of adsorption of Mn (II) metal ions. For this purpose granular activated charcoal was prepared by using Cordia Macleodii tree bark and used for the adsorption of Mn (II) from aqueous solution. Granular activated charcoal was characterized by using FTIR and SEM techniques. Adsorption capacity of Cordia Macleodii tree bark granular activated charcoal for Mn (II) retrieval was investigated by employing batch equilibration method as a function of pH, contact time, initial metal concentration, adsorbent dose, and temperature to determine the efficiency of adsorbent. The adsorption data were found to fit well with the Langmuir model and Freundlich model. The kinetic models, namely pseudo-first order, pseudo second order and elovich model where used to describe the kinetics of Mn (II) ions adsorption on granular activated charcoal. Pseudo second order was the best of the three kinetic models to successfully describe the adsorption. Thus the self-prepared granular activated charcoal under investigation has been proved to be agood economical adsorbent material for Mn (II) removal from aqueous solution.

Keywords: Manganese (II), Granular activated charcoal, Adsorption, *Cordia Macleodii*, Kinetics

---

INTRODUCTION

There are twenty metals which are classified as toxic which directly alters in the environment and causes various hazards to human as well as animals [1]. Manganese is one of the toxic pollutants which causes several environmental and public health problem. Manganese is used in variety of industrial applications like ceramics, dry battery cell, electrical coils and many alloys hence large quantity of manganese discharge in the environment. Manganese is one of the most difficult elements to remove from surface water [2-4]. However manganese has a adverse effect when it cross the permissible limit. According to W.H.O. 0.05 mg/L is the maximum concentration dose of manganese admissible in drinking water [5]. Many studies have been reported for Mn (II) removal in the past such as ion exchange, column, passive treatment system [6-8]. The material used in these processes include rice husk [9], activated carbon [10], orange peel [11], neem leaf [12], red mud [13], sawdust [14] etc.

Activated carbon has been widely used for the removal of various pollutants [15]. Carbon – based materials are very well known as an adsorbent for removal of poisonous heavy metal ions and dyes from aqueous solutions [16]. Adsorbents are usually porous solids, and adsorption occurs mainly on the pore walls inside particles. Activated carbons are commonly prepared by two basic processes: (i) Physical or gas activation method, and (ii) Chemical activation. The choice of activation method is also depending upon the starting material and whether a low or high density, powdered or granular carbon is desired [17].

In the present study granular activated charcoal is prepared from *Cordia macleodii* tree bark and used as an adsorbent to remove manganese from aqueous solution by adsorption.

MATERIALS AND METHODS

Preparation of adsorbent

Cordia Macleodii tree bark were collected from the road side of pusla village, Amravati district, Maharashtra state, India and wash to removes any mud present on the surface of the bark by deionised water several times then dried in the sunlight. After it completely dry then it is converted into granular activated charcoal by using muffle furnace.

Activation of Adsorbent

The prepared granular activated charcoal (GAC) was further activated with water and nitric acid in 1:1 proportion to increase the porosity of GAC. For activation to the 10 gram of GAC 100 ml of H_2O + HNO_3in 1:1 proportion were added and stir for about 48 Hr at room temperature. The acid treated adsorbent was thoroughly washed with hot distilled water to remove acidity. The product was finally dried and used as an adsorbent.

Characterization of adsorbent

The prepared adsorbent was characterized by using FTIR and SEM technology. FTIR shows that there are present of carbonyl group and carboxylate ion. Analysis of adsorbent before and after metal ions adsorption shifting or reductions of bands were found. Results of FTIR are depicted in table no.2 and shown in figure 1 and 2. Surface morphology was analysed by using SEM. Figure 3 shows that the SEM of prepared granular activated charcoal. From the figure 3 it is observed that surface of the adsorbent have tiny holes having rough surface while after adsorption this tiny hole gets converted into rough surface because of adsorption of metal ions. Metal ions cover the surface of adsorbent shown in figure 4.

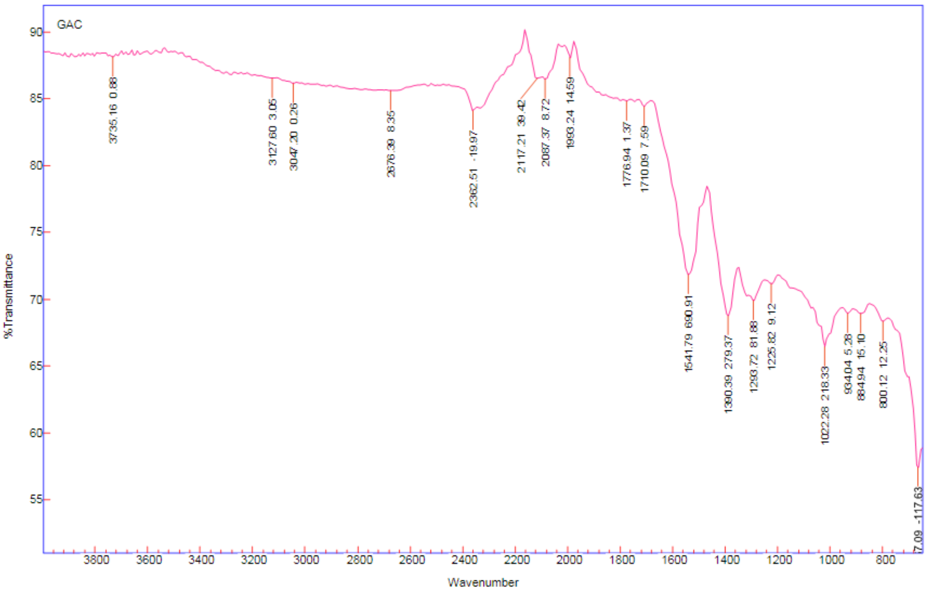


Figure 1. FTIR of GAC

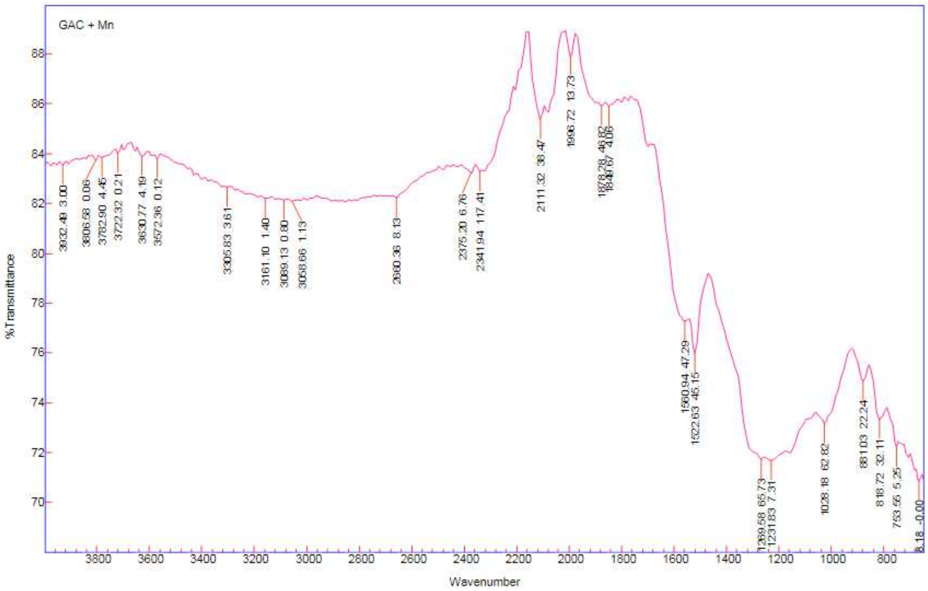


Figure 2. FTIR of GAC after Mn (II) adsorption

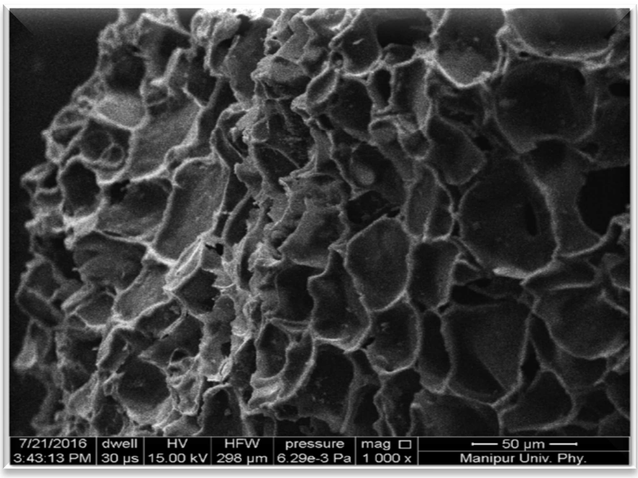


Figure 3.SEM of GAC

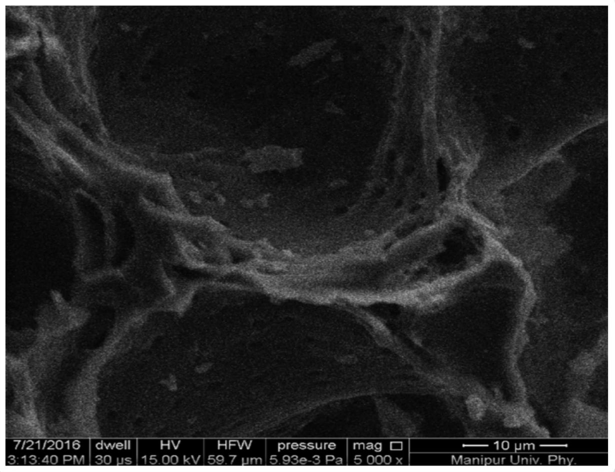


Figure 4. FTIR of GAC after Mn (II) adsorption

Preparation of stock solution

A stock solution of manganese solution used in this study was prepared by dissolving an accurate quantity of 2.86 gram of manganese metal in 1000 ml deionised water. Other concentrations were prepared from this stock solution by dilution. The entire chemicals used were analytical grade and volumes of solution were made up with the help of deionised water.

The apparatus used are UV-Visible spectrophotometer 117, pH cum Potentiometer EQ-631, Rotary Shaker.

RESULTS AND DISCUSSION

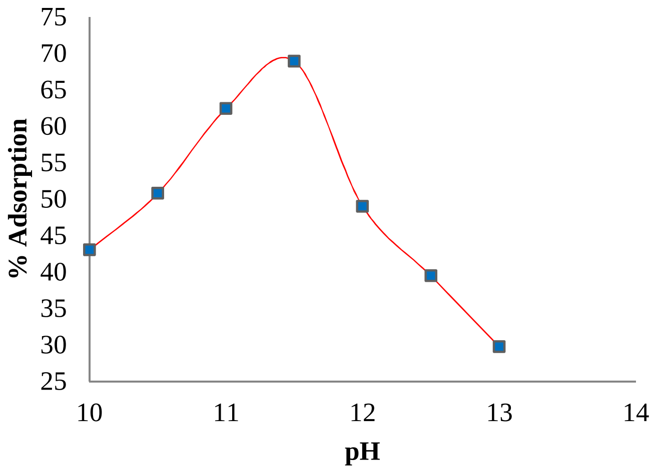
Effect of pH

Figure 5 shows the effect of pH on adsorption of Mn (II) ions on GAC is studied in the range 10 to 13 pH. The percentage removal of Mn (II) ions increases up to pH 11.5 thereafter decreases. From this study is observed that removal of Mn (II) metal ions is highly pH dependent. The maximum removal efficiency at pH 11.5 was found to be 68.93% using initial metal ions concentration 10.6551 mg/L. From experimental value it is observed that as the metal ions/carbon ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decrease in adsorption efficiency.

Effect of contact time

The experiment is conducted to measure the effect of contact time on Mn (II) removal by batch method (initial metal concentration 11.4310 mg/L, pH 11.5, temperature 28± 1°C) by taking 0.5 gram of adsorbent. At equilibrium the removal efficiency was found to be 64.10%.

As observed from the Figure 6, the initially rapid adsorption gradually gave way to adsorption at a slow rate. Thus, it was observed from the study that the removal Mn (II) by adsorption onto granular activated charcoal increased rapidly in the beginning and then slowly until equilibrium time was reached.



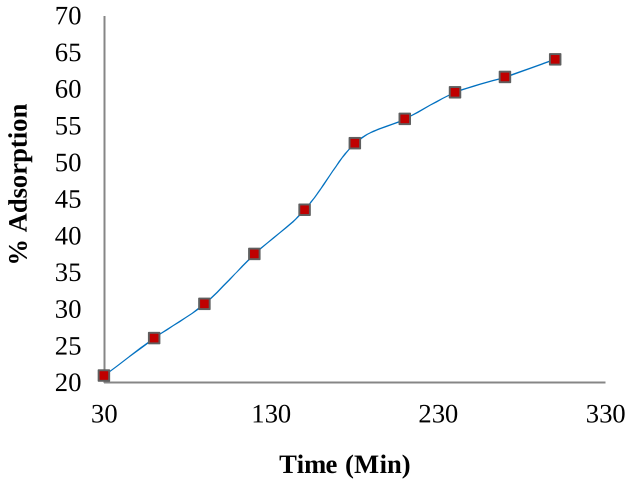


Figure 5.Effect of pH on Mn (II) removal Figure 6. Effect of contact time on Mn (II) removal

Effect of adsorbent dose

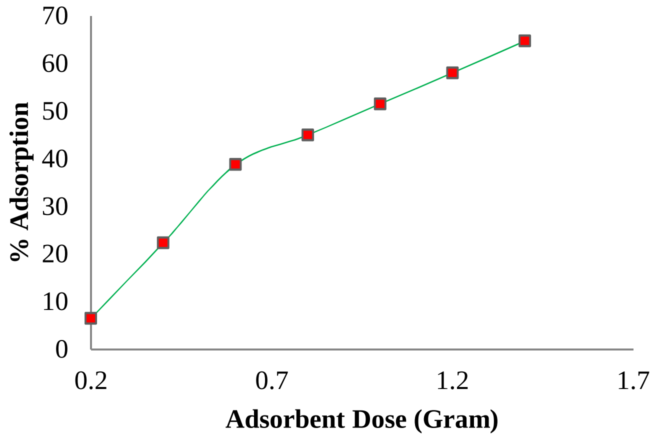
The effect of adsorbent dose is very important to find out the optimum amount of GAC required for the removal of Mn (II) metal ions. The study were carried out by taking 200 ml of 11.3034 mg/L initial concentration of metal ion at pH 11.5 and varying the amount of adsorbent from 0.2 to 1.4 gram result are shown in Figure 7. The percentage removal of Mn (II) metal ions was found to be increase exponentially with the increase in adsorbent dose. The increase in metal ions uptake is due to the increase in adsorption sites resulting from the increased dose of adsorbent, especially at higher dose.

Effect of initial metal ions concentration

In the present study, investigations were carried to study effect of initial metal ions concentration of Mn (II) on adsorption behaviour. The study was carried out by taking the 7.53, 13.60, 18.68, 23.55, 29.06, and 34.48 mg/L initial concentration of Mn (II) with an optimum pH value and shaken for about 3 hours. It was found that as the concentration of metal ions solution increases the adsorption capacity decreases due lack of availability of adsorption sites and hence the amount of metal ions adsorbed on the adsorbent surface is less shown in figure 7.

Effect of Temperature

Study was carried out by taking the 11.77 mg/L concentration of Mn (II) at pH 11.5. The adsorption has been found to increase with an increase in temperature from 25° to 65°C. Increase in adsorption capacity of HNO_3 treated GAC with temperatures indicates an endothermic process. At temperature 65°C the percentage removal was found to be 75.98% shown in figure 9.



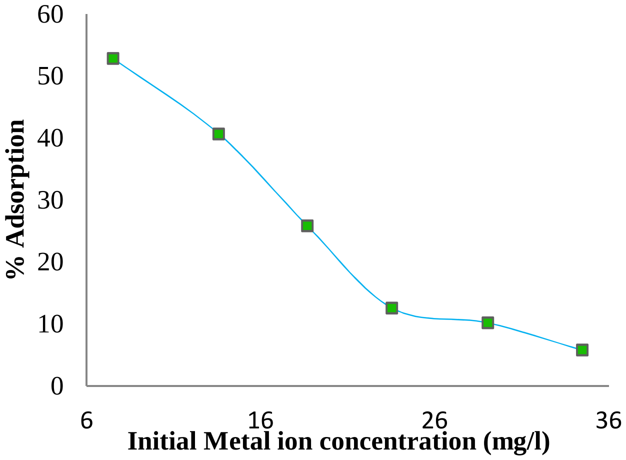


Figure 7.Effect of adsorbent dose on Mn (II) removal on Mn (II) removal

Figure 8.Effect of initial metal ions concentration

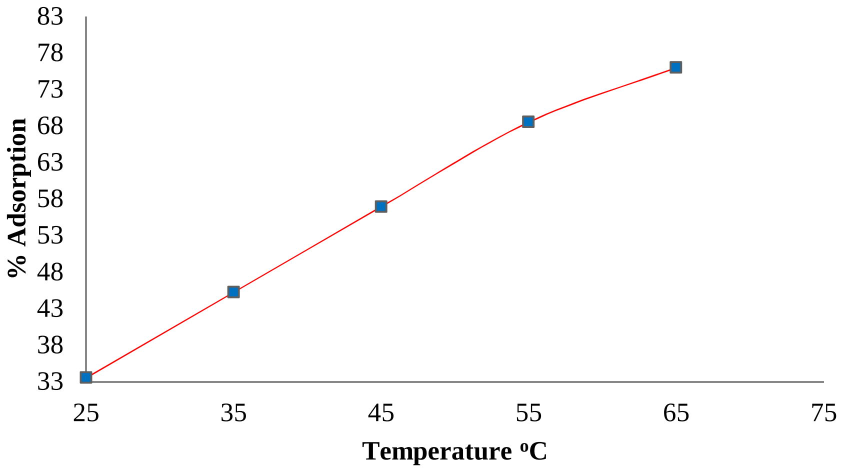


Figure 10. Effect temperature on Mn (II) removal

Adsorption isotherm

Adsorption isotherm study is important to study the mechanism of how the metal ions interact with granular activated charcoal surface. In the present investigation, the adsorption of Mn (II) metal ions onto GAC was studied by Langmuir and Freundlich models.

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm results are shown in Table 1. Q^o values found to be 4.52. Value of K_L lies between 0 and 1 indicate the favourable adsorption. It indicates the applicability of Langmuir adsorption isotherm. The calculated value $R^2$0.978 confirm the applicability of Langmuir adsorption isotherm shown in figure 10.

The Langmuir isotherm [18] model can be given as:

$$\frac{1}{q_e} = \frac{1}{Q^0 b} \times \frac{1}{Ce} + \frac{1}{Q^0}$$

The Langmuir constant Q^o is a measure of adsorption capacity and b is the measure of energy of adsorption. In order to observe whether the adsorption is favourable or not, a dimensionless parameter 'R' obtained from Langmuir Isotherm. The values of Q^o and b were evaluated from the intercept and slope of linear plots of $1/q_e$ vs. $1/C_e$ respectively.

$$R = (1 + b \times Cm)^{-1}$$

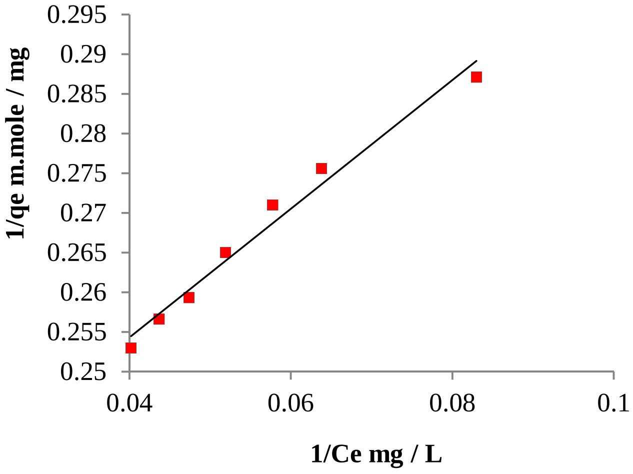
The value of R indicated the type of the isotherm to be either unfavourable (R>1), linear (R=1), favourable (0<R<1) or irreversible (R=0). Where, b is Langmuir adsorption constant and Cm is the maximum initial solute concentration used in the Langmuir isotherm.

Freundlich Adsorption Isotherm

The linear form of Freundlich isotherm model is

$$\text{Log } q_e = \text{B. log } C_e + \log K_f$$

Where, B and K_f are Freundlich constant. These constants represent the adsorption capacity and the adsorption intensity respectively. q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of adsorbate. Linear plot of log q_e Vs log C_e are applied to confirm the removal on Mn (II) metal ions shown in table 1 and figure 11. The values of B and K_f are calculated from the intercept and slope respectively.



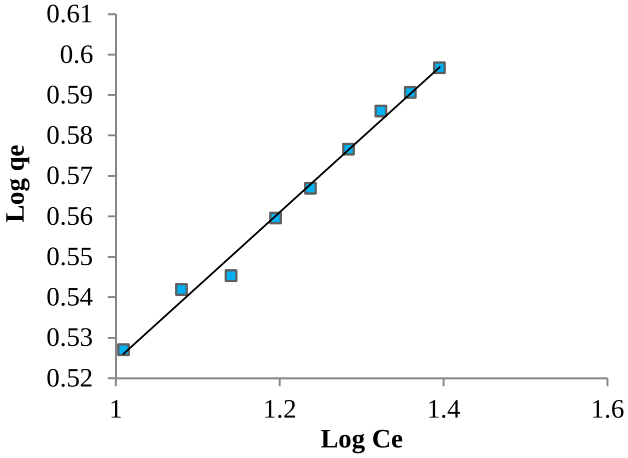


Figure 10.Langmuir adsorption isotherm **Figure 11. Freundlich adsorption isotherm**

Adsorption Kinetics

The rate of adsorption of Mn (II) on HNO_3 treated Granulated Activated Charcoal was studied by using the first order kinetic model, Pseudo second order kinetic and Elovich models are used to test the experimental data.

First order kinetics

The rate of adsorption of Mn (II) on Granulated Activated Charcoal was studied by using the first order rate equation proposed by Lagergren.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t$$

Pseudo Second order models

To describe Mn (II) adsorption the linear form of second order kinetic equation can be written as:

$$\frac{t}{q_t} = \frac{1}{q_e} \times t + \frac{1}{k_2 . q_e^2}$$

Here, the value of t/q_t is calculated from different agitation time's t and graph is drawn between t/q_t and t.
Here slope is $1/q_t$ and y-intercept is

$$\text{y} - \text{Intercept} = \frac{1}{k_2 . q_e^2}$$

$$k_2 = \frac{1}{\text{y} - \text{Intercept}. q_e^2}$$

Elovich Model

Linear form of this Elovich model equation is

$q_t = \frac{1}{\beta} Int + \frac{1}{\beta}$ In (α.β)

Here, slope = 1/β and y-intercept = $\frac{1}{\beta}$In (α.β)

Graph is plotted between q_t versus log t and shown in figure 14.The results obtained from kinetic study are depicted in table 1.

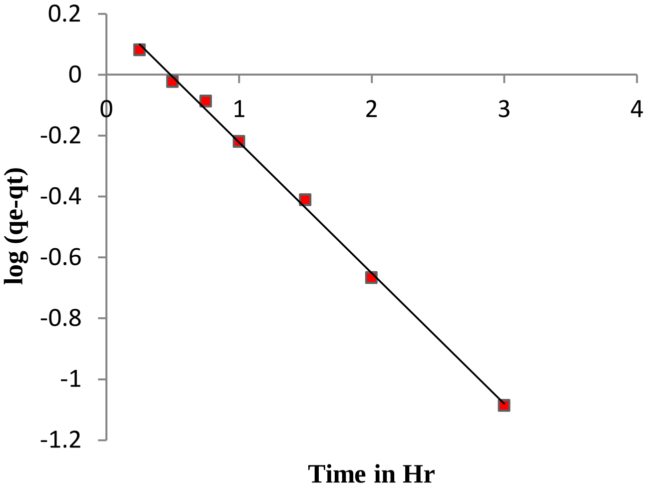


Figure 12.Lagergren plot

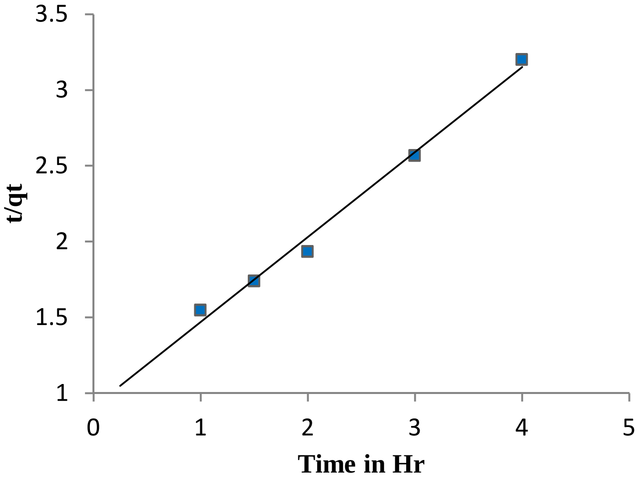


Figure 13. Pseudo second order plot

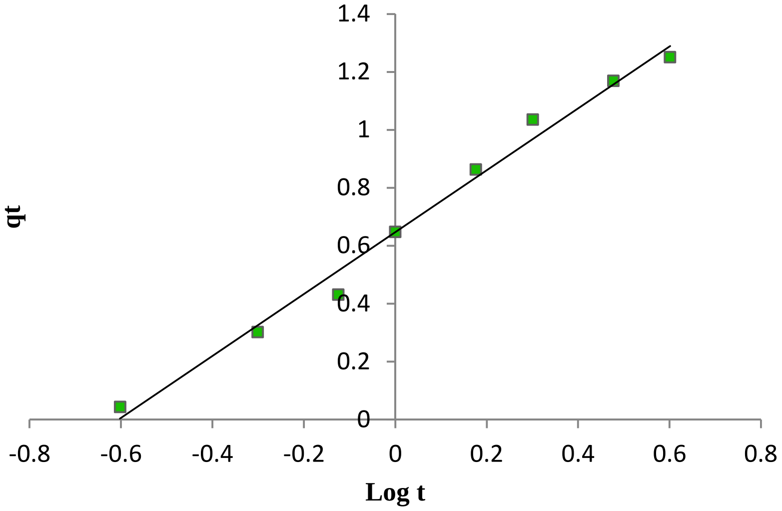


Figure 14. Elovich model

Table 1.Isothermal constants and Kinetic model values

Isotherm Model	Parameters		Kinetic Model	Parameters	
Langmuir Adsorption Isotherm	Q^o	4.524	First order	K_L	0.987
	b	0.011		q_e	1.610
	K_L	0.053		R^2	0.997
	R^2	0.978	Pseudo second order	q_e	1.780
Freundlich Adsorption Isotherm	K_f	2.187		K_2	0.347
	B	0.183		R^2	0.990
	R^2	0.991	Elovich model	α	4.290
				β	0.936
				R^2	0.988

Table 2.Position of FTIR bands in GAC and GAC after Mn (II) adsorption

Sr. No	Band position, cm^{-1}		Description
	GAC	GAC – Mn (II)	
1	800	881	S-O stretching
2	1022	1028	Si-O stretching vibration
3	1390	-------	Al-O as a Si cage
4	1541	1522	C=C stretching vibration in carboxylic chain
5	1710	1849	C=O stretching
6	2117	2111	$C \equiv C$ stretching
7	2362	2375, 2341	Carboxylate ion (-COO^-)

CONCLUSION

Batch adsorption studies for the removal of Mn (II) from aqueous solutions have been carried out using nitric acid treated granular activated charcoal as adsorbents. Results from this study highlight the feasibility of granular activated charcoal prepared from *cordia macleodii* tree bark as alternative low-cost adsorbent for the removal of Mn (II) metal ions from aqueous solution. The obtained results may be summarized as follows:

- The presence of functional groups in the adsorbent favours metal ion binding through complexation.
- Langmuir isotherm well describes the Mn (II) adsorption on adsorbent.
- The pH variation studies showed that the adsorption process for the adsorbents is highly pH dependent. At pH11.5 maximum removal was efficiency found to be 68.93%.
- Increase in contact time and adsorbent dosage leads to increase in Mn (II) adsorption due to increased number of adsorption sites.
- The kinetic study shows that the test data fits the pseudo-second order kinetics well.

Acknowledgements
Authors are very much thankful to Dr. D.V. Atkare, Principal of Mahatma Fule Art`s, Commerce and Sitaramji Chaudhari Science College Warud, for providing necessary facilities to carry out the research work. Authors are also very much thankful to SEM In-charge, Department of Physics, Manipur University, Imphal for providing SEM facility. We are also thankful to Principal of Art`s, Commerce and Science College, Kiran Nagar Amravati for providing FTIR facility.

REFERENCES

[1] Kortenkamp, M. Casadevall, S.P. Faux, A. Jenner, R.O.J. Shayer, N. Woodbridge, P. O'Brien, *Arch. Biochem. Biophys.*,**1996**, 329, 199208.
[2] R.P. Richards, S.N. Foellmi, Utility battles iron and manganese: Public Works, **1985**, 116 (6), 9195.
[3] G.R. Watzlaf, Chemical stability of manganese and other metals in acid mine drainage sludge: Bureau of mines information circular 9183, Proceedings of the mine drainage and surface mining restoration conference, pittsburgs, PA, USA, **April 1988**,17-22, p. 8390.
[4] R.S. Grippo, W.A. Dunson, *Environmental toxicology and chemistry*,**1996**, 15, 19551963.
[5] W.H.O. "Manganese in drinking water", guidelines for drinking water quality, **2011**.
[6] V.P. Evangelou, U.M. Sainju, Xiao Huang, Advances in research and technology: St. Joseph, M.I., American society of agricultural engineers, publication,**1992**, 14-92, p. 304316.
[7] J. A.Gordon, J. L. Burr, National symposium on mining, hydrology, sedimentology and reclamation, **1987,** KY Lexington, university of Kentucky college of engineering, 383393.
[8] Hedin R.S, Nairn R.W. and kleinmann RLP, Passive treatment of coal mine drainage: Bureau of mines information circulation 9389,**1994**, p. 35.
[9] G. McKay, G. Ramprasad, P.P. Mowli, *Water, Air, Soil Pollut.*,**1986**, 29, 273.
[10] Y.C. Sharma, Uma, S.N. Upadhyay, F. Gode, *J. Appl. Sci. Environ. Sanitation*, **2009**, 4, 21.
[11] C. Namasivayam, N. Muniasamy, K. Gayathri, M. Rani, K. Ranganathan, *Bioresour. Technol.*,**1996**, 57, 37.
[12] K.G. Bhattacharya, A. Sharma, *Dyes Pigm*.,**2005,** 65, 51.
[13] V.K. Gupta, I.A. Suhas, V.K. Saini, *Ind. Eng. Chem. Res*., **2004**, 43,1740.
[14] V.K.C. Grag, M. Amita, R. Kumar, R. Gupta, *Dyes Pigm*.,**2004**, 63, 243.
[15] Y.C. Sharma, Uma, S.N. Upadhyay, F. Gode, *J. Appl. Sci. Environ. Sanitation,***2009**, 4, 21.
[16] F. Mendez, G. Fernandez, *Desalination*, **2007**,206, 147.
[17] R. Ansari et al, *Int.J. ChemTech Res*., **2009**,1(4), 859864.
[18] Langmuir I.,*Jour Ameri. Chem. Soc*., **1918**,40,1361–1403.