

Adsorption, Kinetics and Equilibrium Studies on Removal of Mn (II) From Aqueous Solutions Using Surface Modified Granular Activated Charcoal as a Low-Cost Adsorbent

Atul K. Wanjari* and Umesh E. Chaudhari

Department of Chemistry, Mahatma Fule Art's, Commerce and Sitaramji Chaudhari Science College, Warud, Sant Gadge Baba Amravati University, Republic of India
atulrdik@gmail.com

Available online at: www.isca.in, www.isca.me

Received 27th October 2016, revised 2nd December 2016, accepted 18th December 2016

Abstract

The aim of this paper was to investigate adsorption of Mn (II) metal ions from aqueous solution by DOSS (Dioctyl sodium sulfosuccinate), SDBS (Sodium dodecylbenzenesulfonate) and SDS (Sodium dodecyl sulphate) an adsorbed chelating species on granular activated charcoal (GAC) which is prepared from *Cordia Macleodii* Tree Bark. The adsorbent dose, contact time, initial metal ions concentration, temperature, pH were determined and adsorption isotherms were obtained for Mn (II) metal ions. Kinetic data reveals that adsorption mechanism follows pseudo second order model also fitted to Freundlich and Langmuir adsorption isotherms. The surface modified GAC were characterised by SEM-EDAX and FTIR technology.

Keywords: Adsorption, Manganese, Kinetics, Batch Study, Granular Activated Carbon, *Cordia Macleodii*.

Introduction

It is difficult to remove heavy metals naturally from the environment¹. All heavy metals have maximum permissible limit prescribed by W.H.O. above that concentration this heavy metals are highly toxic². In India there are more than 7500 industries which are responsible for pollution but out of that more than 4500 put up effluent treatment plant³. There are various technologies available for the removal of these toxic metal ions from wastewater to adequate level. Few studies are reported to remove toxic pollutants and to treat wastewater by using low cost adsorbent like granular activated carbon⁴, pecan shell-based granular activated carbon⁵, Fly ash, brick kiln ash⁶ etc. From the last some years many researcher reported many processes to remove toxic metal ions by chemical precipitation (by adding alkali), membrane filtration (hybrid flotation), ion exchange (chelating ion exchange polymer), physico-chemical method like coagulation and activated carbon prepared from various tree bark or commercial activated charcoal⁷. Adsorption technique considered as most effective process for the removal of heavy metal ions by using activated carbon⁸.

There are many low cost adsorbents are used like industrial waste and agricultural waste like coconut shell, rice straw etc.⁹. In the present study we prepared a granular activated charcoal from *Cordia Macleodii* tree bark and used it as a low cost adsorbent by surface modification.

Materials and Methods

Preparation of adsorbent and surface modification: The granular activated charcoal used as low cost adsorbent prepared

from a *Cordia Macleodii* tree bark. The bark first washed with deionised water then dried bark is converted into granular activated charcoal by using muffle furnace. The prepared granular activated charcoal was further activated by nitric acid and surface modification of GAC was done as describe in our previous work¹⁰. The surface modification of adsorbent was done by using Dioctyl sodium sulfosuccinate, Sodium dodecylbenzenesulfonate, and Sodium dodecyl sulphate and surface modified GAC were designated as GAC-DOSS, GAC-SDBS and GAC-SDS.

Batch Study: 2.86 gram of manganese bromide was dissolve in 1000 ml of deionised water to prepare stock solution. Solution required to carry out experiment was prepared from this stock solution by dilution it with deionised water. The entire chemicals used were analytical grade and volumes of solution were made up with the help of deionised water. The dried amount of loaded GAC (0.5 gram) was taken in 250 ml reagent bottle and standard solution of various concentration of Mn (II) was added to it and system is equilibrated by shaking the content of the flask at room temperature. The purple coloured complex was measured at 460 nm by periodate method¹¹. The UV-Visible spectrophotometer (117) was used to measure the adsorption of Mn (II) metal ions.

Percentage of Adsorption: The removal percentage of Mn (II) was calculated by using simple formula:

$$\% \text{ Adsorption} = \frac{(C_o - C_e)}{C_o} \times 100$$

Where, in equation C_o and C_e represented the initial concentration and final concentration in solution (mg/L).

Results and Discussion

Adsorption Isotherms: Equilibrium state provides the linear relationship between concentration of metal ions in solution and amount of metal ions adsorbed on the adsorbent, which was analysed by studying adsorption isotherm. To study the adsorption isotherm Langmuir and Freundlich adsorption isotherms are mainly used¹²⁻¹³.

Langmuir Model: The Langmuir adsorption isotherm is mainly depends upon the maximum adsorption related to saturated monolayer on the surface of the adsorbent¹⁴. The Langmuir's isotherm model linearly represented as:

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

The Langmuir constant Q^0 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^0 and b were evaluated from the intercept and slope of linear plots of $1/q_e$ vs. $1/C_e$ respectively.

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

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 C_m is the maximum initial solute concentration used in the Langmuir isotherm.

Freundlich Model: It helps to investigate the nature of adsorption and the adsorption capacity of an adsorbent. The linear form of Freundlich isotherm model is $\log q_e = B \cdot \log C_e + \log K_f$

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. Plot of $\log q_e$ Vs $\log C_e$ was also found to be linear. The values of B and K_f are calculated from the intercept and slope respectively.

Langmuir isotherm and Freundlich isotherm results are shown in Figures-1, 2 and parameters are depicted in Table-1.

Adsorption Kinetics: To study the mechanism of adsorption of Mn (II) kinetics, three models were tested namely; First order kinetic model, Pseudo second order kinetic and Elovich model.

First Order Kinetics: The kinetics of Mn (II) adsorption was studied from the time versus % removal curves. The rate kinetics of Mn (II) adsorption on the surface modified adsorbent was analysed using the first order rate kinetics proposed by Lagergren. This can be given as:

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

Where: q_e is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg/g), q_t is the amount of solute adsorbed at any given time t and k_1 is the rate constant.

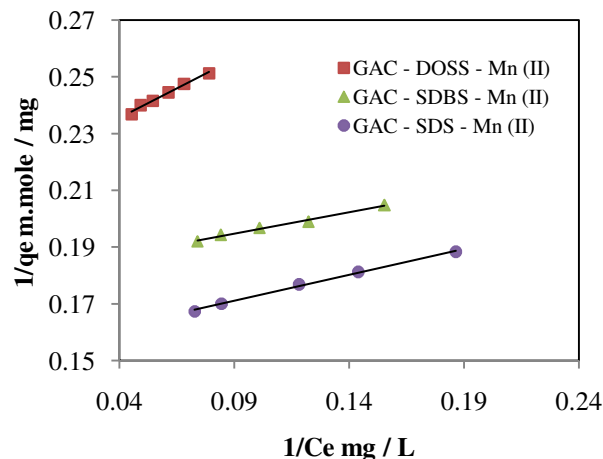


Figure-1
Langmuir adsorption isotherm

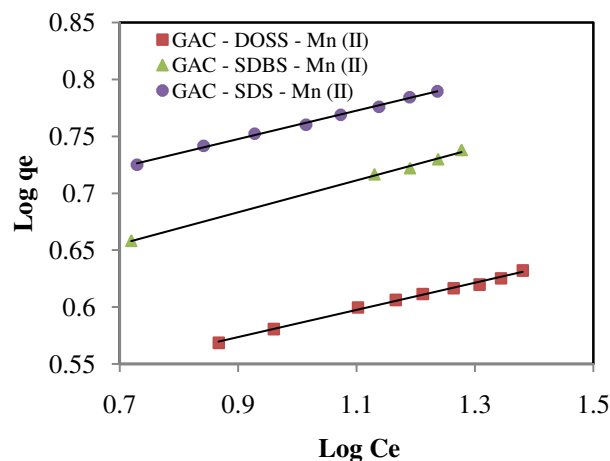


Figure-2
Freundlich adsorption isotherm

Pseudo Second Order Kinetic Model: Pseudo second order model is based on the assumption of chemisorptions of the adsorbate on the adsorbent. This model can be represented by following equation.

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

Here, the value of t/q_t is calculated from different agitation time's t and a graph is drawn between t/q_t and t . However the linear plot between t/q_t and t is the so called ratio correlation in that t present in both abscissa and coordinate. This plot has been widely used for kinetics study.

Elovich Model: The Elovich or Roginsky-Zeldovich equation is generally expressed as follows.

$$q_t = \frac{1}{\beta} \ln \alpha t + \frac{1}{\beta} \ln (\alpha \beta)$$

$$\frac{dq_t}{dt} = \alpha \exp (-\beta \cdot q_t)$$

Where, α is called initial adsorption rate in (mg/g/min) and β is desorption constant (g/mg). Linear form of this equation is

Where q_t is the amount of Mn (II) adsorbed by adsorbent at a time t , α is the initial Mn (II) adsorption rate [mmol/(g min)] and β is the desorption constant (g/mmol). The optimum values of kinetic parameters are given in Table-2 and shown in Figures-3, 4 and 5.

Table-1
Isotherm constants for Mn (II) adsorption

System	Langmuir				Freundlich		
	Q^0	b	R	R^2	K_f	B	R^2
GAC – DOSS - Mn (II)	4.5871	0.0116	0.0530	0.989	2.9241	0.119	0.995
GAC – SDBS - Mn (II)	5.5248	0.0097	0.0508	0.990	3.6057	0.139	0.997
GAC – SDS - Mn (II)	6.4935	0.0082	0.0532	0.997	4.3151	0.124	0.997

Table-2
Kinetic model value for Mn (II) adsorption

System	First order			Pseudo second order			Elovich model		
	K_L	q_e	R^2	q_e	K_2	R^2	α	β	R^2
GAC-DOSS-Mn (II)	0.932	1.90	0.997	2.31	0.4004	0.997	8.36	0.7627	0.990
GAC-SDBS-Mn (II)	0.822	1.88	0.998	2.62	0.4439	0.997	15.16	0.7610	0.992
GAC-SDS-Mn (II)	0.893	2.04	0.999	2.92	0.4148	0.999	17.47	0.6779	0.993

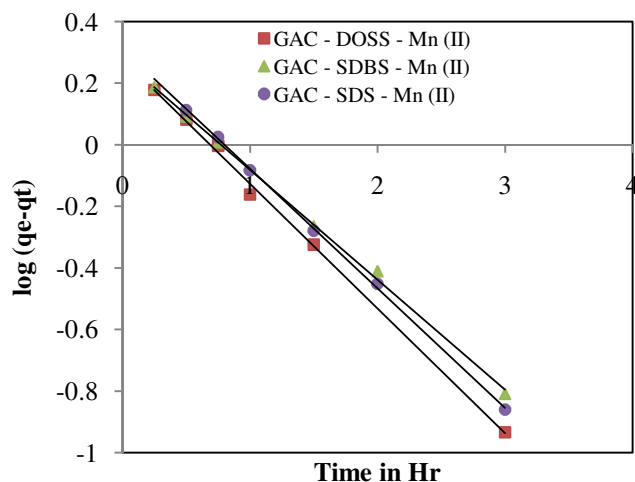


Figure-3
Lagergren plot

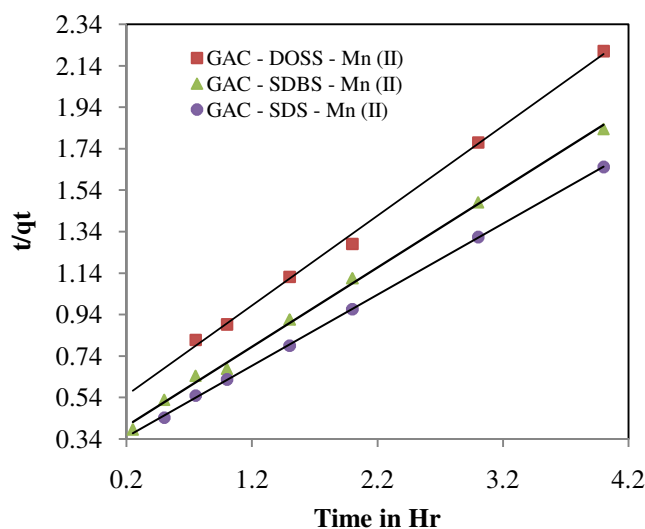


Figure-4
Pseudo second order plot

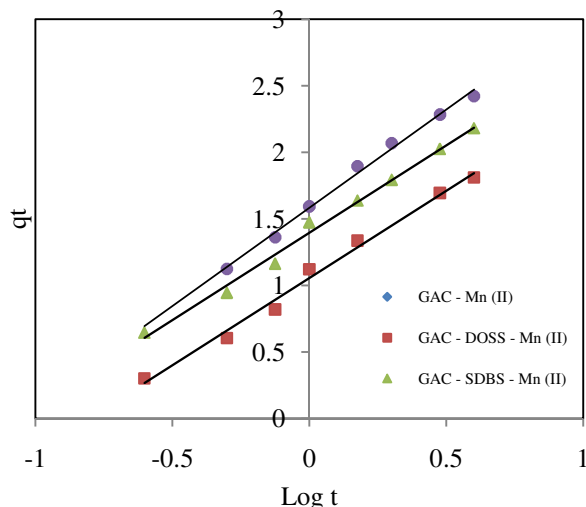


Figure-5
 Elovich model plot

Schematic adsorption mechanism: The possible adsorption mechanism of Mn (II) on granular activated charcoal loaded with SDBS shown in Figure-6. Some factors played an important role to bind the metal ions with loaded GAC which are electrostatic attraction, ion exchange and complexation. SDBS have a hydrophilic head and due to loading it with GAC this head played a vital role to attract metal ions towards itself and increases the adsorption capacity of GAC towards Mn (II) metal ions removal.

Effect of pH on Mn (II) Adsorption: The role of pH on Mn (II) adsorptions shown in Figure-7. pH directly affects on the properties of the adsorbent.. The result indicates that Mn (II) removal is highly pH dependent. Effect of pH from the 10-13 range was analysed by taking initial metal ions concentration 10.65 mg/L keeping all the parameter constant (Dose = 0.5 gram, contact time = 3 Hr, temperature = $27 \pm 1^\circ\text{C}$). Results

indicates that at high pH value (pH = 11.5) the surface of the impregnated GAC becomes highly negatively charge due to which Mn (II) metal ions adsorption increases via electrostatic attraction.

Effect of contact time on Mn (II) Adsorption: In order to study the effect of contact time on the removal of Mn (II) metal ions, study was carried out with 0.5 gram loaded GAC using initial Mn (II) concentration 11.43 mg/L at an initial pH 11.5. Figure-8, shows the result of Mn (II) removal as a function of contact time. It was observed that removal of Mn (II) metal ions initial rapidly increases with increase in contact time but thereafter remains somewhat constant. The adsorption capacity is rapid at the beginning of the process and due to increase in contact time no further changes was observed. It is found that GAC loaded with SDS has greater adsorption capacity than GAC-SDBS and GAC-DOSS.

Effect of adsorbent dose on Mn (II) Adsorption: The effect of adsorbent dosage on the amount of Mn (II) adsorption was studied by taking initial concentration of solution 11.10 mg/L separately with 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4 grams of adsorbent at temperature 27°C with 3Hrs contact time and 1000 rpm shaking speed. UV-Vis spectrophotometer (117) was used to measure the percentage of adsorption of Mn (II) metal ions filtrate. It is found that as the dose of adsorbent increases the removal of Mn (II) metal ions increases shown in Figure-9.

Effect of initial metal ions concentration: In order to evaluate the effect of Mn (II) metal ions concentration, 0.5 gram of loaded GAC added to 200 ml solution of Mn (II) metal ion by varying concentration 7.53, 13.60, 18.68, 23.55, 29.06, 34.48 mg/L. The result shows that the adsorption of Mn (II) metal ions decreases with increase in concentration of adsorbate because of lack of adsorption sites at higher concentration shown in Figure-10.

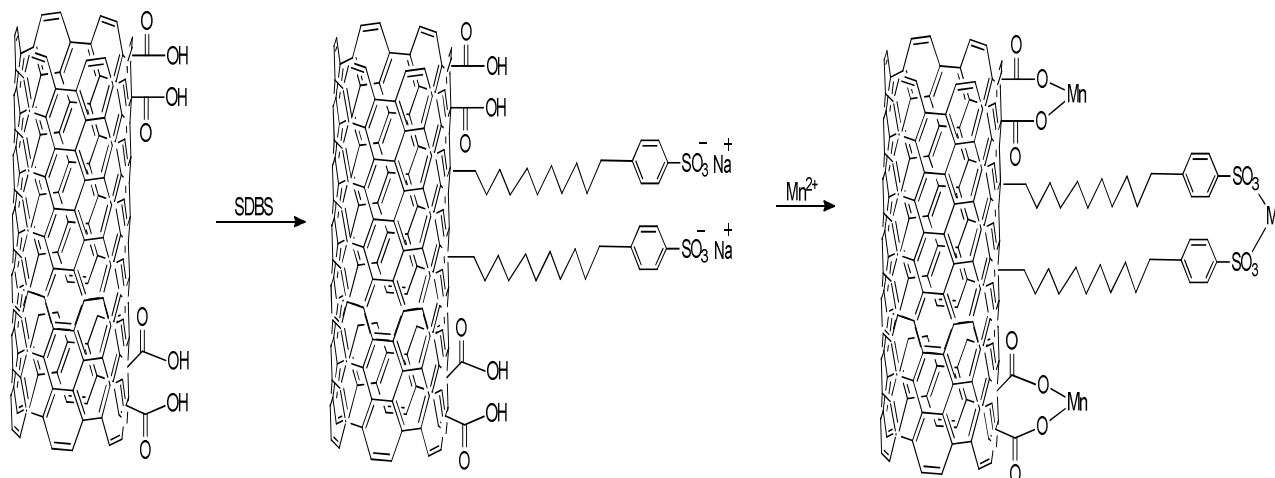


Figure-6
 Showing schematic representation of mechanism of adsorption

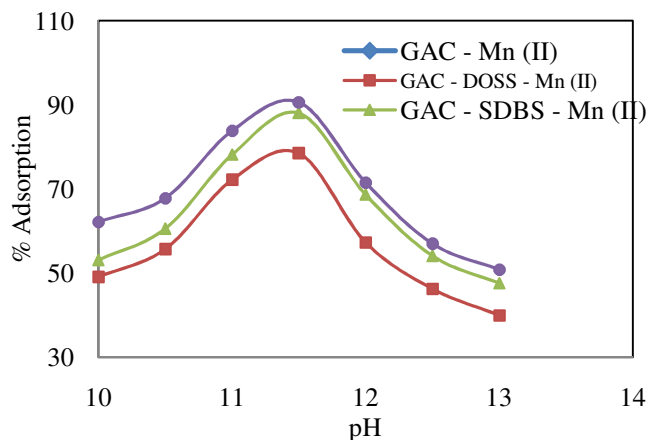


Figure-7
 Effect of pH

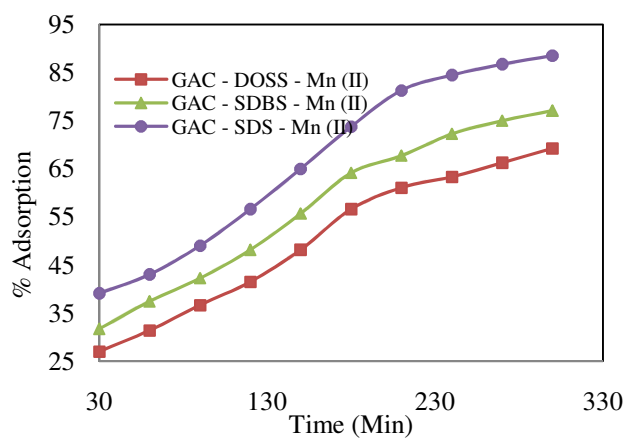


Figure-8
 Effect of contact time

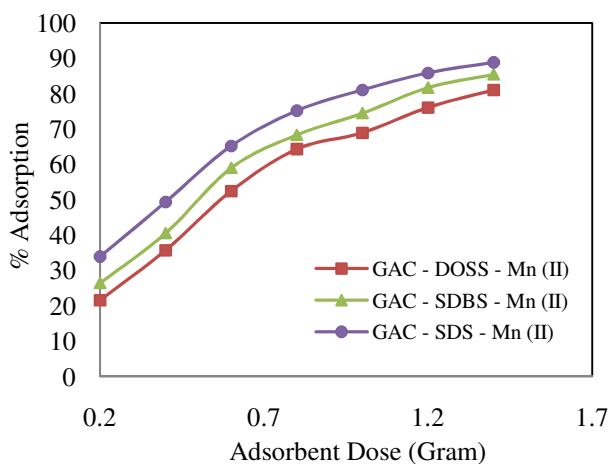


Figure-9
 Effect of adsorbent dose

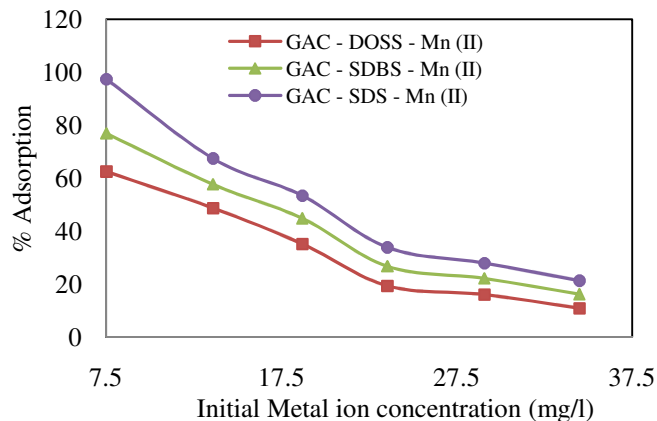


Figure-10
 Effect of initial metal ions concentration

Effect of Temperature: 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. Study was carried out at pH 11.5 and at 1000 rpm with contact time 3 hours. Temperature directly affects of porosity of adsorbent. As the temperature increases porosity increases and percent of adsorption increases shown in Figure-11.

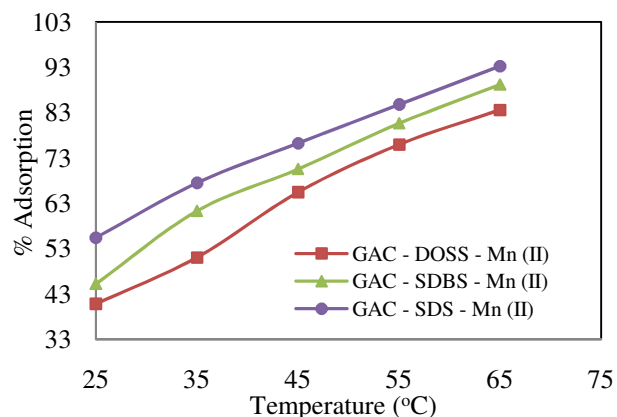


Figure-11
 Effect of temperature

SEM-EDAX and FTIR characterization: SEM-EDAX images of loaded granular activated charcoal before and after Mn (II) metal ions adsorption shown in Figures-12, 13, 14 and 15. Comparison of these micrographs before and after Mn (II) adsorption shows that there is an adsorption of Mn (II) metal ions on loaded granular activated charcoal. Characterization of adsorbent by FTIR technology provides an idea about functional groups present in the adsorbent. It also suggests the mechanism of binding and interaction of functional groups with metal ions. The band observed before and after metal ions adsorption on to loaded GAC shown in Table-3. After Mn (II) metal ions adsorption on loaded GAC showed shifting or reduction in peaks. From which it is conclude that functional groups are involved in adsorption mechanism.

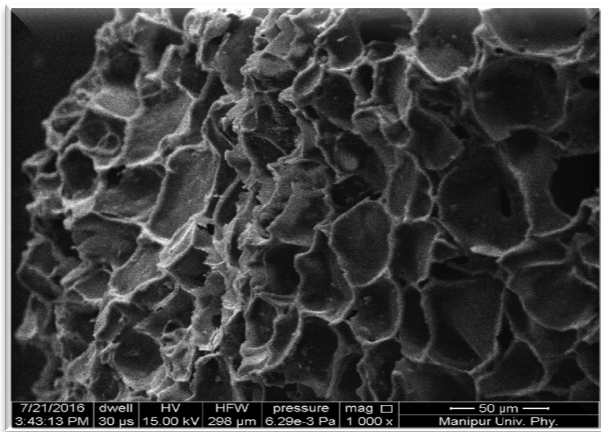


Figure-12
 SEM monograph of virgin GAC

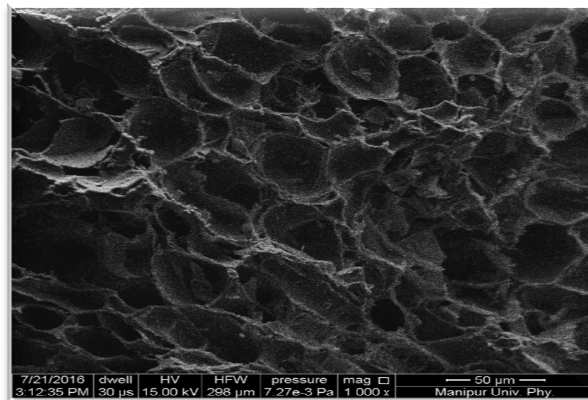


Figure-14
 SEM monograph of GAC loaded with DOSS after Mn(II) metal ion adsorption

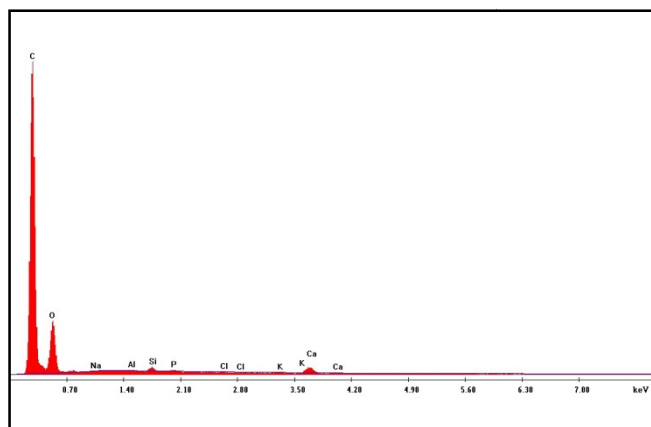


Figure-13
 EDAX monograph of virgin GAC

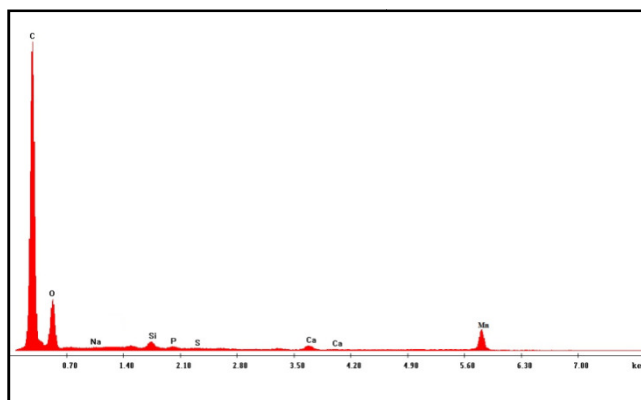


Figure-15
 EDAX monograph of GAC loaded with DOSS after Mn(II) metal ion adsorption

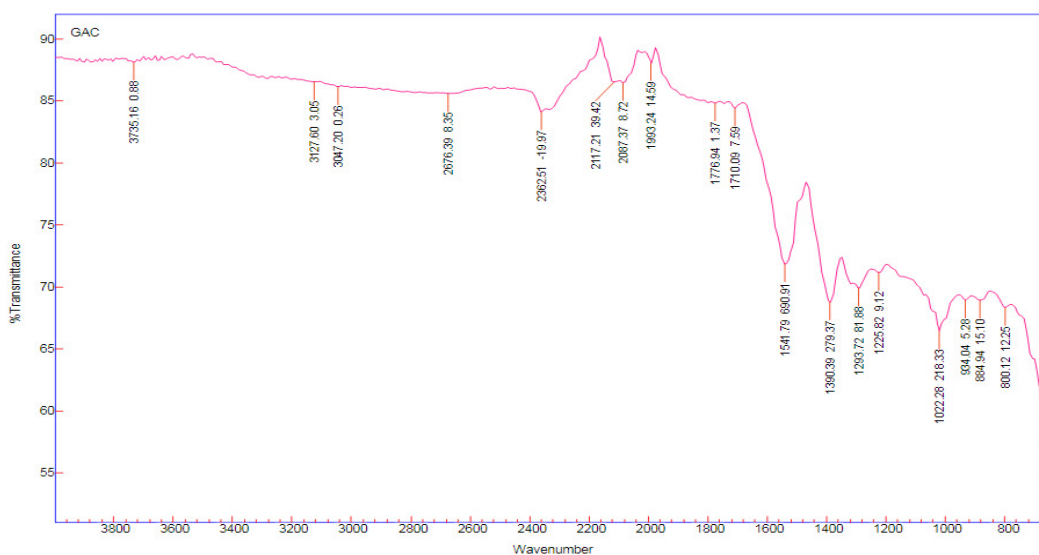


Figure-16
 FTIR spectra of virgin GAC

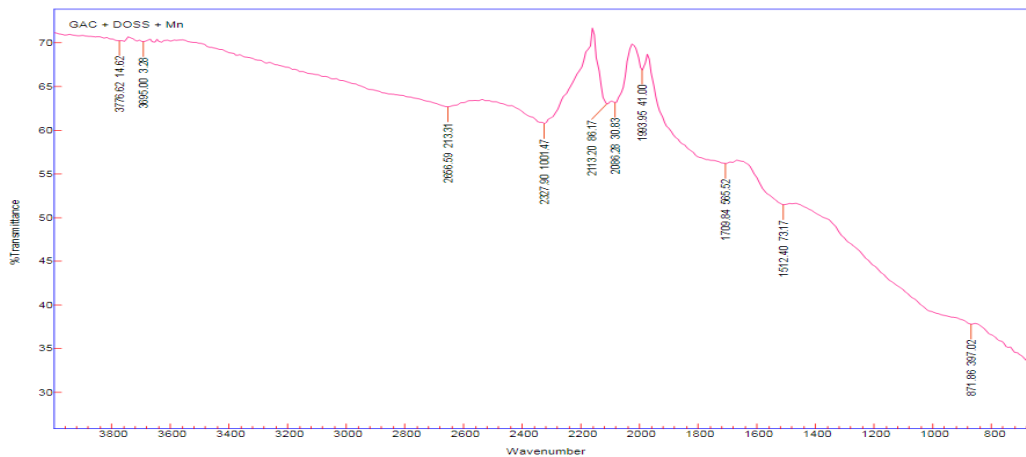


Figure-17
FTIR spectra of GAC loaded with DOSS after Mn (II) adsorption

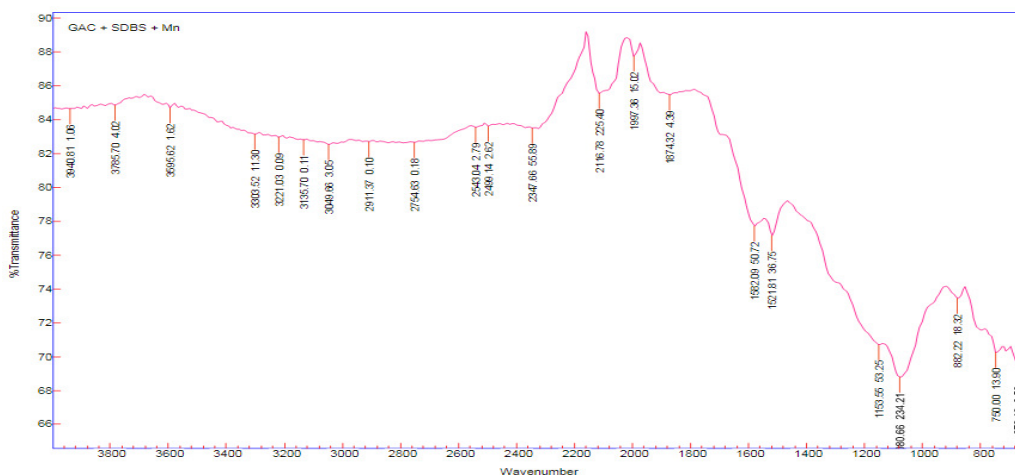


Figure-18
FTIR spectra of GAC loaded with SDBS after Mn (II) adsorption

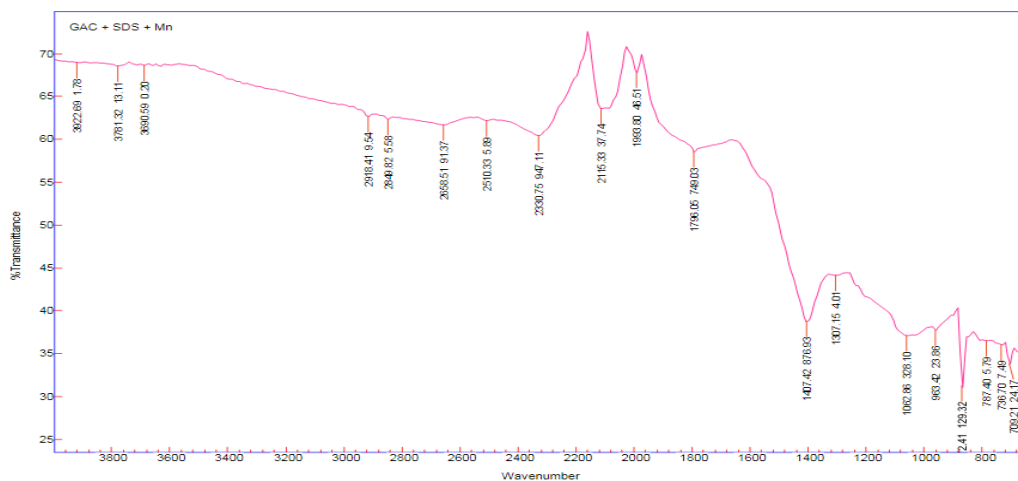


Figure-19
FTIR spectra of GAC loaded with SDS after Mn (II) adsorption

Table-3
Positions of FTIR bands in GAC and Loaded GAC after Mn (II) adsorption

Sr. No.	Band position (cm ⁻¹)				Description
	GAC	GAC – DOSS - Mn (II)	GAC – SDBS - Mn (II)	GAC – SDS - Mn (II)	
1	800	871	884	872	S-O stretching
2	1022	-----	1080	1062	Si-O stretching vibration
3	1390	-----	-----	1307	Al-O as a Si cage
4	1541	1512	1582	1407	C=C stretching vibration in carboxylic chain
5	1710	1709	1874	1796	C=O stretching
6	2117	2113	2116	2115	C ≡ C stretching
7	2362	2327	2347	2330	Carboxylate ion (-COO ⁻)

Conclusion

The surface modified granular activated charcoal with DOSS, SDBS, and SDS causes a dramatic increase in its adsorption capacity for the adsorption of Mn (II) metal ions. Among the two isotherms tested Langmuir isotherm was best fitted with experimental data. The results are summarised as follows. i. The removal of Mn (II) metal ions founds to be highly pH dependent, at pH 11.5 maximum removal efficiency was obtained. ii. SEM-EDAX and FTIR confirms the adsorption of Mn (II) metal ions. The FTIR analysis showed that different functional groups are involved in the adsorption which is observed by either shifting or reduction in bands positions. iii. The removal capacity of Mn (II) metal ions increases with increase in contact time, temperature and adsorbent dose while decrease by varying initial metal ions concentration. iv. Pseudo second order model was best fitted for Mn (II) removal among the three models tested. v. From the experiment data removal efficiency of adsorbent increases in the following order GAC-SDS > GAC-SDBS > GAC-DOSS.

Acknowledgements

We are very much thankful to Principal of institute Dr. D.V. Atkare 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. Siti Nur Aeisyah Abas, Mohd Halim Shah Ismail, Md Lias Kamal and Shamsul Izhar (2013). Adsorption Process of

Heavy Metals by Low-Cost Adsorbent: A Review. *World Appl. Sci. J.*, 28(11), 1518-1530.

2. Babel S. and Kurniawan T.A. (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 5(7), 951-967.
3. Tyagi P. (1998). Law and implementation of industrial wastewater pollution control. *Water Sci. Technol.*, 24, 5-13.
4. Crittenden J.C., Vaitheeswaran K., Hand D.W., Howe E.W., Alieta E.M., Tate C.H., McGuire M.J. and Davis M.K. (1993). Removal of dissolved organic carbon using granular activated carbon. *Water Res.*, 27, 715-721.
5. Bansodea R.R., Lossoa J.N., Marshallb W.E., Rao R.M. and Portierc R.J. (2004). Pecan shell-based granular activated carbon for treatment of chemical oxygen demand (COD) in municipal wastewater. *Bioresour. Technol.*, 94, 129-135.
6. Devi R. and Dahia R.P. (2006). Chemical oxygen demand (COD) reduction in domestic wastewater by fly ash brick kiln ash. *Water Air Soil Pollut.*, 174, 33-46.
7. Orhan Y. and Buyukgungor H. (1993). The removal of heavy metals by using agricultural wastes. *Water Sci. Technol.*, 28, 247-255.
8. Huang C.P. and Blankenship D.W. (1984). The removal of Mercury (II) from dilute aqueous solution by activated carbon. *Water Res.*, 18, 37-46.
9. Macchi G., Maroni D. and Tiravarthi G. (1986). Uptake of Mercury by exhausted coffee grounds. *Environ. Technol. Lett.*, 7, 431-444.
10. Wanjari A.K. and Chaudhari U.E. (2016). Removal of Cr (VI) from aqueous solution using granular activated

- charcoal prepared from cordia macleodii tree bark and surface modified granular activated charcoal: A comparative study via spectroscopic characterization. *International jour. of Engineering Sci. & research technology*, 5(10), 304-316.
11. Jeffery G.H., Bassett J., Mendham J. and Denney R.C. (1989). Vogel Textbook of Quantitative Chemical Analysis., 5th Edition, 684. ISBN 0-582-44693-7.
 12. Langmuir I. (1916). The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.*, 38, 2221-2295.
 13. Freundlich H.M.F. (1906). Über die biosorption in lösungen. *Z. Phys. Chem.*, 57, 385-470.
 14. Ajaelu Chijioko John, Ibironke, Oluwafunke Lara, Adedeji, Victor and Olafisoye Oladunni. (2011). Equilibrium and Kinetic Studies of the Biosorption of Heavy Metal (Cadmium) on *Cassia siamea* Bark. *American-Eurasian Journal of Scientific Research*, 6 (3), 123-130.