



## Adsorption characteristics of manganese (II) on granular activated carbon

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### ABSTRACT

In the present investigation the surface of granular activated carbon was modified by organic ligand for removal of  $Mn^{2+}$  ions from aqueous solution. Experiment was carried out in batch mode at constant temperature of  $25 \pm 1^\circ C$ . Some readily available derivatives of benzene were used for surface modification of GAC. To enhance the capacity to adsorb manganese. GACs were loaded with organic ligand. The equilibrium adsorption data was better fitted to the Langmuir and Freundlich adsorption model. Study was also extended to evaluate the surface area occupied by manganese in the formation of monolayer on GAC.

**Keywords:** Adsorption, Mn (II), Granular Activated Carbon(GAC), 3-Nitrophthalic Acid (3-NPTA), Filtrasorb100 (F-100), Filtrasorb 816 (F-816).

### INTRODUCTION

In present day context water pollution is the biggest hazard for all forms of life. The environmental pollution has been the most remarkable side effect of rapid industrialization and growing population of the world. Today, almost all the things, which are most necessary to the human beings, are more or less contaminated by toxic substances.

Manganese is common contaminant in ground water, as a divalent ion  $Mn^{2+}$  and it is considered a pollutant mainly because of its organoleptic properties. The World Health Organization (WHO) has set a guideline value 0.05 mg/L of manganese in drinking water [1]. Water gets polluted by manganese ions coming from many industries mainly pyrolusite  $MnO_2$  treatment, steel alloy, dry cell batteries, glass and ceramic, paint and varnish, ink and dyes, match and fireworks. A substantial part of water used for potable use shows contamination significantly exceeding the maximum contaminant level. Thus it is an important and necessary for the researchers to develop appropriate methods to check the deterioration of the environment. Numbers of methods have been developed by the workers for the removal of heavy metals like ion exchange, solvent extraction, chemical precipitation, biological operation, filtration etc [2-8]. But adsorption of heavy metals by activated carbon and modified activated carbon proved to be the most economically viable technique in this application.[9-19]. In present study adsorption isotherms were established and the results modeled by the Langmuir and Freundlich isotherm.

### MATERIALS AND METHODS

All the chemicals used in experiment were analytical reagent grade. The manganese solution was prepared by dissolving requisite  $MnSO_4$  (E-Merck) in freshly prepared distilled water. In present study granular activated carbons namely F-816 and F-100 supplied by Calgon Carbon Corporation Ltd. Pittsburg PA USA were used as adsorbent. Each grade of carbons was first subjected to size fractionation to obtain a particles of desired size using a sieve shaker (M/s Jayant Test Siever Mumbai) and the particles retained in between  $840\mu$ - $1400\mu$  were used in all experiment. These particles were washed several times with boiled distilled water until clear lechate was obtained

and collected in petridish. Finally the samples were dried in an oven at a temperature of 100-110°C, cooled at room temperature and stored in desiccators until use.

A ten solutions of known concentration of  $Mn^{2+}$  ions were prepared from main stock solution by diluting with distilled water. Potassium periodate method was used to form the complex with  $Mn^{2+}$  ions [20]. Then absorbance of each solution was measured spectrophotometrically at 525 nm of wavelength using Chemito-spectoscan UV 2700, Double beam UV-Vis Spectrophotometer. The Beer's law calibration curve was established by plotting the graph between absorbance versus concentration. In the present work 3-Nitrophthalic acid was selected as organic ligand to modify the surface of GAC. It was first purified and recrystallized by standard method. The experimental melting point of 3-Nitrophthalic acid (218.5°C) compared with literature value (219°C) [21]. For determining adsorption isotherm, 0.5 gm of the dried GAC was taken in each clean shaking bottle and 200 ml of acid solution of a specific concentration was shaken for 5 hrs using remi stirrer at about 500 rpm. The solution was then filtered off and the carbon was washed several time thoroughly with distilled water. This carbon was transferred to shaking bottle and then 200 ml  $Mn^{2+}$  ion solution of  $P^H = 5$  was added to it. The mixture was then stirred for 5 hrs at constant temperature of  $25 \pm 1^\circ C$ . The initial and final concentration of the  $Mn^{2+}$  ion in mg /L was then estimated using mathematical equation obtained from calibration curve. The batch adsorption experiments were repeated to ensure reproducible result.

## RESULTS AND DISCUSSION

Adsorption isotherms are essential for the description of how metal ion concentration interact with carbon surface and also useful to optimize the use of granular activated carbon as a adsorbent for the removal of manganese.

Adsorption of  $Mn^{2+}$  ions on ligand loaded GAC was studied by batch technique. The uptake of  $Mn^{2+}$  on the loaded GAC was calculated from equation

$$q_e = (C_0 - C_e) \times \frac{V}{W}$$

Where,

$q_e$  = Concentration of  $Mn^{2+}$  on the ligand loaded GAC in mg/mmol of ligand at equilibrium,

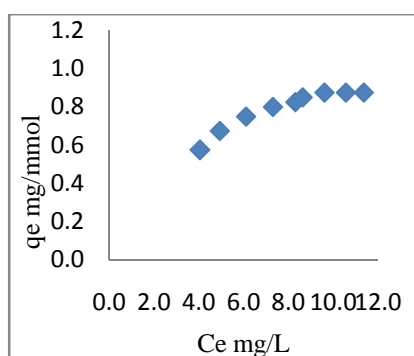
$C_0$  = Initial concentration of  $Mn^{2+}$  in solution in mg/L,

$C_e$  = Equilibrium concentration of  $Mn^{2+}$  in solution in mg/L,

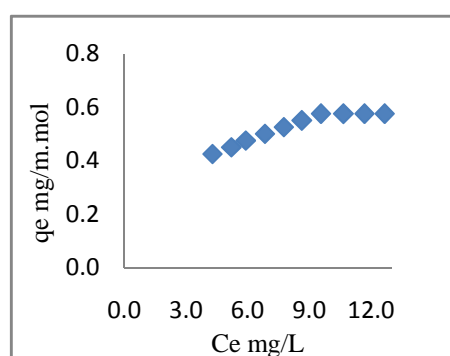
$V$  = Volume of solution in Lit,

$W$  = Weight of the carbon .

The adsorption isotherms of ligand loaded GAC obtained by plotting  $q_e$  and  $C_e$  are shown in Fig-1 and Fig-2.



**Fig-1 Adsorption Isotherm**  
System: F-816-3NPTA- $Mn^{2+}$



**Fig-2 Adsorption Isotherm**  
System: F-100-3NPTA- $Mn^{2+}$

Adsorption isotherm:

The adsorption equilibrium data were fitted to the Langmuir and Freundlich isotherm.

The most important Langmuir model of monolayer adsorption of manganese ions on the surface of carbon sites is expressed in the linear form. As per Langmuir theory, the non linear equation can be represented by

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

The linearised form of Langmuir isotherm can be expressed as

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

Where,  $Q^0$  =(monolayer adsorption capacity) amount adsorbed per unit weight of the carbon forming a complex monolayer on the adsorbent surface,  $b$  = Langmuir constant. A plot of  $1/C_e$  versus  $1/q_e$  found to be linear indicating the applicability of Langmuir model.

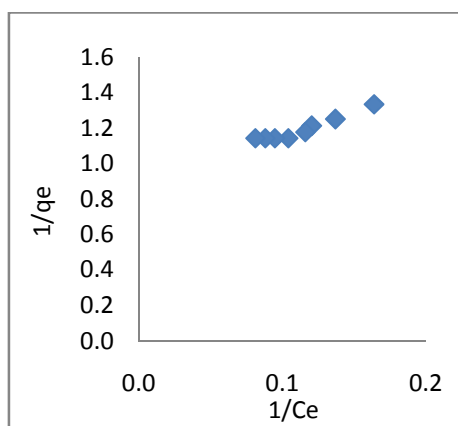
The Freundlich model is an empirical equation describes the heterogeneous surfaces and multilayer adsorption and is expressed in non linear form as

$$q_e = k \cdot C_e^{\frac{1}{n}}$$

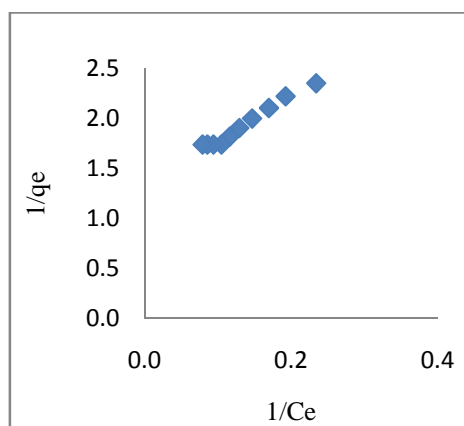
It may be linearised as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where the constant  $K_f$  and  $1/n$  of the Freundlich model related to the adsorption capacity and adsorption intensity respectively, which depends on the heterogeneity of the material. A plot of  $\log q_e$  versus  $\log C_e$  was fairly showing validity of Freundlich equation over a range of concentration. The slope of  $1/n$  ranging between 0 and 1 is a measure of the surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Fig-3 to Fig- 6 illustrate the plot of Langmuir and Freundlich isotherm for F-816-3-NPTA- $Mn^{2+}$  and F-100-3-NPTA- $Mn^{2+}$ . The value of  $K_f$ ,  $1/n$ ,  $b$ ,  $q_{max}$  and  $Q^0$  for F-816-3-NPTA- $Mn^{2+}$  and F-100-3-NPTA- $Mn^{2+}$  are shown in Table No.1. F-816-3-NPTA- $Mn^{2+}$  systems show the superiority over F-100-3-NPTA- $Mn^{2+}$  for the adsorption process.



**Fig-3 Langmuir Adsorption Isotherm**  
System: GAC-F-816-3-NPTA- $Mn^{2+}$



**Fig-4 Langmuir Adsorption Isotherm**  
System: GAC-F-100-3-NPTA- $Mn^{2+}$

The saturation of monolayer by adsorbate gave the value of  $q_e$  was used for determination of surface area of the adsorbent. For this purpose a plot of  $1/q_e$  versus  $1/C_e$  helped in determination of  $1/Q^0$  and hence  $Q^0$ . The surface area of the carbon through  $Mn^{2+}$  adsorption can then be represented as

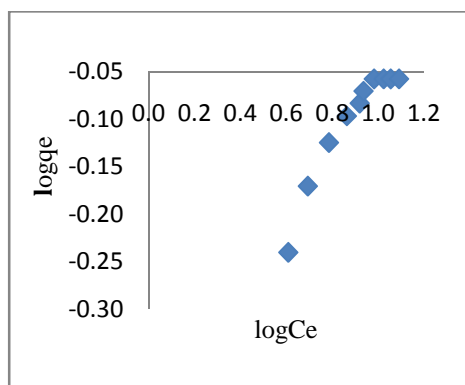
$$S = N Q^0 A$$

Where,

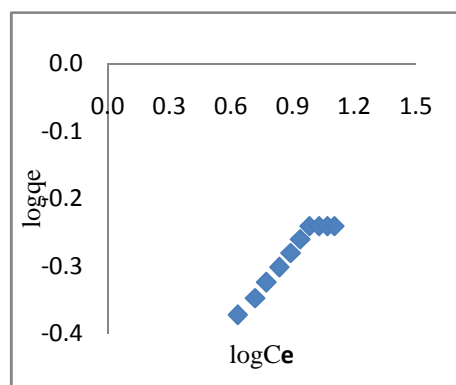
$S$  = Surface area of adsorbent  $cm^2/g$

$N$  = Avogadro number

$A$  = Cross section area of the adsorbate molecule



**Fig-5 Freundlich Adsorption Isotherm**  
System:GAC-F-816-3-NPTA-Mn<sup>2+</sup>



**Fig-6 Freundlich Adsorption Isotherm**  
System:GAC-F-100-3-NPTA-Mn<sup>2+</sup>

Thus it is possible to determine the surface area of ligand loaded GAC at the saturation level when a monolayer of the Mn<sup>2+</sup> would cover entire surface of GAC adsorbent.

The determination of surface area occupied by a single Mn<sup>2+</sup> ion, were calculated using the expression given by Brunauer and Emmet.

$$A = 4 \times 0.866 [M/\sqrt{4N_a \cdot d}]^{2/3}$$

Where,

M=Atomic weight of Manganese [22]

N = Avogadro number

d = Density of Manganese (7.3 gm/cm<sup>3</sup>) [23]

The values of S obtained from Q<sup>0</sup> and S' obtained from q<sub>max</sub> are fairly comparable and are reported in the Table-2.

**Table-1 Langmuir and Freundlich Isotherm Constants**

Sr.No	System	Langmuir Constant		Freundlich Constant		qmax(mg/m.mole)
		Q <sup>0</sup>	b	1/n	K <sub>f</sub>	
1	GAC-F-816-3-NPTA-Mn <sup>2+</sup>	1.1494	0.3020	0.3650	0.3724	0.8750
2	GAC-F-100-3-NPTA -Mn <sup>2+</sup>	0.7468	0.3030	0.3060	0.2761	0.5750

The numerical value of K<sub>f</sub> and 1/n for GAC F-816 are 0.3724 and 0.3650 respectively. The fractional value of 1/n indicates that the surface of GAC is of the heterogeneous type with an exponential distribution of energy site. The higher numerical value of K<sub>f</sub> confirms the significant affinity of Mn<sup>2+</sup> ions for granular activated carbon. The value of Freundlich and Langmuir constants indicate the superiority of GAC -F-816 over GAC-F-100, in the removal of Mn<sup>2+</sup> from aqueous phase.

**Table No-2 Surface Area of GACs**

Sr. No.	System	Area	S	S'
1	GAC-F-816-3-NPTA-Mn <sup>2+</sup>	5.875×10 <sup>16</sup> cm <sup>2</sup>	2.961×10 <sup>2</sup> cm <sup>2</sup> /g	2.254×10 <sup>2</sup> cm <sup>2</sup> /g
2	GAC-F-100-3-NPTA-Mn <sup>2+</sup>	5.875×10 <sup>16</sup> cm <sup>2</sup>	1.89×10 <sup>2</sup> cm <sup>2</sup> /g	1.481×10 <sup>2</sup> cm <sup>2</sup> /g

## CONCLUSION

In the present investigation, it is concluded that GACs are unique adsorbents for the removal of manganese ions from aqueous phase. The adsorptive ability of F-816 is higher than F-100. This is due to the fact that activated carbon have high surface area and high microporous characters.

The results indicate the GAC is an effective adsorbent for the removal of Mn(II) ions from aqueous solution under the tested experimental condition and could be useful in the treatment process of industrial wastes or the analytical application.

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