

# STUDIES ON DIFFUSION APPROACH OF $Mn^{2+}$ IONS ONTO GRANULAR ACTIVATED CARBON

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## ABSTRACT

*In present investigation attempts have been made to use commercially available carbon Norit 1240+ (N-1240+), filtratorb 820 (F-820) and filtratorb 400 (F-400) in removal of metal ions from aqueous phase. Batch mode experiments were carried out to obtain adsorption isotherms of  $Mn^{2+}$  ions onto Granular Activated Carbon in conjunction with resorcinol at constant temperature  $25 \pm 0.5$  °C. The present study deals with the determination of adsorptive capacity of adsorbents in removal of  $Mn^{2+}$  ions from synthetically prepared waste water. The adsorption isotherms and kinetics of  $Mn^{2+}$  on granular activated carbon have been determined at pH in the range of 5 to 6. Experimental results demonstrate that the N-1240+ has a significant capacity for adsorption of  $Mn^{2+}$  as compared to selected GAC from waste water.*

**Keywords:** about four key words separated by commas

## 1. INTRODUCTION

The effluents of industries such as electroplating, mining operations and tanneries contain heavy metal ions to certain extent [1]. The presence of heavy metal ions in the water bodies has been a matter of major concern due to their toxic effect on mankind. Unlike organic pollutants the majority of which are susceptible to biological degradation, heavy metal ions will not degrade into harmless end-product [2]. There are several methods used for treatment of metal contaminated effluents such as chemical precipitation [3-5], coagulation, flocculation [6-8], reverse osmosis [9], ultra-filtration [10], electro-dialysis [11], flotation [12], ion exchange [13] and membrane processes [14] are employed for the treatment of toxic metals. They have their innate advantages and limitations in application. Among them adsorption process is preferred because of its high efficiency, easy handling and its cost effectiveness [15]. Adsorption has been found to be superior technique used for removal of heavy metals from waste water because of its initial cost and simplicity of design [16]. Several co-workers used activated carbon as a adsorbent for scavenging the heavy metals such as Cd, Cu, Cr, Pb Mn etc. from waste water [17]. This technique is more popular in potable water treatments [18-20]. Furthermore activated carbon is effective in removing taste and odor causing compounds and many metals [21]. Granular Activated Carbon is widely accepted for the removal and recovery of toxic metals because of its low cost and high affinity towards the metal ions [22-26]. Manganese is an essential element for human health. Manganese and its compounds are introduced into natural water from a variety of industrial wastes. In drinking water source secondary maximum contaminant level (SMCL) for manganese must not exceed 0.05 mg/L [27]. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause diseases like parkinson, lung embolism and bronchitis. In this connection work was started in laboratory to remove manganese metal using coal based GAC in conjunction with ligand which are capable of forming a complex with the manganese and thus help in its recovery. In present work surface modification of GAC is achieved by using organic ligand such as resorcinol. Resorcinol is 1,3-Dihydroxy benzene containing two OH groups make it sufficiently polar, so it is soluble in polar solvent.

## 2. MATERIALS AND METHODS

Commercial Granular Activated Carbons namely filtratorb 820 (F- 820) and filtratorb 400 (F-400) supplied by Calgon Carbon Corporation, Pittsburgh, USA and Norit 1240+ supplied by Norit Netherland, B.V. were used as adsorbents. Approximately of equal size particles were obtained by using sieve (M/s Jayant Test Sieves, Mumbai) and particles retained between 1400 micron and 1600 micron were used in the present study. The GACs particles were considered fit for use when the distilled water obtained after washing was visibly clear and then dried in an oven at a temperature of 100-110°C for one hour and stored in  $CaCl_2$  desiccator until use. All chemicals used were of AR grade. A stock

solution of  $Mn^{2+}$  ions was prepared by dissolving required quantity of Manganese Sulphate (E. Merck) in freshly prepared distilled water. Various concentrations of  $Mn^{2+}$  ions were prepared from the stock solution in 50 ml measuring flask. Then volume was made up to the mark with distilled water Spectrophotometrically, Beer's law standard calibration curve was established for  $Mn^{2+}$ , from these standard solutions [28]. A sample of resorcinol was recrystallised by the routine method. The purity of sample was tested from the measurement of melting point of resorcinol. The observed melting point  $109.5^{\circ}C$  was compared with the literature value ( $110^{\circ}C$ ) [29]. All experimental systems were carried out in batches of five units at a time. For adsorption isotherm study 0.5 GM of the GAC and 200 ml of 0.001M resorcinol solution were taken in each clean reagent bottle and stirred for about five hours using Remi stirrers (Type L-157 M/s Remi Udyog, Mumbai, India) in a constant temperature bath at around 500 RPM. The solution was then filtered off and the carbon was washed thoroughly with distilled water. This carbon was then transferred to a clean shaking bottle of wide mouth and then 200 ml of manganese solution of  $pH = 5$  were added carefully. The  $pH$  of the experimental solution was adjusted using nitric acid, sodium hydroxide and buffer solutions when required. The system was then stirred for five hours completely with the same speed at constant temperature  $25 \pm 0.5^{\circ}C$ . The initial and final concentrations of the  $Mn^{2+}$  were then determined spectrophotometrically (Type 166 Systronics India Ltd.) at a wavelength of 525 nm.

### 3. EXPERIMENTATION FOR KINETICS STUDY

To study the kinetics of  $Mn^{2+}$  ions, 1 gm of GAC and 400 ml of 0.001 M resorcinol solution were shaken for about five hours in a round bottom flask. The weight of GAC and concentration of  $Mn^{2+}$  was fixed throughout the kinetic study. The solution was removed by decanting and inverting the flask, keeping carbon particles at side. The loaded carbon particles were then shaken with 400 ml of  $Mn^{2+}$  ion solution at  $pH=5$  at around 500 RPM. The time of the addition of carbon was noted as  $t = 0$ . Thereafter aliquots of 5 ml samples of experimental solution were pipette out from the flask by momentarily interrupting the stirrer. The first four readings were noted at 15 minute time intervals, the next two readings were noted at 30 minute intervals and the final two readings were noted at a time interval of one hour. The residual concentrations of  $Mn^{2+}$  ion  $C_o$  and  $C_e$  in mg/L in the sample were estimated using mathematical equation computed from the standard curve.

### 4. RESULTS AND DISCUSSION

Five stirring systems were arranged at a time in a constant temperature bath. The equilibrium concentration of manganese on loaded GAC was determined using the following expression.

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

Where,

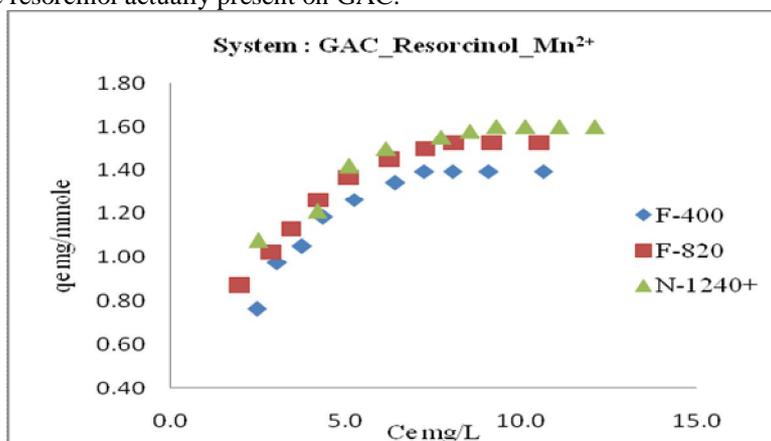
$q_e$  = Concentration of manganese on the resorcinol loaded GAC in mg/millimoles.

$C_o$  = Initial concentration of manganese in solution in mg /L,

$C_e$  = Final concentration of manganese in solution in mg/L;

$V$  = Volume of solution in liters;

$W$  = Millimoles of the resorcinol actually present on GAC.



**Figure 1: Adsorption Isotherm**

A plot of  $q_e$  versus  $C_e$  represented an adsorption isotherm of resorcinol loaded Granular Activated Carbon, (N-1240+, F-820 and F-400) is given in the figure 1. The comparative adsorption capacities (saturation values of  $q_e$ ) of  $Mn^{2+}$  ion on different grades of loaded GAC used in the present work can be assumed from figure 1. The  $q_e$  values for different GAC at the saturation level are in the order given below.

$$N-1240+ > F-820 > F-400$$

The plots of  $\log q_e$  versus  $\log C_e$  and  $1/q_e$  versus  $1/C_e$  showed linearity indicating the validity of the Freundlich equation as well as Langmuir equations in the entire range of concentrations used in this work. The Langmuir equation is useful to evaluate the surface area of the adsorbent under the present experimental conditions. Estimations of the specific surface areas of loaded GAC are based upon measurement of the capacity of the adsorbent for a selected adsorbate having a well accepted molecular cross sectional area. This is done by using  $Q^0$  which obtained from Langmuir plot and related to surface area of the adsorbent as,

$$S = Na Q^0 A$$

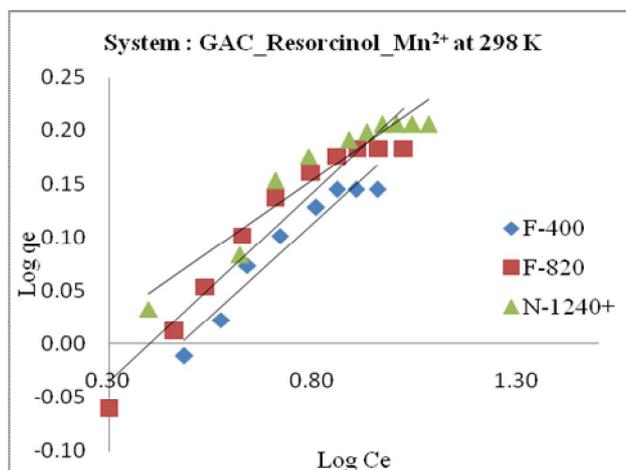
Where,

S = Surface area of the adsorbent,  $m^2/gm$

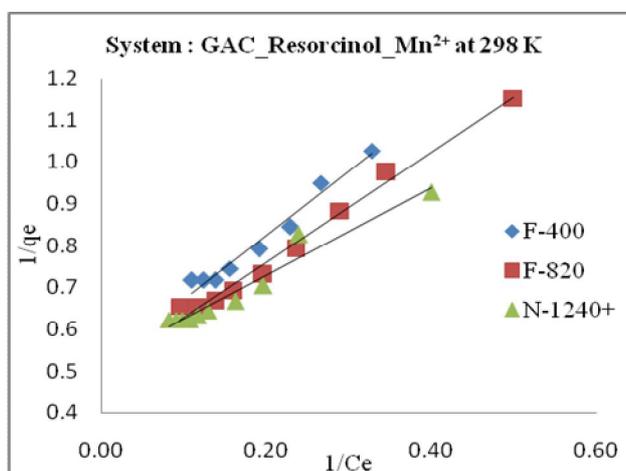
Na = Avogadro number

A = Cross sectional area of the adsorbate molecule,  $m^2$

The values of  $q_{e,max}$  and regression coefficients ( $R^2$ ) are given in Table 1.



**Figure2:** Langmuir Adsorption Isotherm



**Figure 3:** Freundlich Adsorption Isotherm

**Table 1:**  $q_{e,max}$  (mg/m.mole) and regression coefficient  $R^2$  for adsorption of Manganese ion from solution by GAC containing adsorbed ligand (Resorcinol)

Sr. No.	Adsorption System	$q_{e,max}$	Regression Coefficient ( $R^2$ )
1	F-400_Resorcinol_Mn <sup>2+</sup>	1.3947	0.9700
2	F-816_Resorcinol_Mn <sup>2+</sup>	1.5263	0.9870
3	N-1240+_Resorcinol_Mn <sup>2+</sup>	1.6053	0.9500

**Table 2:** The values of Langmuir constant, Freundlich constant, cross-sectional area of the adsorbate and surface area of resorcinol loaded GAC covered by Mn<sup>2+</sup>

Sr. No.	Systems	Langmuir Constants		Freundlich Constants		A cm <sup>2</sup>	S cm <sup>2</sup> /gm	S' cm <sup>2</sup> /gm
		Q <sup>0</sup>	b	K	1/n			
1	F-400_Resorcinol_Mn <sup>2+</sup>	1.9305	0.3383	0.6839	0.3480	5.8274 x 10 <sup>-16</sup>	3.5633 x 10 <sup>3</sup>	4.9320 x 10 <sup>3</sup>
2	F-816_Resorcinol_Mn <sup>2+</sup>	2.0080	0.3804	0.8570	0.1630	5.8274 x 10 <sup>-16</sup>	3.8944 x 10 <sup>3</sup>	5.1301 x 10 <sup>3</sup>
3	N-1240+_Resorcinol_Mn <sup>2+</sup>	2.0493	0.3879	0.9371	0.1320	5.8274 x 10 <sup>-16</sup>	4.1011 x 10 <sup>3</sup>	5.2352 x 10 <sup>3</sup>

The apparent values of surface area S' evaluated from q<sub>e</sub>max and S evaluated from q<sup>0</sup> are given in Table 2. The above Table clearly shows the fact that manganese is inaccessible to the inner pores of the GAC and it adsorbed superficially on the surface of GAC.

### 5. THE RATE OF EXCHANGE OF MANGANESE WITH GAC

From the initial concentration of manganese C<sub>0</sub> and the concentration of manganese at different time intervals C<sub>t</sub> values of  $\bar{q}$  were estimated by the procedure given in the experiment. The plots of approach to equilibrium, i.e. of both  $\bar{q}$  versus t and  $\bar{q}^*$  versus t, are given in figures 4, 5 and 6. In the adsorption process diffusion arises from a concentration gradient either in the fluid phase or on the solid phase. When diffusion involves separation of solute from the fluid phase to the sorbent phase it is called particle phase diffusion or homogeneous diffusion described by an effective diffusion coefficient D. The driving force for pore diffusion is the concentration gradient of the adsorbate in the pore space and characterized by pore diffusion coefficient D<sub>p</sub>. Alternatively, surface diffusion, which occurs after adsorption due to migration of the adsorbed molecules along the pore walls may be represented in terms of the gradient of the amount of the adsorbate on the pore walls. This is characterized by the surface diffusion coefficient D<sub>s</sub>. It is often observed that one of the two types of the above mentioned diffusional processes could be treated under certain specified conditions, which are specific to the cases. Several investigators have estimated pore diffusivities in the agitated tank, [30] while some have proposed a method where surface diffusion is the rate controlling [31]. This method has been subsequently modified subject to certain limitations and reasonable conclusions have been drawn from it.

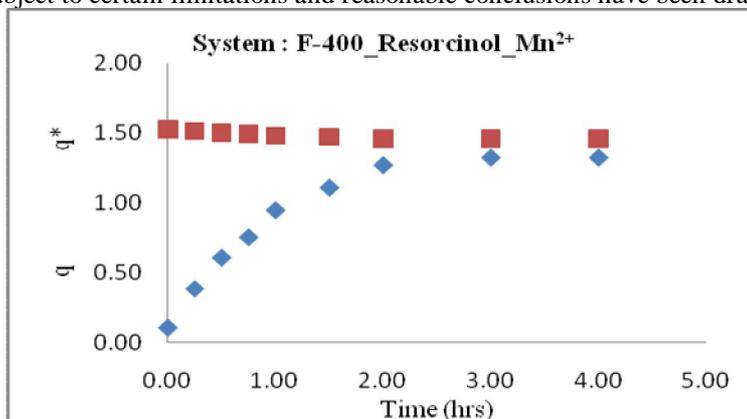


Figure 4: Approach to Equilibrium plots of  $\bar{q}$  and  $\bar{q}^*$  versus time

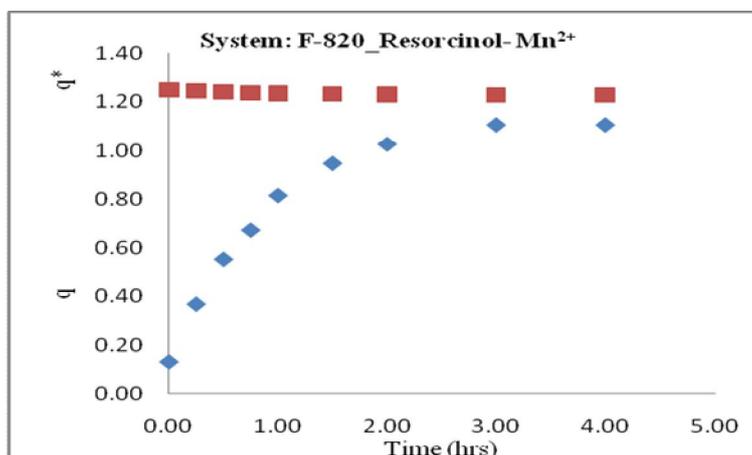
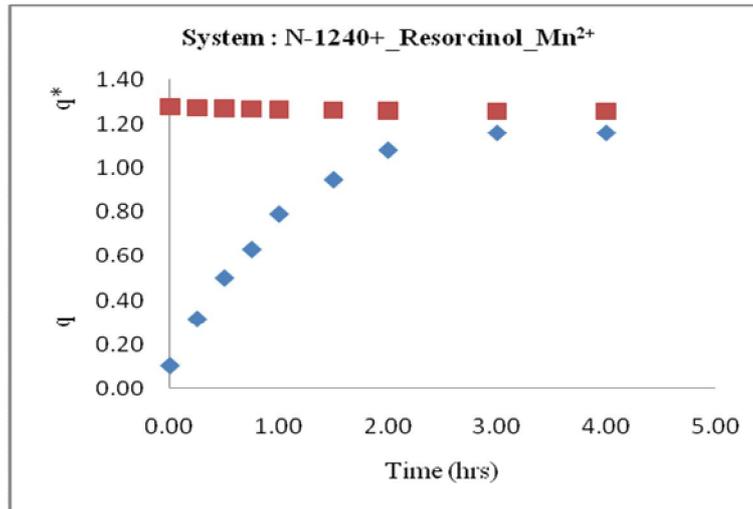


Figure 5: Approach to Equilibrium plots of  $\bar{q}$  and  $\bar{q}^*$  versus time



**Figure 6:** Approach to Equilibrium plots of  $\bar{q}$  and  $\bar{q}^*$  versus time

Glueckauf and Coates [32] first suggested the linear driving force (LDF) method in which the rate of adsorption by a spherical particle is considered to be the product of surface area, an effective mass transfer coefficient and a driving force consisting of the difference between the bulk average concentration in the spherical particle  $\bar{q}$  and the surface concentration  $\bar{q}^*$ . Glueckauf proposed the most common form of linear driving force (LDF) equation which is as follows

$$\frac{d\bar{q}}{dt} = \frac{15D}{a^2} (\bar{q}^* - \bar{q})$$

Where,

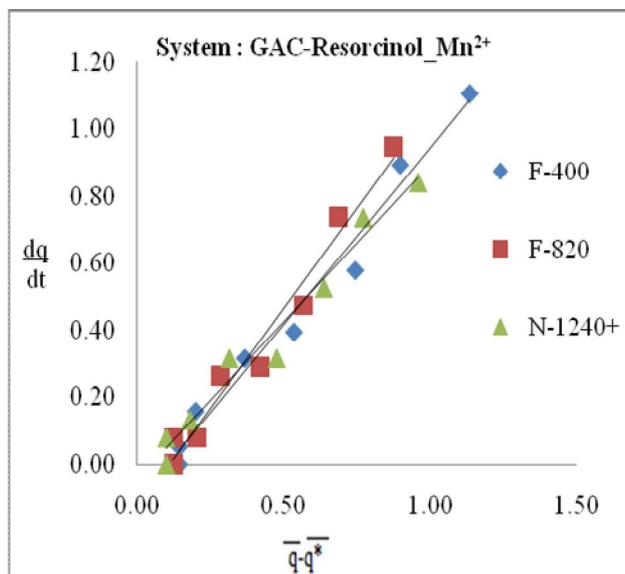
D = Diffusion coefficient in solid phase

a = Radius of the spherical particle

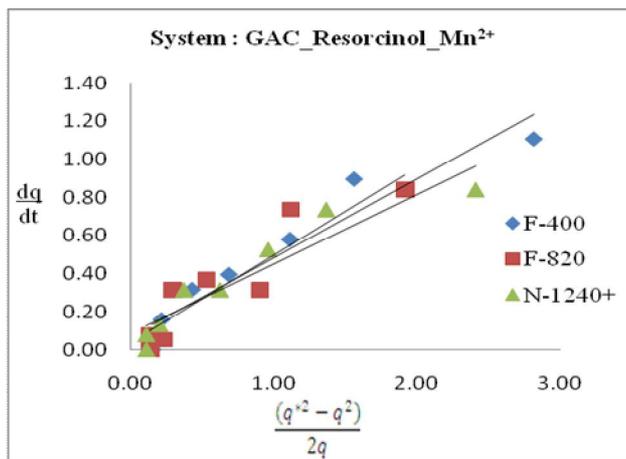
The LDF method is inadequate to distinguish between surfaces and pore diffusion. Vermuelen [33] proposed the following Quadratic Driving Force (QDF) expression to determine the diffusion coefficient

$$\frac{d\bar{q}}{dt} = \pi^2 \frac{15D}{a^2} \left( \frac{\bar{q}^* - \bar{q}}{2\bar{q}} \right)$$

This expression was compared by Glueckauf who concluded that while in most cases this LDF approximation was adequate. The above relation approximated the solution of the solid diffusion model. In both cases it was necessary to simplify assumptions before comparisons could be made. A representative of the LDF and QDF plots are given in Fig. 7 & 8. In the present work, the QDF equation has been used to obtain the values of D, the diffusion coefficient, and is given below in table no. 3.



**Figure 7.** Linear Driving Force Plot



**Figure 8.** Quadratic Driving Force

**Table 3:** The values of diffusion coefficient of resorcinol loaded GAC covered by Mn<sup>2+</sup>

Sr. No.	Systems	D Values (cm <sup>2</sup> /Sec)
1	N-1240+_Resorcinol_Mn <sup>2+</sup>	7.7188 x 10 <sup>-8</sup>
2	F-820_Resorcinol_Mn <sup>2+</sup>	7.7652 x 10 <sup>-8</sup>
3	F-400_Resorcinol_Mn <sup>2+</sup>	8.7477 x 10 <sup>-8</sup>

From these values it is seen that all the D values are in the range of that encountered for surface diffusion phenomena.

## 6. CONCLUSION

The present study investigated the feasibility of GAC used as a low cost adsorbent for the removal of manganese from aqueous solution. The sorption capacities of GAC's were evaluated using Freundlich and Langmuir adsorption models. In the present study the uptake of Manganese on to N-1240+ was found to be considerably higher than other GAC. The adsorption isotherms obtained from the present work may be helpful in designing industrial adsorption columns. The values of diffusion coefficient clearly indicate that the adsorption process of Mn<sup>2+</sup> on GAC involved surface diffusion phenomena.

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