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Influence of Surface Characteristics of Adsorbent and Adsorbate on Competitive Adsorption Equilibrium

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ABSTRACT

In the present study the adsorption behaviour of manganese from aqueous solution on to ligand loaded Granular Activated Carbon (GAC) was investigated. The study was carried out to examine the potential and effectiveness of Granular Activated Carbon to remove manganese through adsorption from aqueous solution. The experimental adsorption data showed good correlation with the Freundlich and Langmuir isotherm models. The results demonstrate that the filtrasorb 816(F-816) has a significant capacity to adsorbed of manganese (II) as compared to filtrasorb 300 (F-300) from wastewater.

Key words : Adsorption, Manganese, GAC F-300, GAC F-816, Resorcinol.

INTRODUCTION

The presence of heavy metal ions in the environment has been a matter of major concern due to their toxicity to human life. Unlike organic pollutants the majority of which are susceptible to biological degradation, heavy metal ions will not degrade into harmless end-product[1]. Even though heavy metal ions can be removed by physical-chemical methods such as chemical precipitation, membrane separation[2-3] and ion exchange but adsorption has been shown to be economical alternative for removing metals from water[4-6]. However adsorption by activated carbon had been reported as a technically and economically viable technology for heavy metal removal[7-8]. Surface properties of activated carbon have been shown to play an important role in the adsorption process[9-11]. Activated carbon is highly porous material, therefore it provides an extremely high surface area for accumulation of metal content. The equivalent surface area of one pound of activated carbon ranges from 60 to 150 acres[12]. Adsorption using activated carbon is popular in potable water treatments[13-15]. Activated carbon is effective in removing taste and odour causing compounds and many metals[16]. Several workers [17-21] studied the adsorption of metals and dyes by using granular activated carbon. Manganese occurs naturally in many surface water and ground water sources and in soils that may erode into this water in drinking water sources. In drinking water source secondary maximum contaminant level (SMCL) for manganese must not exceed 0.05 mg/L[22].

In this connection work was initiated in laboratory to scavenge manganese metal using coal based GAC containing adsorbed ligand which are capable of forming a chelate with the manganese and thus help in its recovery. For this purpose Resorcinol has been chosen in present work. Resorcinol is 1,3-Dihydroxy benzene, It is acidic and two OH groups make system sufficient polar, so it is soluble in polar solvent water.

MATERIALS AND METHODS

In the present work commercially available Granular Activated Carbon namely filtrasorb 816 (F- 816) and filtrasorb 300 (F-300) gifted by Calgon Corporation, Pittsburgh, USA were used as adsorbents. These were first subjected to the size fractionation and only the particles of size ranging between 1400 micron to 1600 micron were recovered. The GAC was then washed with boiled distilled water 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 chemical used were of AR grade. A stock solution of manganese ions was obtained by using a solution of Manganese Sulphate (E. Merck, 99 % purity). It was standardized volumetrically by EDTA using Erio Black T as an indicator. Spectrophometrically, Beer's law calibration curve was established for Mn^{2+} [23] using series of standard manganese sulphate solutions . A sample of resorcinol was recrystallised by the routine method. The experimental melting point of resorcinol (109.5°C) was compared with the literature value (110 °C)[24]. All experiments were carried out in batches of five units at a time. For determining the adsorption isotherm of manganese ion on the different grades of carbon containing adsorbed ligand such as resorcinol, 0.5 gm of the GAC were taken in clean shaking bottles and 200 ml of 0.001M. resorcinol solution was shaken for about five hours using Remi Stirrers (Type L-157 M/s Remi Udyog, Mumbai, India) in 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 and then 200 ml of manganese solution at a pH = 5 was added carefully. The system was then stirred for five hours completely with same speed maintaining the temperature at 25 ± 0.5 °C. The initial and final concentration of the manganese ion was then determined spectrophotometrically (Type 166 Systronics India Ltd.) .

RESULTS AND DISCUSSION

The mathematical interpretation of the adsorption isotherms is studied using the two popular models, namely Freundlich and Langmuir. The adsorption isotherms for different grades of granular activated carbon are shown in Fig.1 and 2. The slope of the isotherms indicates the high affinity between sorbent surface and adsorbate molecules. The amount of manganese on the ligand loaded GAC was determined using the equation

$$q_e = (C_o - C_e) \times V/W$$

where,
q_e = Concentration of manganese ion on the ligand loaded GAC in mg/millimoles of ligand
C_o = Initial concentration of manganese ion in solution in mg/L.
C_e = Final concentration of the manganese ion in solution in mg/L.
V = Volume of solution in litres
W = Millimoles of the ligand actually present on GAC.

The correlation of the experimental adsorption data with Langmuir and Freundlich model was undertaken to gain an understanding adsorption behaviour and the heterogeneity of the adsorbent surface. The mathematical expression for the Langmuir model in terms of manganese ion concentration in solution Ce(mg/L) in equilibrium with that on ligand loaded GAC q_e (mg/millimoles) is given by

$$q_e = \frac{Q^0 bCe}{1+bC_e}$$

The linearised form of Langmuir isotherm is

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

Where Q° and b are Langmuir constants.

Freundlich equation is on the other hand represented by

$$q_e = k_f .\ C_e^{1/n}$$

The equation may be linearised as

Fig 1
Adsorption Isotherm
System : F-300 -Resorcinol -Mn^{2+} at 298K

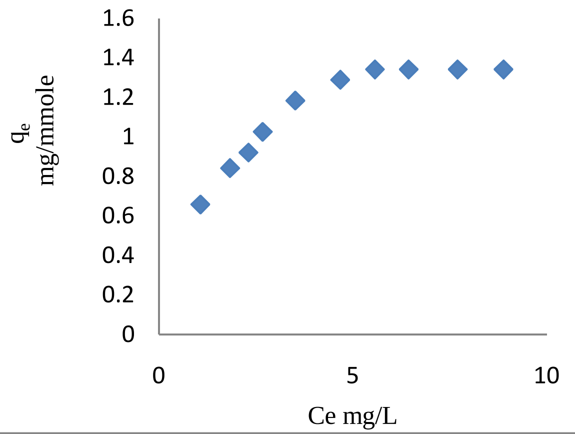


Fig 2
Adsorption Isotherm
System : F-816 -Resorcinol -Mn^{2+} at 298K

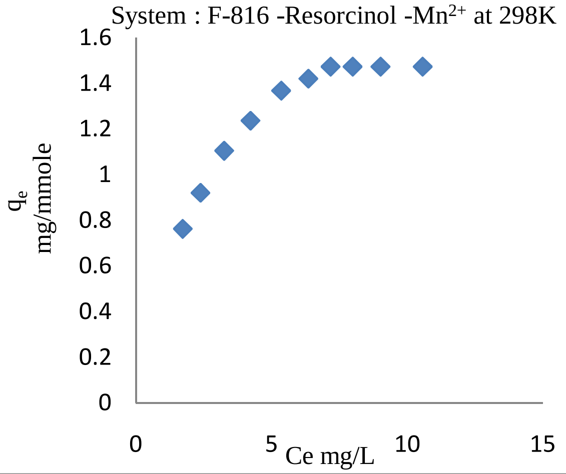


Fig 3
Langmuir Adsorption Isotherm at 298 K
System : GAC-F-300-Resorcinol - Mn^{2+}

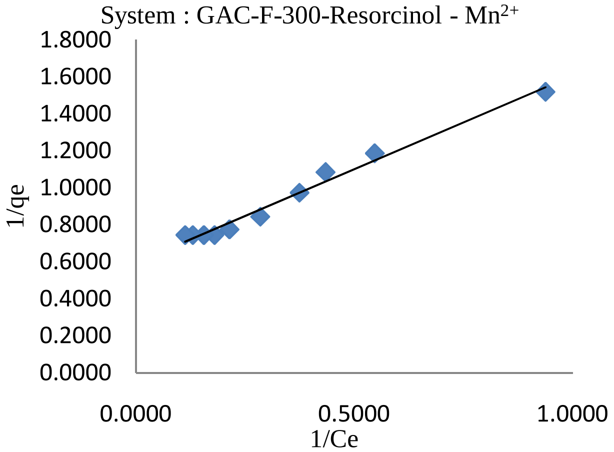


Fig 4
Langmuir Adsorption Isotherm at 298 K
System : GAC-F-816-Resorcinol - Mn^{2+}

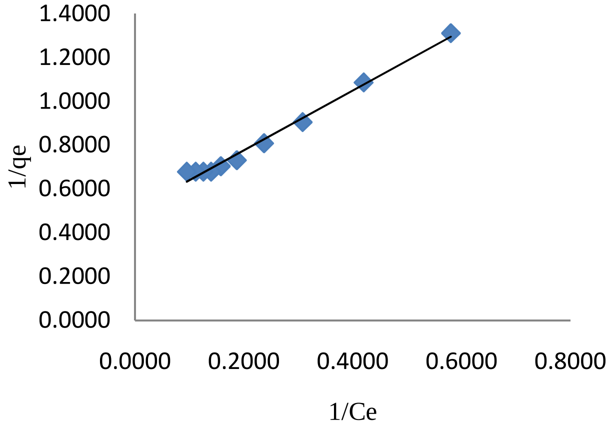


Fig 5
Freundlich Adsorption Isotherm at 298 K
System : GAC-F-300-Resorcinol - Mn^{2+}

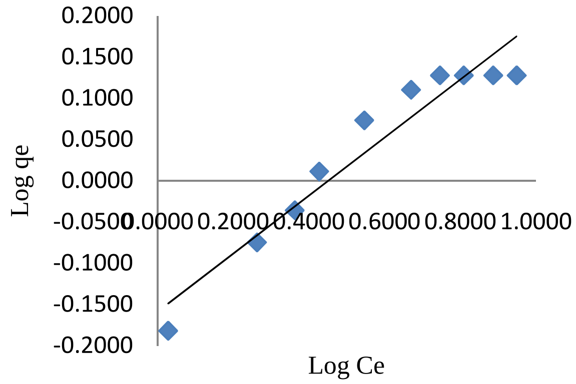
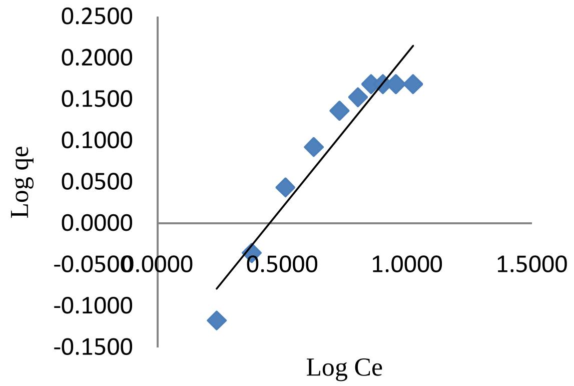


Fig 6
Freundlich Adsorption Isotherm at 298 K.
System : GAC-F-816-Resorcinol - Mn^2



$\log q_e = \log k_f + 1/n \log C_e$

Where k_f and 1/n are Freundlich constants.

Fig.3 to 6 illustrate the plot of Langmuir and Frendlich isotherms for GAC F-300 and F-816. The plots of $1/q_e$ versus $1/C_e$ were found to be linear indicating the applicability of Langmuir model. The parameters Q° and b are Langmuir constants relating to the sorption capacity and adsorption energy respectively.

Table 1: Values of q_e max (mg/m.mole) Langmuir equation and R^2 for adsorption of manganese ion from solution by GAC containing adsorbed ligand (Resorcinol)

Sr. No.	System	F-300 - Resorcinol-Mn^{2+}	F-816 - Resorcinol -Mn^{2+}
1	q_e max	1.3421	1.4736
2	Stat.Parameters R^2	0.983	0.988

The comparative adsorption capacities (saturation values of q_e) of manganese ion on different grades of GAC used in the present work can be assessed from Fig. 1 and Fig. 2.

The surface area of the carbon through such manganese adsorption can be represented as

S= Na. Q°. A

Where, S = Surface area of adsorbent, m^2/g
Na = Avogadro number
A = Cross-sectional area of the adsorbate molecule m^2.

The value of A were calculated using the expression given by Brunauer and Emmet.

$$A = 4x0.866\ [M/4\sqrt{2}\ Na\ .\ d]^{2/3}$$

Where, M = Atomic weight of manganese,
Na = Avogadro number.
d = Density of manganese[25]

The trend in the q_e values at the saturation level are in the order F-816 > F-300.

Table 2

Sr. No.	System	F-300 - Resorcinol-Mn^{2+}	F-816 - Resorcinol -Mn^{2+}
1	Qo	1.6778	1.9841
2	A	5.8274×10^{-16} cm^2	5.8274×10^{-16} cm^2
3	S	4.2874×10^3 cm^2/gm	5.0702×10^3 cm^2/gm

Further the essential characteristics of the Langmuir isotherm can be describe by separation factor R_L ; which is defined as

$$R_L = \frac{1}{1 + bC_i}$$

Where C is the initial concentration of manganese and b is the Langmuir Constant . 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

CONCLUSION

Experimental studies would be quite useful in developing an appropriate technology for removal of heavy metal ions from contaminated industrial effluents. In the present work, the ligand loaded granular activated carbon showed high adsorption capacity in the removal of manganese ion from aqueous solution. The adsorption isotherms of the manganese on different grades of carbon loaded with resorcinol clearly shows that F-816 adsorbs manganese to a greater proportion as compared to F-300. Adsorption was found to be in good agreements with Langmuir isotherm which indicates monolayer adsorption. Application of the Freundlich and Langmuir isotherm models gave good representations of the experimental data for manganese sorption by GAC .

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