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Research Article

COMPARATIVE STUDIES ON THE CAPABILITY AND BEHAVIOUR OF ADSORPTION OF Mn^{2+}ON GRANULAR ACTIVATED CARBON

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ABSTRACT

Investigation was conducted in the batch mode for studying removal of Mn^{2+} from aqueous phase by adsorption on granular activated carbon (GAC) modified by ligand such as 3-Aminophenol. The study was carried out to examine efficiency of GAC to remove Mn^{2+} ion through adsorption from aqueous solution at constant temperature of 25$\pm$0.5 °C. The adsorption isotherm was determined and tested for adherence to the Freundlich and Langmuir models. The results demonstrate that the filtrasorb 820 (F-820) has a significant capacity to adsorbed of Mn^{2+} as compared to other grades of carbon.

Keywords: Adsorption, Manganese, GAC F-400, GAC F-816, GAC F-820.

INTRODUCTION

The metal pollution in water resources due to the indiscriminate disposal of toxic metals has been causing worldwide concern for the last decades. The metals like Chromium, Copper, Lead, Mercury, Iron and Manganese etc are significantly toxic to human being and ecological environment[1,2]. Manganese is one of such heavy metal which occurs naturally in many surface water, ground water sources and in soil that may erode into this water in drinking water sources. Manganese in surface water is a micro nutrient but elevated concentrations are toxic to aquatic life and humans and affectsdrinking water quality[3]. Its removal from aqueous solution is most difficult problem in many countries[4-7].

Even though heavy metal ions can be removed by physical, chemical methods such as chemical precipitation, membrane separation[8,9] and ion exchange, but adsorption has been shown to be economical alternative for removing metals from water[10-12]. A number of adsorbent materials have been studied for their ability to remove heavy metals and they have been sourced from natural materials and biological wastes of industrial processes[13]. However, adsorption by activated carbon had been reported as a viable technique used for heavy metal removal[14-15].

Surface properties of activated carbon have been shown to play an important role in the adsorption process[16-18]. 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[19]. Adsorption using activated carbon is popular in potable water treatments[20-22].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[23-27].

3-Aminophenol is an aromatic amine and aromatic alcohol with molecular formula

$C_6H_4(NH_2)(OH)$ is selected as a ligand to modify the surface of GAC.

MATERIALS AND METHODS

In the present studythree Granular Activated Carbons namely filtrasorb 400 (F- 400), filtrasorb 816 (F- 816) and filtrasorb200 (F-200) gifted by CalgonCarbon Corporation, Pittsburgh, USA were used as adsorbents. These GACs were first subjected to the size fractionation and only the particles of size ranging between 1400 micron to 1600 micron were recovered. The GAC particles of desired size were then washed several times with boiled distilled water until clear water obtained 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 prepared by dissolvingrequired quantity of Manganese Sulphate (E. Merck). The stock solution was further diluted with distilled water to desired concentration for obtaining the series of solutions. Spectrophotometrically, Beer's law calibration curve was established for Mn^{2+}, using series ofstandard manganese sulphate solutions[28]. A sample of 3-Aminophenol was recrystallised by the routine method. The experimental melting point of 3-Aminophenol (120.5°C) was compared with the literature value (121 °C)[29]. All experiments 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. 3-Aminophenol solution were taken in clean reagent bottle and stirred for about five hours using Remi Stirrers (Type L-157 M/s RemiUdyog, 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 of pH = 5 was added carefully. The pH of the adsorptive solution was adjusted using nitric acid, sodium hydroxide and buffer solutions when required. The system was then stirred for five hours completely with same speed at constant temperature 25 ± 0.5 °C. The initial and final concentration of the Mn^{2+}were then determined spectrophotometrically (Type 166 Systronics India Ltd.) at a wavelength of 525 nm

RESULTS AND DISCUSSION

The mathematical interpretation of the adsorption isotherms for different grades of GAC was studied using the two popular models, namely Freundlich and Langmuir. These isotherms for different grades of granular activated carbon are shown in Fig.1 and 2. The amount of manganese on the GAC,chemically modified by ligand (3-Aminophenol) was determined using the equation

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

where,

q_e = Concentration of Mn^{2+}on the ligand loaded GAC in mg/millimoles of ligand

C_o = Initial concentration of Mn^{2+}in solution in mg/L.

C_e= Final concentration of the Mn^{2+}in solution in mg/L.

V = Volume of solution in litres

W = Millimoles of the ligand actually present on GAC.

The mathematical expression for the Langmuir model in terms of Mn^{2+}concentration in solution C_e(mg/L) in equilibrium with that on ligand loaded GAC q_e (mg/millimoles) is given by

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

It can be written in its liberalized form as follows

$$\frac{1}{q_e} = \frac{1}{Q^{\circ} b} \times \frac{1}{C_e} + \frac{1}{Q_0}$$

Where,

Q° the Langmuir constant related to the adsorption capacity and b is the other Langmuir parameter related to the energy of adsorption.

Freundlichmodel can be take the following form.

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

The equation may be linearised as follows

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

Where,

kf and 1/n are Freundlich constants.

Fig.3 to 6 illustrate the plot of Langmuir and Freundlich isotherms for GAC F-400, GAC F-816 and GAC F-820 in combination with ligand. The plots of 1/qeversus 1/Ce were found to be linear indicating the applicability of Langmuir model. The parameters Q° and b areLangmuir constants relating to the sorption capacity and adsorption energy respectively.

All the values of q_{emax} (mg/m.mole) Langmuir equation and regression coefficient R^2 for adsorption of manganese ion fromsolution by

GAC containing adsorbed ligand (3-Aminophenol) are reported in Table 1.

The comparative adsorption capacities (saturation values of q_e) of Mn^{2+} on different grades of GAC usedin the present work can be assessed from Fig. 1 and Fig. 2.

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

$$S= Na. Q°. A$$

Where,

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

Na = Avogadro number

A = Cross-sectional area of the adsorbate molecule cm^2.

The value of A was 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[30]

The apparent values of surface area S' evaluated from $q_e$max are found to be comparablewith S(obtained from Q^0) to some extent. .

The trend in the q_e values at the saturation level are in the order

F-820-3-Amino phenol-Mn^{2+}> F-816-3-Amino phenol-Mn^{2+}> F-400-3-Amino phenol-Mn^{2+}.

The values of Langmuir constant, Freundlich constant, Cross-sectional area of the adsorbate andSurface area of adsorbent for adsorption of manganese ion from solution by GAC containing adsorbed ligand (3-Aminophenol) are reported in Table 2.

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

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

Where,

C=The initial concentration of manganese

b = Langmuir Constant.

The values of R_L for all isotherm of Mn^{2+} was found to be in between 0 to 1 indicate favorable adsorption[31].

The value of separation factorR_L, indicates the nature of the adsorption process as in Table 3

CONCLUSION

The removal of Mn2+ from aqueous solution using different grades of carbons was found to be cheap and effective process. The adsorption isotherms of the manganese on different grades of carbonsin combination with 3-Aminophenol clearly shows that F-820 adsorbs manganese to a greater extent as compared to other grades of carbon namely F-816, F-400. Application of the Freundlich and Langmuir isotherm models gave good representations of the experimental data for manganese sorption by GAC.

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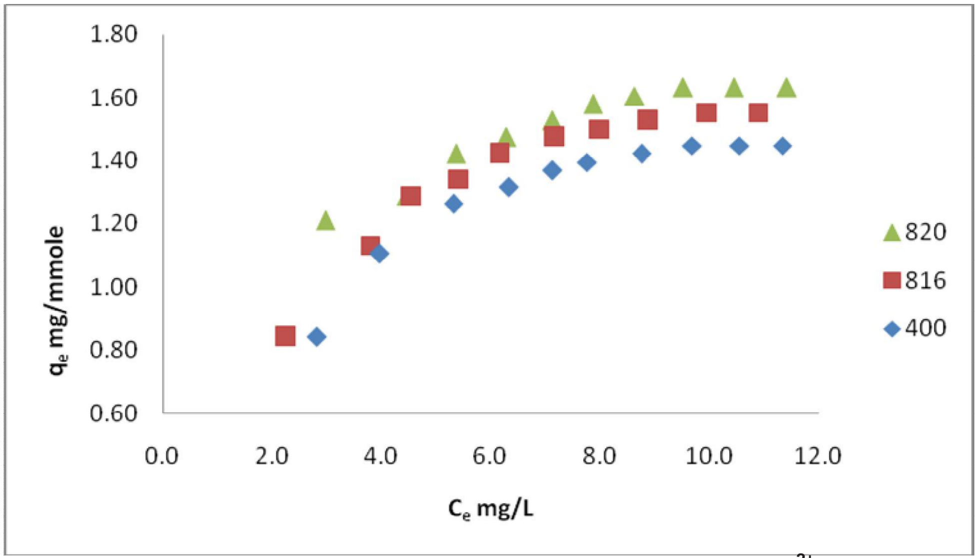

Fig. 1: Adsorption Isotherm System: 3-Aminophenol-Mn^{2+}- GAC

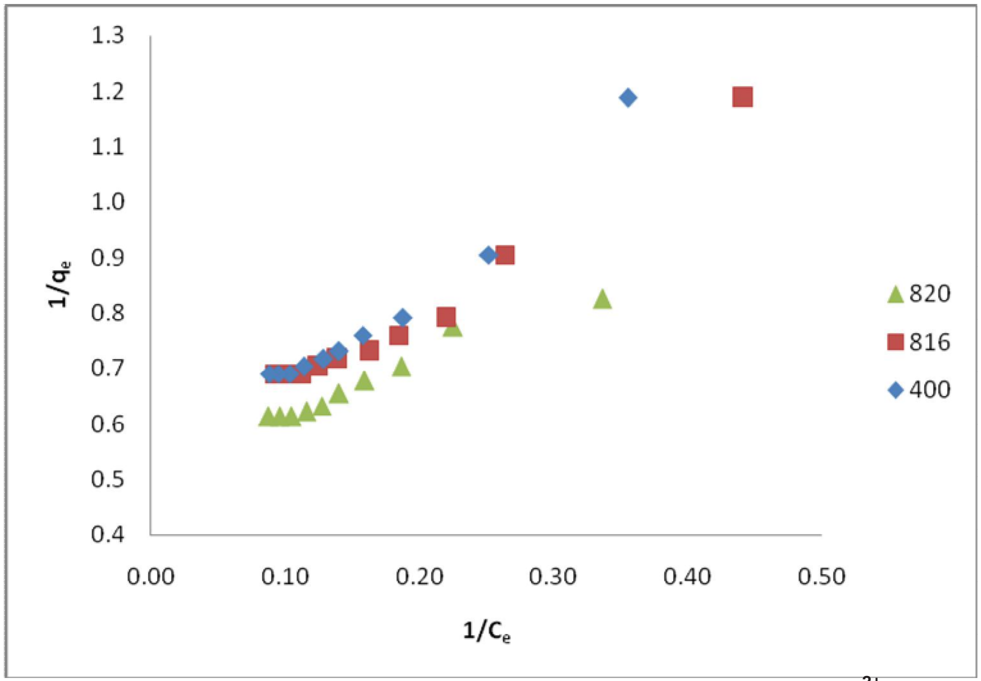

Fig. 2: Langmuir Adsorption Isotherm System: 3-Aminophenol-Mn^{2+}- GAC

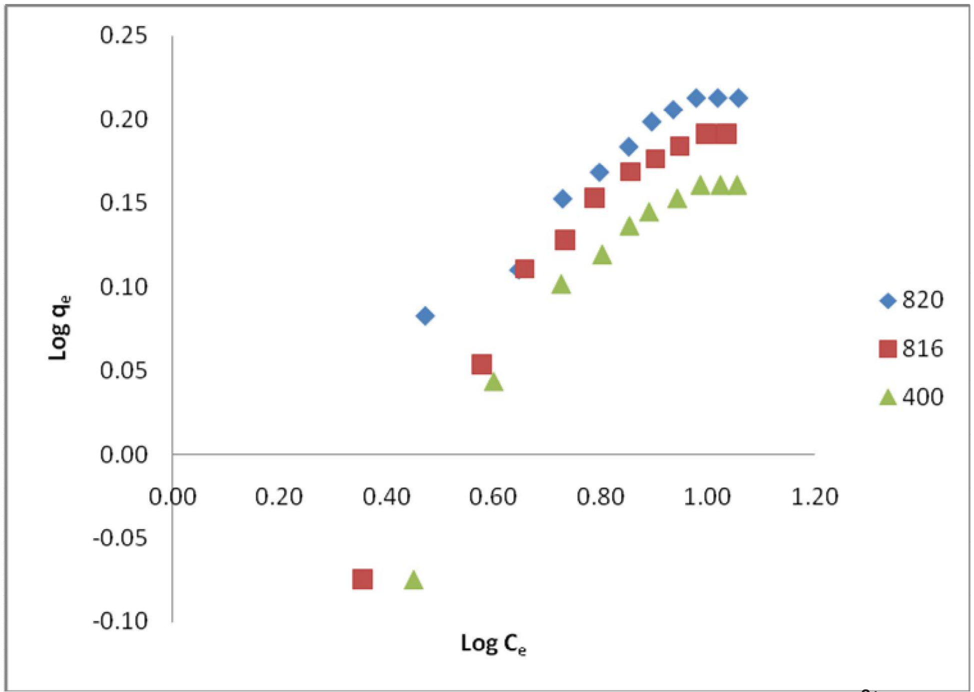

Fig. 3: Freudlich Adsorption Isotherm System: 3-Aminophenol-Mn^{2+}-GAC

Table 1: q_{emax} (mg/m.mole) and regression coefficient R^2 for adsorption of manganese ion from solution by GAC containing adsorbed ligand (3-Aminophenol)

Sr. No.	Adsorption System	$q_{e\ max}$	Rgression Coefficient (R^2)
1	F-400-3Aminophenol-Mn^{2+}	1.4473	0.9810
2	F-816-3Aminophenol-Mn^{2+}	1.5526	0.9650
3	F-820-3Aminophenol-Mn^{2+}	1.6316	0.9780

Table 2: The values of Langmuir constant, Freundlich constant, Cross-sectional area of the adsorbate and Surface area of adsorbent for adsorption of Mn^{2+} from solution by GAC containing adsorbed ligand (3-Amino phenol)

S. No.	System	Langmuir constants		Freundlich constants		A cm^2	S cm^2/gm	S' cm^2/gm
		Qo	b	k	1/n			
1	F-400-3-Aminophenol-Mn^{2+}	1.8315	0.3970	0.9397	0.186	5.8274×10^{-16}	4.6791×10^3	3.6977×10^3
2	F-816-3-Aminophenol-Mn^{2+}	2.0408	0.5157	0.9440	0.172	5.8274×10^{-16}	5.2138×10^3	3.9665×10^3
3	F-820-3-Aminophenol-Mn^{2+}	2.0876	0.3783	0.9484	0.147	5.8274×10^{-16}	5.3336×10^3	4.1684×10^3

Table 3: RL values and Nature of adsorption process

R_L	Value Nature of adsorption process
$R_L>1$	Unfavorable
RL= 1	Linear
$0<R_L<1$	Favorable
$R_L = 0$	Irreversible

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