EQUILIBRIUM STUDIES IN ADSORPTION OF HEAVY METALS USING MODIFIED GRANULAR ACTIVATED CARBON

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ABSTRACT

In the present research, batch experiments were carried out to study the adsorption capacity of manganese onto granular activated carbon. Activated carbons F-100 and F-300 were modified by using 3-Aminobenzoic Acid as an organic ligand at constant temperature $25 \pm 0.5^\circ\text{C}$. For determination of adsorption isotherms both the selected granular activated carbons were first loaded with 3-Aminobenzoic acid and then agitated at about 500 rpm. A microporous structure of selected adsorbent was found to be more effective as it provides a large surface area to approaching metal ions. The adsorption data fitted well with the Langmuir model as compared to the Freundlich model. From the experimental observation, it can be concluded that granular activated carbon F- 300 showed more ability to adsorbed Mn^{2+} ions from an aqueous solution than F-100.

Keywords: GAC, Filtrasorb, F-100, F-300 Manganese ion, Heavy metals, Isotherm, 3-Aminobenzoic acid

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INTRODUCTION

Major industries of Indian economic development such as chemical, paper pulp, petroleum refineries, tanneries and textile discharged excessive amounts of heavy metals into water bodies which adversely affect human beings and the environment. Non-degradable heavy metals cause multiple diseases due to their magnification through the food chain. Therefore, the removal of heavy metals from wastewater is of utmost priority to safeguard the health and the environment. Neurological disorder similar to Parkinson's disease is mainly caused due to the intake of manganese metal.¹⁻³ The World Health Organization suggested a permissible value of 0.05 mg/L for manganese in drinking water.⁴ A substantial part of the groundwater used for potable use shows contamination significantly exceeding the maximum permissible level. The presence of high concentrations of manganese in water causes hazardous physiological problems. A wide range of processes have been recommended by researchers for the removal of heavy metals from wastewaters include chemical precipitation⁵⁻⁶, coagulation and flocculation⁷⁻¹⁰, ion exchange¹¹, adsorption, and membrane processes.¹² However in most of the methods there occurs continuous input of chemicals and requires high capital to install the project.¹³ Therefore, an efficient and cost-effective method is needed particularly for chemical industries. Adsorption is a very effective and economical method. It produces relatively little sludge, and therefore, is used for the removal from wastewaters.¹⁴⁻¹⁷ Activated carbon has the strongest physical adsorption forces or the highest volume of adsorbing porosity of any material known to mankind.

Activated carbon is a granular, solid, black powdered and microcrystalline or a pelletized substance. It is a non-graphitic form of carbon with high porosity and a large surface area. This property is known for its high capacity to bind heavy metals by adsorption. Many researchers used readily available activated carbon as a low-cost adsorbent for scavenging heavy metals from aqueous solutions.¹⁸⁻²⁴ To investigate the adsorption capacity of Manganese onto the granular activated carbon batch experiment was conducted. Two empirical models namely, Freundlich and Langmuir adsorption isotherms were used in this study.

EXPERIMENTAL

Material

Analytical grade chemicals were used for preparing all required solutions. In all experimental work, for preparation of the synthetic solution, distilled demineralized water was used. A Granular Activated Carbon namely F- 100 (filtrisorb100) and F-300 (filtrisorb 300) gifted by Calgon Carbon Corporation, Pittsburgh, USA were used as adsorbents for adsorption of heavy metals. The selected grade of carbon was sieved by using a sieve shaker. The particle size ranging between 1400 μ to 1600 μ were collected in a Petri dish. To remove the adhered impurities, these particles were washed several times with hot distilled water. All the particles were collected in a clean Petri dish and dried in an oven at a temperature of 100-110°C for one hour. After cooling, it was then stored in CaCl₂ desiccator until use.

Method

Ten solutions of specific concentrations were prepared in 250 ml volumetric flask by using a stock solution of Manganese sulphate (E.Merck). A calibration curve of Beer's law was established for Mn²⁺ by measuring the absorbance of different solutions at wavelength 520 nm using Chemito-spectroscan UV2700 Double beam UV-VIS Spectrophotometer. All batch experiments were carried out in a set of five units at a time. Ligand embedded activated carbon was developed by using 0.5g carbon and 200 ml of 0.001 M 3-Aminobenzoic Acid solution. This mixture was then stirred in a broad mouth glass bottle for five hours at around 500 rpm using a Remi stirrer (Type L-157 M/s Remi Udyog Mumbai). The shaking was carried at a constant temperature of 25 $\pm$ 0.5°C throughout the experiment. The stirred solution was then filtered off and the carbon particles loaded with ligand were washed thoroughly with distilled water. These particles were then kept in a clean shaking bottle. In the same shaking bottle, 200 ml of Manganese solution of definite concentration at a pH = 5 was added carefully. The system was again stirred for five hours continuously with the same temperature at the same speed. The initial and final concentration of the Manganese ion was then determined spectrophotometrically using Beer's law equation established from the graph plotted between absorbance and concentration of Manganese solution.

RESULTS AND DISCUSSION

In the present study two models, namely, Freundlich and Langmuir were used for mathematical interpretation of the adsorption isotherms. The adsorption isotherms for F-100 and F-300 grades of granular activated carbon are shown in Fig.-1 and Fig.-2. The slope of the isotherms indicates the high affinity between the adsorbent surface and adsorbate molecules.

The adsorption amount of Manganese on the ligand loaded GAC at the equilibrium step was determined using the equation:

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

Where,

q_e = Concentration of Mn²⁺ on the ligand loaded GAC in mg/mmol of ligand,

C_0 = Initial concentration of Mn²⁺ in solution in mg/L,

C_e = Final concentration of Mn²⁺ in solution in mg/L,

V = Volume of the solution in Lit,

W = Weight of the carbon taken.

The adsorption isotherms of ligand loaded GAC obtained by plotting q_e and C_e are shown in Fig.-1 and Fig.-2. The adsorption behavior of solutes on specific adsorbents is described by adsorption isotherms. These are superbly describing equilibrium between the concentration of the dissolved solute and the amount of solute that accumulated on the sorbent. In the present study, adsorption data for adsorbate concentrations are used to describe the two popular models namely Freundlich and Langmuir. The sorption isotherm is the mathematical model, which gives an interpretation for the adsorbate species behavior between solid and liquid phases.²⁵

Langmuir Isotherm

The model assumed that there is only a monolayer of an adsorbate on the surface of the adsorbent. It represents the distribution of equilibrium for the metal ions between the solid and liquid phases. No

additional layer formation occurs once the monolayer is formed on the surface of the adsorbent.²⁶ This is valid for monolayer adsorption onto a surface of adsorbent where a finite number of identical sites is available with regular energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.²⁷ This indicates that the accumulation of metal ions takes place on a homogeneous surface by monolayer sorption without any interaction with the adsorbed ionic species.²⁸⁻²⁹

The linearized form of the Langmuir equation is represented as-

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

Where,

Q^0 = Maximum amount of adsorbate adsorbed per unit weight of the adsorbent forming a complex monolayer on the surface of the adsorbent,

C_e = Equilibrium concentration of adsorbate solution in mg/L,

q_e = Amount of adsorbate adsorbed on adsorbent in mg/mmol,

b = Langmuir constant related to the affinity of the binding site.

The slope and intercept give the values of b and q_e max called Langmuir constants obtained from the graph plotted between $1/q_e$ versus $1/C_e$, are shown in Fig.-3 and Fig.- 4.

Freundlich Isotherm

It is based on the principle that the sorption of metal ions occurs on a heterogeneous surface by monolayer adsorption. The theory states that the ratio of the amount of solute adsorbed onto a known mass of sorbent to the solute concentration in the solution at different concentrations is not constant. An equation is derived to model the multilayer sorption and the sorption on heterogeneous surfaces. The Freundlich model is described by the following equation.³⁰

The linearised form can be written as-

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

Where,

q_e = Amount of Manganese ion on ligand adsorbed GAC,

C_e = Concentration of Manganese ion at equilibrium in mg/L,

n = Freundlich constant represents the heterogeneity of the adsorption surface,

K_f = Constant indicates the relative adsorption capacity of the carbon.

The plots of $\log q_e$ against $\log C_e$ was fairly showed the validity of Freundlich equations over a range of concentration are shown in Fig.-5 and Fig.-6. The values of Freundlich constants n and K_f were evaluated from the slope and intercept of the plot $\log q_e$ and $\log C_e$. Q^0 and b called Langmuir constants and n and K_f called Freundlich constant are reported in Table-1.

The experimental data were tested for both the model. From the results of R^2 value, it was observed that Langmuir adsorption isotherm provides a better fit for the experimental data of the selected metal than the Freundlich model. The apparent surface area of granular activated carbon S and S' were calculated from the values of q_e max and Q^0 . The value of q_e max was obtained from the plot of C_e versus q_e and Q^0 was obtained from the Langmuir plot of $1/q_e$ versus $1/C_e$, which is used to evaluate the surface area. The values of q_e max, surface area S and S' for F-100 and F-300 are reported in Table 2. The surface area is calculated by using the following equation,

$$S = \frac{q_{e \max}}{\text{Atomic weight of Mn}} N_a \times A$$

Where,

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

N_a = Avogadro number,

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

Fig.-1: Adsorption Isotherm System:
F-100 3-Aminobenzoic acid Mn^{2+}

Fig.-2: Adsorption Isotherm System:
F-300 3-Aminobenzoic acid Mn^{2+}

Fig.-3: Langmuir Adsorption Isotherm System:
F-100 3-Aminobenzoic acid Mn^{2+}

Fig.-4: Langmuir Adsorption Isotherm System:
F-300 3-Aminobenzoic acid Mn^{2+}

Fig.-5: Freundlich Adsorption Isotherm System:
F-100_3-Aminobenzoic acid_ Mn^{2+}

Fig.-6: Freundlich Adsorption Isotherm System:
F-300_3-Aminobenzoic acid_ Mn^{2+}

Table -1: Constants of Langmuir and Freundlich Adsorption Isotherm

S. No.	System	Langmuir Constants		R^2	Freundlich constants		R^2
		Q^0	B		$1/n$	K_f	
1	F-100_3Aminobenzoic acid Mn^{2+}	0.7238	0.1739	0.909	0.3930	0.1849	0.865
2	F-300_3Aminobenzoic acid Mn^{2+}	0.7743	0.1860	0.960	0.3740	0.2108	0.920

Table -2: Values of Surface Area for Different Adsorption Systems

S.No.	System	q_{emax}	$S \text{ cm}^2/\text{g}$	$S' \text{ cm}^2/\text{g}$
1	F-100 3 Aminobenzoic acid Mn^{2+}	0.4750	1.2236×10^3	1.8761×10^3
2	F-300 3-Aminobenzoic acid Mn^{2+}	0.5250	1.3524×10^3	1.9945×10^3

CONCLUSION

A novel ligand embedded activated carbon was developed for enhancing its adsorptive capacity. The result suggested that the modified adsorbent is composed of a variety of co-coordinating centers. The adsorbents were found to be stable in water and no ligand leakage was noticed after soaking the adsorbent for five hours. The adsorption capacity of GAC-F-300 is found to be appreciably high as compared to GAC-F- 100. This can probably be due to the high surface area of GAC-F-300 and more coordinating sites available for approaching metal ion during adsorption. The adsorption data were fitted in both Langmuir and Freundlich isotherm but the Langmuir model was best fitted for the adsorption of Manganese as confirmed from its regression value. These experimental studies on coal-based adsorbents would be quite useful in developing appropriate technology for the removal of heavy metal ions from contaminated industrial effluent. It could be concluded that granular activated carbon modified with the organic ligand is a potential and active adsorbent for the removal of Manganese ions from its aqueous solution and industrial wastewater remediation.

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