

Adsorption Study of Copper(II) on F100 Granular Activated Carbon by Adsorption Technology

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ABSTRACT

The main purpose of this work was to exploit low cost and efficient sorbents for the removal of copper from aqueous solution using F-100 Granular Activated carbon. It was observed from the experimental results that almost 90-100% copper can be removed from the aqueous solution. Adsorption kinetics and equilibrium have been investigated as a function of initial copper ion concentration, contact time, concentrations and adsorbent dosage. The commercially activated carbon was found to be cost effective and has good efficiency to remove copper ions from aqueous solution.

Keywords : Activated carbon, Adsorption, Copper, Aqueous solution

Introduction

The presence of heavy metals in the environment is a major concern due to their toxicity for many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products. Therefore, the elimination of heavy metals from water and waste water is important to protect public health. Although some trace metals are considered as essential plant nutrients. Most heavy metals are of considerable health and environmental concern because of their toxicity and bioaccumulative behavior²⁻⁴. Pb²⁺, Cu²⁺, Fe³⁺ and Cr³⁺ are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders². They are also common ground water contaminants at industrial and military installation. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phyto extraction, ultrafiltration, reverse osmosis and electro dialysis⁵⁻⁸. The use of alternative low cost materials as sorbents for the removal of heavy metals has been emphasized recently. Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals at trace quantities⁹. The present study was undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated F-100 carbon for the removal of copper(II) ions in aqueous solution. The effects of parameters such as initial copper ion concentration, adsorbent dosages, contact time. The batch experiments were done for studying the effectiveness of adsorbent dosage, contact time, initial concentration, for the maximum removal of copper from aqueous solutions.

The Langmuir and Freundlich adsorption isotherms were used to verify the adsorption.

Materials and Methods:

Power requirement : All power needed for running electric appliances was obtained from an Automatic Servo stabilizer, 5 KVA capacity (M/s Dandekar Electricals Pvt. Ltd., Nagpur).

Distilled water : The present work involved estimation of metal ions in solution and hence good quality of distilled water was necessary for preparing experimental solutions. The distilled water obtained from

laboratory distills water still (M/s. Kumar, Industries Mumbai, Capacity 1.5 lit/hour). Distilled water thus obtained was preferably prepared a fresh before use, as and when needed, and stored in a Borosil 5 liter flat bottom flask provided with a glass stopper.

Glasswares:All glasswares in laboratory were standard glass wares obtained from M/s Borosil, Bombay. Before use these glass wares were thoroughly washed with chromic acid & several times with distilled water & dried in oven.

Electric Oven:In this laboratory NEOLAB electric oven was used which had an arrangement to regulate the temperature to the required value.

Mechanical Shaker :A mechanical shaker (Remi Model No. RS-24, Remi Instrument Ltd., Mumbai) was used for agitation of GAC with solution for some adsorption experiments. The shaker was especially useful for adsorbing the metals on Granular Activated Raw Carbon and Granular Activated Oxidized Carbon. Usually the experimental samples could be shaken for around 12 hours, but for certain system it was necessary to shake it for longer periods. For this purpose an electronic timer was fabricated in this laboratory with the help of electrical engineering section of this Institute. This timer helped in switching on the shaker for approximately 3 minutes while switching it off for same period during the next 3 minutes.

pH Meter: The digital pH meter used in this laboratory was an LI-120 model (M/s ELICO, Pvt. Ltd. Hyderabad , India) and standardized using potassium hydrogen phthalate buffer of pH 4.01 at 25° C.

Spectrophotometer:All Spectrophotometer measurements were done on a Systronics Digital Spectrophotometer Model 166, India Ltd that was readily available in this laboratory using 1 cm matched cuvettes.

ThermostatBath: A thermostat arrangement, which was an essential requirement for agitating the loaded carbon with metal ion solution and for all subsequent kinetic runs was fabricated in the laboratory using a 50 liter plastic through which employed distilled water and had provision for heating and cooling of the bath liquid. With the help of a contact thermometer the heater & the cooling pump were operated through an electronic relay separately. By this help, all systems run at a uniform temperature of $28^{\circ} \pm 0.1^{\circ}\text{C}$. Since the temperature in the course of experimentation was usually above the ambient temperature of the laboratory for most parts of year, it had to be cooled, for this purpose an old refrigerating unit provided with a heavy-duty compressor was employed. The cooling coils of the unit were dipped in a bucket of water. Cold water produced by this unit was circulated with the help of circulating pump through the thermostat bath liquid and with such a unit it was possible to run the thermostat continuously at the temperature of $28^{\circ} \pm 0.1^{\circ}\text{C}$ during the entire work. Once all these facilities were readily available it was possible to plan adsorption studies as also to carry out rate of adsorption in the present work.

Apparatus

All absorbance measurements are taken by Digital Spectrophotometer (Type-166, Systronics India Ltd.) with matched cells of 1 cm optical path length.

Reagents and Chemicals

Variety of carbon of Calgon Corporation Filtrasorb used namely F-100 Pittsburg (USA). All the reagents and chemicals used are of A.R. Grade. Cupric Sulphate (E. Merck India Ltd.) was used for the preparation of standard Copper solution and it was diluted proportionately to prepare the experimental solution. Nitroso-R-Salt, sodium acetate solution used in the experiment were of Analytical Grade HNO₃ from E. Merck India Ltd. was also used for oxidizing the carbon surface.

Surface area

Estimation of the specific surface area of granular activated carbon are based upon measurement of the capacity of the adsorbent expressed in mol/gm of GAC and related to the surface area using Langmuir equation for monomolecular adsorption. The relation relates the surface area to the monolayer capacity factor by the relation:

$$S = N_a \cdot Q^{\circ} \cdot A$$

Where, S = Surface area of the adsorbent in m²/g; N_a = Avagadro's number;

Q^o = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface in mg/g; A = Cross sectional area of the adsorbate molecule in m².

Since the values of Q^o can be obtained from Langmuir plots of 1/q_e versus 1/C_e, the value of S for any particular GAC sample can be calculated. Here, q_e is the concentration of metal ion on GAC in mg/g of Carbon and C_e is equilibrium concentration of adsorbate in solution in mg/L. The occupied surface area of adsorbent by Cobalt ion due is calculated from the following expression

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

Where, M = Atomic weight of Cobalt I, N_a = The Avagadro number, d = the density of Cobalt Using M = 58.70, N_a = 6.023 x 10²³ and d = 9.0

Modification of Granular Activated Carbon

In the present work an effort has been made to modify the carbon surface by using oxidizing agents called as chemical modification of the surface. This acid treatment oxidizes the porous carbon surface, enhanced the acidic property, removes the mineral elements and improved the hydrophilic of surface¹⁰.

ADSORPTION ISOTHERM OF COPPER METAL ION ON RAW GAC.

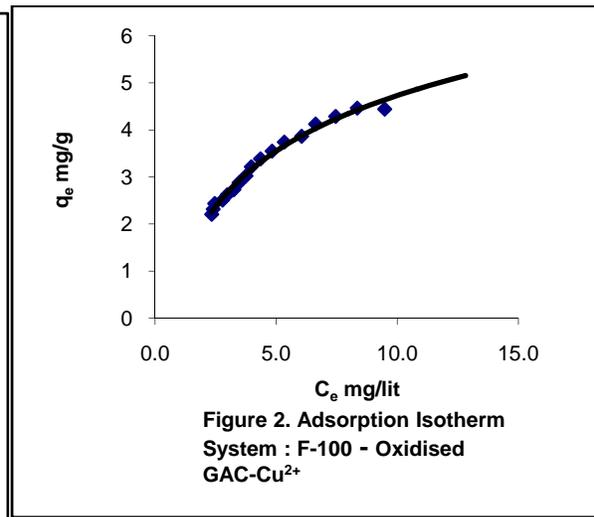
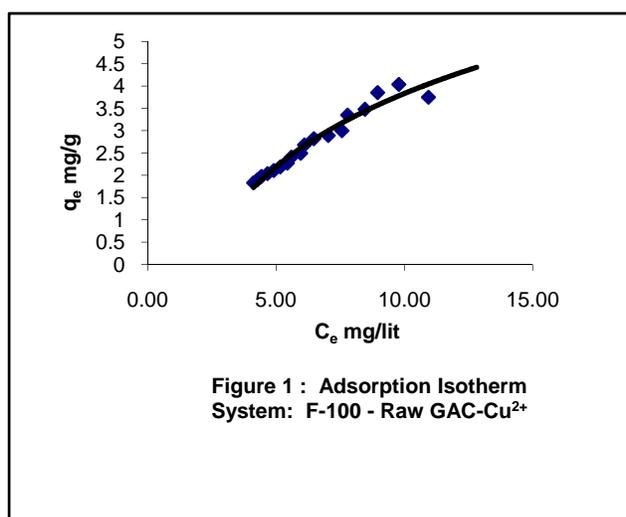
The adsorption isotherms of metal ions like Cr, Ni, Co and Cu on various grades of raw GAC and oxidized GAC i.e. F-400, F-300, F-200, and F-100 as mentioned in previous chapter. These results are summarized in **Tables 1 & 2 and Figure 1** These Figures at equilibrium show a plot of solid phase concentration of metal ions (mg/gm) versus the equilibrium concentration of metal ions in solution (mg/lit). The equilibrium was attained in 6 hours as observed by test experiments. This was verified by conducting the experiments for prolonged periods of time, until no detectable changes in equilibrium concentration values C_e could be observed. An equilibrium between the adsorbate in solution and the adsorbate on the carbon, there is a definite distribution of the adsorbate between the solution and the solid phase which is also a measure of the position of the equilibrium in the adsorption process. A relation who governs these two aspects is referred to, as an Adsorption Isotherm. The relation between these two quantities under isothermal condition is called as an adsorption isotherm. i.e. plot of q_e versus C_e. q_e is calculated by using the expression.

Table 1 Adsorption Isotherm System: F-100 - Raw GAC-Cu²⁺

Sr. No.	Metal ion	Grades of raw GAC	Q ⁰ g/mg	A 10 ⁻¹⁶ cm ²	S cm ² /gm	S' cm ² /gm
1	Cu ²⁺	F-100	30.303	5.559	1.015 x10 ¹⁰	1.623 x10 ¹⁰

Table 2 Adsorption Isotherm System : F-100 - Oxidised GAC-Cu²⁺

Sr. No.	Metal ion	Grades of modified GAC	Q ⁰ g/mg	A 10 ⁻¹⁶ cm ²	S cm ² /gm	S' cm ² /gm
1	Cu ²⁺	F-100	71.429	5.559	2.256 x 10 ¹⁰	2.737 x 10 ¹⁰



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

Where

q_e= Concentration of metal ion on GAC in mg/gm of carbon

C_o = Initial concentration of metal ions in solution in mg/liter.

C_e= Equilibrium concentration of metal ions in solution in mg Per liter.

V = Volume of solution taken in liters.

W = Weight of carbon taken in grams.

Several types of isothermal adsorption relations may occur, the most common being the case where the adsorption leads to the deposition of an apparent single layer of adsorbate molecule on the surface of the adsorbent. The Langmuir adsorption while for multimolecular adsorption more complex adsorption models are to be considered.

The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface.

Using the values of q_e and C_e the Langmuir equation could be expressed as follows ⁴

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

Where Q° = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface in mg/gm.

C_e = equilibrium concentration of adsorbate in solution in mg./lit.

Q_e = amount of adsorbate adsorbed per unit weight of adsorbent in mg/gm.

b = Langmuir constant

Rearranging the above expression

$$1/q_e = 1/(Q^\circ \cdot b \cdot C_e) + 1/Q^\circ$$

A plot of $1/q_e$ versus $1/C_e$ should be linear if Langmuir adsorption were

Permitting calculation of Q° . The value of Q° being known, the surface area of the adsorbent could be determined. However, it must be cautioned that the Langmuir equation may not be strictly valid over the range of concentrations used in the present work and only a mathematical analysis of the experimental data would substantiate this point.

The Langmuir equations for these systems also help in determining the surface area of the adsorbent under the present experimental conditions. Estimation of the specific surface area of GAC are based upon measurement of the capacity of the adsorbent expressed in mol/gm of GAC and related to the surface area using either the Langmuir equation for monomolecular adsorption or the B.E.T equation for multimolecular adsorption. The relation relates the surface area to the monolayer capacity factor by the relation:

$$S = N_a \cdot Q^\circ \cdot A$$

Where,

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

N_a = Avagadro's number

A = Cross sectional area of the adsorbate molecule in m^2 .

Since the values of Q° can be obtained from Langmuir plots of data, it is possible to calculate the value of S for any particular GAC sample.

The Freundlich equation is an empirical equation and is often used as means of data description and generally agrees quite well with the Langmuir equation in a large number of cases. It is used for adsorption of gases and has been extended to dissolved solute over moderate to low concentrations of adsorbates.

$$\text{The equation is } q_e = k C_e^\beta$$

Where q_e and C_e have the same significance as mentioned before and k and β are Freundlich constants.

This relation is indicative of the adsorption capacity and intensity. It is verified by using the relation in the form.

$$\log q_e = \log k + \beta \log C_e$$

Preparation of the solution of the Copper ion and its estimation.

A standard copper solution was prepared by dissolving 0.8524 gm of hydrated cupric chloride (E. Merck India Ltd.) in 500ml of distilled water. A drop of conc. HCl was added to it to prevent hydrolysis of the solution. It was generally used within a time period of a week and was prepared fresh as and when needed. 10ml of the above stock solution was taken in different small conical flasks. To it 10ml of dilute ammonia solution was added followed by 5-10 drops of Murexide indicator. The solution turned yellow. It was then titrated against a standard 0.01 M EDTA solution when the color changed from yellow to pink at the end point. The amount of copper in solution was estimated as per standard procedure¹¹. Working standard solutions were prepared by appropriate dilution of this stock solution. For the preparation of a standard Beer's Law plots a copper solution of the concentration range of approximately 10^{-4} M was prepared. Then various aliquots of this copper ion solutions were pipette out in several small conical flasks provided with a clean rubber stoppers. To it 10 ml o buffer solution (citric acid + liquid ammonia) of the pH = 8.5 was added followed by 10 ml of the sodium diethyldithiocarbamate solution. 20 ml of the chloroform was then added to each of the conical flasks were shaken vigorously for about 2 minutes. Both the layers were then allowed to separate and the organic layer extracted carefully with the help of a glass syringe and was taken in a clean dry test tubes. A pinch of anhydrous sodium sulphate was added through a spatula to each of these test tubes and shaken. This helped in removing residual moisture in the extract. It was then filtered through a Whatman filter paper and the absorbance of the extract was measured at 435 nm using the spectrophotometer against the pure chloroform as standard¹² The absorbance was measured immediately in order to avoid loss due to the evaporation of the chloroform layer. A graph between the absorbance versus concentration of copper ion in solution gave a standard Beer's Law plot. A working equation was derived between these values through regression analysis of data, which was used in all subsequent calculations purposes.

Result & Discussion

Characterization of Adsorbent

In the present work, carbon namely Filtrasorb F-100 was used for isotherm study. A plot of q_e versus C_e represented an adsorption isotherm with F-100 Raw carbon & F100 Oxidized carbon are given in Fig. 1(a-b). A remarkable increase in adsorption capacity is observed in Fig. 1(a-b) case of oxidized F-100 granular activated carbon.

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