Surface technology- adsorption and kinetic of heavy metal ions on modified granular activated carbon by batch study and their recovery study

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Abstract. Adsorption is a unit process to control pollution in water and wastewater technology. Carbon adsorption is widely used for the removal of refractory organic compounds from wastewater. GAC (Granular Activated Carbon) is used as an adsorbent for heavy metals like Nickel, Copper, Chromium etc. by modifying it in Modified Granular Activated Carbon. In this work, adsorption of Copper on activated carbons is carried out from oxidation treatments with HNO₃ to GAC. The oxidation treatments determined an increase adsorption capacity on the surface by functional groups. By performing Batch experiments the study of Copper ions from synthetic solution on Modified GAC & their recovery was studied at constant temp 28°C. By varying concentration of Cu²⁺ solution. The parameters for the Langmuir and Freundlich parameters has been also studied by showing maximum adsorption capacity of copper by MGAC. The oxidation treatments determined an increase adsorption capacity on the surface by functional groups.

Keywords. Modified Granular Activated Carbon, Copper sorption, adsorption isotherms, kinetics Models

1. Introduction
Due to industrial expansion all living beings are facing increased amount of organic and inorganic pollutants in the waste water which threat seriously to the human health. Heavy metals are bigger pollutants among many contaminants, namely the presence Ni, Cd, Hg and Ar in the environment has a adverse effect on living being. Hence, these heavy metals affect human organs like, kidney, thyroid, nervous system, mental retardation, birth defects and different types of cancer [1]. It has been noted that, as there was need of fresh sources of drinking water which we get by water separation process. An adsorbent of a high adsorption capacity and low cost for removing various pollutants from contaminated water; inorganic & organic traces from water [2]. A various techniques, i.e. filtration, precipitation, reverse osmosis, ion exchange, chemical, etc., have been developed for treatment of waste water , among these, adsorption, as a simple, convenient to control water pollution[1], also for handling low concentration waste streams and severe treatment levels [3]. In adsorption study, adsorption isotherms are important tools that provide to measure the maximum adsorption capacity as well as the best operating conditions of the adsorption system [4,5,6,7,8]. The aim of this study was to study various factors that shown the efficiency toward Cu adsorption of Modified Activated Carbon and Granular Activated Carbon, which was subjected to oxidation treatments with like nitric acid. The main purpose of this work is to analyze and evaluate the effect of initial concentration of metal ions in
aqueous solution and adsorbent particle quantity on metal adsorption by GAC in agitated batch adsorption. Finally, the analysis of kinetic aspects of the adsorption systems was also studied.

1.1 Materials and Methods

a. Glasswares: M/s Borosil, Bombay were used.
b. Balance: weighing balance used (electronic balance) having accuracy of ± 0.001mg.
c. Mechanical Shaker: For agitation of GAC, Shaking machine is used.
d. pH Meter: LI-120 model of digital pH meter used in this laboratory.
e. Spectrophotometer: A Systronics Digital Spectrophotometer was used.
f. Thermostat Bath: For agitating purpose carbon loaded with metal ion solution a thermostat arrangement, set in the laboratory.
g. Choice of adsorbent from the various grades carbons available in this laboratory. Activated carbon plays very important role in all wastewater treatment technology. Calgon Corporation Filtrasorb varieties namely F-400 grades of carbons readily available in the laboratory.

1.1.1. Experimental Arrangement

Preparation of the solution of the Copper ion and its estimation. Hydrated cupric chloride (E. Merck India Ltd.) a standard copper solution of 0.8524 gm was prepared. In each conical flask 20 ml of the chloroform was added and stirred for 2 to 3 minutes. Then layers were separated extraction of the organic layer with the help of a syringe was done. It was then added in a clean dry test tubes. In each of these test tubes, pinch of anhydrous sodium sulphate was added to remove residual moisture in the extract. Then the absorbance of the extract at 435 nm was measured using the spectrophotometer as standard solution using pure chloroform. [10] The absorbance was measured immediately that follows Beer’s law.

1.1.2 Determination of adsorption isotherm of Copper on of Raw Granular Activated Carbon & Modified Granular Activated Carbon.

Into a round bottom flask Granular activated carbon like F-400 varying weight of GAC was taken carefully for each set of experiment. For determining the adsorption isotherm of Copper ion on different grades of grades of, and fixed concentration of Copper ion in solution was then pour into RB flask. At 28°C for six hours the stirrer was placed in position. The initial and final concentration of Copper ion in mg/lit was then determined spectrophotometrically. Amount of Copper adsorbed on the RGAC was determined by using the following expression with the period of shaking for six hours equilibrium was reached.

By using both values C0 and Ce, the value of qe, the

\[ q_e = (C_0 - C_e) \times \frac{V}{W} \]

Where,

\( q_e \) = Concentration of Copper ion on GAC in mg/gm of carbon
\( C_0 \) = Initial concentration of Copper ions in solution in mg/liter.
\( C_e \) = Equilibrium concentration of Copper ions in solution in mg Per liter.
\( V \) = Volume of solution taken in liters.
\( W \) = Weight of carbon taken in grams.

Thus for each GAC- Copper ion system there is available a set of data for qe and Ce. A plot qe versus Ce then represents a typical adsorption isotherm for the Copper ion on F-400 grades of RGAC (Raw Granular Activated Carbon) & MGAC (Modified Granular Activated Carbon). The data on these isotherm are given in Table 1 & 2, as also log qe, log Ce and 1/qe and 1/Ce values for which are useful test for adherence of adsorption of Copper ions to either the Freundlich or the Langmuir adsorption models. The isotherms and the adherence to Freundlich and Langmuir theories are given in Fig. 1, 1(A), 1(B)& 2, 2(A) & 2(B). Similar procedure is applied for Modified Granular Activated Carbon.

1.1.3. Experimental arrangement
The kinetic study of Copper ion of granular activated carbon. Copper ion solution was taken whose concentration was equivalent to the concentration that was on the descending portion of the lot of $q_e$ versus $C_e$ on the adsorption isotherm curve i.e. where curve just starts showing constancy in the value of $q_e$. The glass stirrer was set in motion when carbon granules were drawn into the solution and the time noted. The concentration of the Copper ion the solution withdrawn at definite time intervals were estimated spectrophotometrically which were designated as $C_t$. The values of the concentration of the Copper ion on the loaded granular activated carbon at the same time intervals was estimated using a similar expression as before namely.

$$q_t = (C_0 - C_t)$$

Where $q_t$ = The concentration of Copper ion on the GAC in the mg/g at a particular time interval $C_0$ = The concentration of the solution at start in mg/lit $C_t$ = The concentration of the Copper ion in the solution at any time $t$ in mg/lit. $W$ = Weight of carbon taken in gm $V$ = Volume of Copper solution in liters.

The rate of adsorption of the Copper metal on different grades of carbon and data represents in Tables 1 & 2. Values of the $q_e$ at different time intervals were then plotted versus these time intervals. $q^*$ represents the equilibrium concentration of metal ion on the loaded GAC at a particular time interval, calculated using determined values of $C_t$ and using the plot of $q_e$ versus $C_e$ finding $q^*$ at $C_e=C_t$ which was $q^*$. A plot both $q$ and $q^*$ were plotted versus different time interval. These curves represent the approach to equilibrium Figure 3 & 4. The difference between the values of $q^*$ and $q$ at any time represented the driving force operative in the process leading to adsorption on the Granular Activated Carbon. It gives values of $dq^*/dt$ calculated at the various time intervals using a computer program developed in this laboratory. At the same time intervals selected values of $q^2 - q$ were also computed from $q^*$ values which were useful to test adherence to the Linear Driving Force (LDF) and Quadratic Driving Force (QDF) Models.

Similar procedure is applied for Modified Granular Activated Carbon.

### 1.1.4. Modification of carbon surface with oxidizing agent

Granular activated carbon modified by concentrated nitric acid and this process is called as chemical modification of the carbon surface, which involved following procedure. In this case about Standard amount of carbon was taken in conical flask and add concentrated nitric acid. It was then boiled by adding a little distilled water. This modified carbon was then agitated with metal ion solution having single system. It was found that there was an increase the adsorption capacity of carbon.

### 1.1.5. Recovery of adsorbed metal ions from the Granular Activated Carbon surface

As discussed above the transition metals like Copper are scavenged by granular activated carbon, it was thought if simultaneous recovery of these metals could be possible. For the recovery there was a need to modify the carbon. The carbon was modified as discussed earlier. It is modified by leaching process with strong desorbing agent nitric acid. In effect it could be visualized as a leaching process. An aliquot of this solution was analyzed calorimetrically for the determination of metal ions.

### 1.1.6 Result and Discussion

| Sr. No. | Metal ion | Grades of raw GAC | $Q^*$/mg | $A_{10^{-16}cm^2}$ | $S$ cm$^2$/gm | $S'$ cm$^2$/gm |
|---------|-----------|-------------------|-----------|-----------------|---------------|----------------|
| 1       | Cu$^{2+}$ | F-400             | 66.667    | 5.559           | 2.106 x 10$^{10}$ | 2.516 x 10$^{10}$ |
Table 2. Modified Isotherm study

| Sr. No. | Metal ion | Grades of modified GAC | Qo g/mg | A $\times 10^{16}$ cm$^2$ | S cm$^2$/gm | S$'$ cm$^2$/gm |
|---------|-----------|-------------------------|---------|---------------------------|-------------|---------------|
| 1       | Cu$^{2+}$ | F-400                   | 166.667 | 5.559                     | 5.264 x 10$^{10}$ | 5.646 x 10$^{10}$ |

Figure 1. Adsorption Isotherm. System: F-400-Raw GAC -Cu$^{2+}$

Figure 1(A) Linearised Freundlich Adsorption Isotherm System: F-400-Raw GAC -Cu$^{2+}$

Figure 1(B) Linearised Langmuir Adsorption Isotherm System: F-400-Raw GAC -Cu$^{2+}$

Figure 2. Adsorption Isotherm System: F-400 -Oxidised (M) GAC in presence of Cu$^{2+}$
A glance of the Tables clearly indicates that the surface area as occupied by the metal ions on the surface of RGAC & MGAC. However utilizing could roughly assess the values of the area occupied by metal ions on the modified GAC when the surface is saturated with a monolayer of metal ion could be roughly assessed by utilizing the values of \( q_{\text{emax}} \) in mg per gm of carbon and converting it to atoms per gm of carbon by the relation.

### 1.1.6. Kinetics of Exchange of Copper with GAC

For kinetic studies of the Copper ion uptake by grades of GAC experimental procedure is mentioned as above. In all cases of adsorption GAC is generally considered to be diffusional in character. Diffusion, results from a concentration gradient in the fluid phase or on the solid phase, where diffusion involves separation of the solute from the fluid phase to sorbent phase it is called particle phase diffusion or homogeneous diffusion described by an effective diffusion coefficient \( D \). Analytical solutions of this equation are available elsewhere in literature [11]. The solutions assumed a number of simple boundary conditions and constant \( D \) but are not easy to use. For this reason Glueckauf and Coates [12]. This LDF equation can be applied for cases where the adsorption isotherm was linear or moderately curved and adsorption took place under conditions close to equilibrium. Various references mentioned in literature clearly indicated that the LDF method although simple, which is very useful method to give idea about the adsorption processes. All the plots of LDF and QDF plots give an idea that, it can be applied for cases where the adsorption isotherm was linear or moderately curved and adsorption took place under conditions close to equilibrium.

In the present investigation it has been observed that the QDF plots were better than the LDF plots.

![Figure 2(A)](image1.png)  
**Figure 2 (A). Linearised Freundlich Adsorption Isotherm F-400-Oxidised GAC -Cu\(^{2+}\) in presence of - Cr\(^{2+}\).**

![Figure 2(B)](image2.png)  
**Figure 2(B) Linearised Langmuir Adsorption Isotherm System: F-400-Oxidised GAC -presence of - Cu\(^{2+}\).**

\[
\text{log } q_e = 0.8238 \text{log } C_e + 0.2248  
\text{R}^2 = 0.9904
\]

\[
\frac{1}{q_e} = 0.86181/\text{C}_e + 0.017
\text{R}^2 = 0.9914
\]

![Figure 3](image3.png)  
**Figure 3. Adsorption phase approach to equilibrium system :RGAC F-400- -Cu\(^{2+}\).**

\[
\text{log q}_e = 0.2238 \text{log C}_e + 0.058
\text{R}^2 = 0.9998
\]

\[
\frac{1}{q_e} = 0.90181/\text{C}_e + 0.0017
\text{R}^2 = 0.9994
\]
Figure 3(A). Quadratic driving force plot
System - GAC F-400-raw carbon -Cu^{2+}

Figure 3(B) Linear driving force plot
system GAC F-400 raw carbon-Cu^{2+}

Figure 4. Adsorption phase approach to equilibrium system : GAC F-400- Oxidised carbon-Cu^{2+}

Fig. no. 4(A):  Quadratic driving force plot
system - GAC. F400-oxidised carbon -Cu^{2+}

Figure 4(B) Linear driving force plot
system : GAC F-400 oxidised carbon-Cu^{2+}
1.1.7. Single solute adsorption and simultaneous recovery.

From the batch experiments of the single solute adsorption system it was observed that the different metal ions were adsorbed up to different extent by the raw GAC. Digesting the adsorbed GAC in concentrated HNO₃ carried out the recovery of copper. The results are given in Tables.

| Table 3. Adsorption of Copper on raw F-400 GAC |
|-----------------------------------------------|
| Sr No | Initial amount of Copper in solution in mg/ml | Final amount of Copper in solution in mg/ml | Amount of Copper adsorbed by GAC in mg/gm |
|-------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1     | 212.1                                         | 209.1                                         | 3.00                                          |
| 2     | 212.1                                         | 207.2                                         | 4.90                                          |
| 3     | 212.1                                         | 207.5                                         | 4.60                                          |

2. Conclusion

In this present work it was noticed that, work was initiated keeping in view that the presence of toxic metals in the wastewater, which could serious effect on living things. As seen from literature studies in recent years adsorption by granular activated carbon is a very effective and economical technique. On raw activated carbon as well as on oxidized carbon adsorption of metal ions involves basic chemistry relating to the diffusion of metal ion in macro and micro pores of the carbon. The following are the important aspects of the present investigation.

When the metal ions adsorbed granular activated carbons were digested with concentrated HNO₃, the metal recovery was very much conclusive. The carbon treated with suitable oxidizing agent played a significant role in the recovery of metal ions. Technique was found to be useful in the separation of particular metal ion from the mixture of metal ions. Modifying the carbon surface with oxidation by Nitric acid in order to obtain maximum recovery of a given metal ion optimized the recovery process.

3. References

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