Effect of Temperature on the Adsorption Behavior of Copper onto Carbonaceous Substrate

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Summary: The adsorption of Cu (II) from aqueous solutions on the surface of activated charcoal was investigated as a function of shaking time, concentration of adsorbate, and shaking temperatures of 25°C, 30°C, 35°C, 40°C, 45°C and 50°C. For this purpose, high purity $CuCl_2$ was used as the heavy metal source and commercial activated charcoal was used as the adsorbent. Adsorption equilibrium was attained within 20 minutes. The adsorption was lower at higher temperatures and vice versa, due to the exothermic nature of the process. Accordingly the energy of activation is small, and thus these reactions are favorable at lower as compared to high temperatures. Freundlich and Langmuir adsorption isotherms were applied to the data and it was found that both equations fitted the data well. The rate constants of adsorption were determined by the first order kinetic equation which provided best fit to the data, indicating that the kinetics of the surface adsorption process are directly proportional to the adsorbate concentration. The adsorption isotherm data was also used for computing the thermodynamic parameters like $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$. Negative value of these parameters show that the interaction of the adsorbate with the adsorbent is spontaneous.

Introduction

Industrialization is a vital force in the economic development of a country. Pakistan needs to achieve higher standards of industrialization for the over all development. At the time of partition (1947) Pakistan had negligible industrial base. Most of the consumer good industries like textile (both cotton and synthetic), chlor-alkali, electroplating, petroleum refining, motor vehicles, mining and metallurgy, explosives, paper and pulp, leather tanning, food, chemical, fertilizer, steel and engineering are now will established in Pakistan. Among these, the textile, steel and engineering, paper and pulps, and leather industries form the largest sub-sector of the country economy [1]

Among the various operations involved in the manufacturing processes of these industries are protective coating, sizing and bleaching, dyeing etc. Metallic salts, sulfuric acid, sodium hydroxide, hydrogen peroxide, starch, oil, soda ash, phenols, dyes stuffs etc., serve as basic raw materials for the above-mentioned industries [2]. These industrial processes on the one hand have provided some valuable products in the market but on the other hand have generated considerable volumes of industrial effluents, as well. These effluents contain many metals, which are neither usually removed, nor are readily detoxified by metabolic activity. As a result they accumulate and cause severe effects to living organisms. Among these metals some are potentially hazardous to human, namely like Ba, Cd, Cu, Ni, Zn, Mn, Vn, etc. [3].

Copper is one of the most important metals used widely in metallic state either as pure metal or an alloy. For all organisms it is an essential micronutrient. It is usually found in high concentration in water and sediments as a result of mining activities, and its use as copper-based fungicides. Its toxic effects include brain damage to mammals.

The quantity as well as the quality of clean water supply is of vital significance for the welfare of mankind. Environmental audits have been made for the identification of pollutants, (both organic and inorganic) by various health authorities, which have reported most of them to be carcinogenic in their mode of action. Therefore, the removal of these cations from industrial effluents is of prime concern and demands special attention.

An amorphous form of carbon, i.e., charcoal, can be prepared from various sources i.e. carbonaceous materials like anthracite, graphite, wood, animal bones, binders such as tars, electrolytic pitches and miscellaneous substances [4-7]. These materials are mixed in definite proportions and are

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carbonized and activated under controlled conditions. The resultant structure carries relatively large cavities interconnected in all dimensions, thereby increasing their tortousity [8]. This porous solid is one of the most effective materials used for the removal of polar and non-polar compounds that have been found in portable waters [10, 30-32]. Because of its combined properties of high permeability, small pore size, activity, inertness to all but highly oxidizing chemicals, resistance to thermal shock and ease of fabrication [9], the activated carbon has applications in industries like food, textile, leather, paper and pulp, sugar, oil, pharmaceutical and portable water treatment [9]. Earlier workers have used activated carbon for the removal of toxic and carcinogenic materials from industrial effluents [7-8], which are introduced into water bodies through different sources [9-11]. Activated carbon can be employed in the form of adsorption bed, columns, and cloths etc. The degree of adsorption is very sensitive to the concentration of adsorbate, solvent system, particle size, nature of the active sites present on the surface, pore size distribution, pH, ash contents and modification of the surface of adsorbent [12-18]. Many earlier investigators have used different techniques for the adsorption of heavy metals using activated charcoal as an adsorbent [19-27] Both physical and chemical adsorption has been investigated in detail [33].

The purpose of this study was to evaluate the effect of temperature on the adsorption behavior of copper onto carbonaceous substrate. To achieve this objective both kinetic and equilibrium studies were performed and various thermodynamic parameters like Gibb's free energy change, Enthalpy change and Entropy change were determined.

Results and Discussion

Surface Area

The surface area of charcoal was determined by Snow's iodine adsorption method [35]. Surface area of the sample was found to be 250.0 m^2/g, which is lower than the surface area range, 400 - 1800 m^2/gm, as given in the charcoal manufacturing standards [28]. This lower surface area may be due to the large size of iodine molecules, which diffuse with difficulty into the smaller micro pores and thus reduce the removal of iodine from its solution. The low surface area of our sample may also be due to the presence of surface functional groups such as chromene, carboxylic acid anhydride, hydroxyl group, phenolic, cyclic peroxide and lactones. These complexes decrease the internal diameter of pores (micro, meso and macro pores and thus reduce the adsorption of iodine. For better results it needs more investigation by BET method [29]

Uptake Study at Different Temperatures

a). Kinetic Studies

The results of the kinetics of the heavy metal adsorption on charcoal are given in fig 1. The affinity of copper towards charcoal surface is due to its incomplete outer shell ($3d^9$, $4s^2$) [34] and as a result has greater interaction with the carbon surface. The results show that with the increase in temperature the rate of adsorption decreases which is due to the exothermic surface reaction. Its energy of activation has thus negative values. The kinetic data was found to obey the first order kinetic i.e.

$$\ln C = \ln C_0 - k t \qquad (1)$$

Where,

C = concentration of Cu solution at time t.
C_0 = concentration at the start of experiment.
k = adsorption rate constant
t = reaction time in minutes

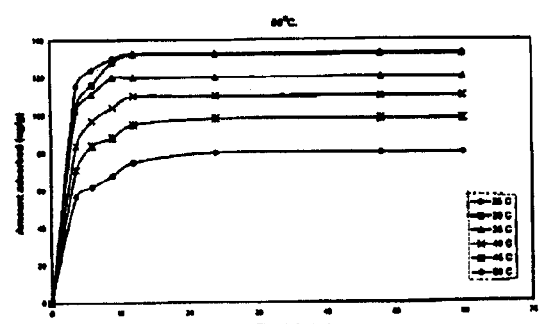

Fig. 1: Kinetic studies of copper on charcoal at temperature, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

The plots of lnC Vs t at different temperatures are shown in fig. 3. It is evident from the plots that up to about twenty minutes the process follow the first order kinetics and give linear plots and then become plateau indicating that equilibrium has been established.

The first order rate constants (k) found from the slopes of the curves at different temperatures are shown in table 1.The activation energy calculated from the slope of the plot lnk Vs 1/T was found to be -32.195 kcal.mol^{-1} .The negative value is due to the exothermic nature of adsorption.

Table 1: Thermodynamic parameters for the adsorption of copper on charcoal

Temp. °C	Rate constant(k) .min^{-1}	$^{+}\Delta G$ K.J. mol^{-1} x 10^{-9}	$^{+}\Delta H$K.J.mol^{-1}	$^{+}\Delta S$.K.J.mol^{-1} deg^{-1} x 10^{-12}
25	0.0447	-2045.453	-10231.135	-3430.67080
30	0.0390	-2079.924	-10405.189	-3430.75448
35	0.0343	-2114.468	-10577.863	-3430.79632
40	0.0283	-2149.136	-10752.880	-3430.83816
45	0.0263	-2183.972	-10927.143	-3431.63312
50	0.0153	-2218.536	-11101.072	-3431.67496

Thermodynamic parameters like enthalpy change $(\Delta H)^{\neq}$, entropy change $(\Delta S)^{\neq}$ and Gibb's free energy change $(\Delta G)^{\neq}$ of adsorption at different temperatures (25^{0}C, 30^{0}C, 35^{0}C, 40^{0}C, 45^{0}C, 50^{0}C) are given in table 1, which were determined using the following equations.

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (2)$$

$$k = kT/h\, e^{\Delta s\neq/R}\, e^{-\Delta H\neq/RT}$$

OR

$$\Delta S^{\neq} = R\,\{\ln(kh/kT) + \Delta H/RT\}$$

Where k = rate constant

K = Boltzmann's constant (1.3806×10^{-23} J. deg^{-1})

$\Delta H^{\neq}$ = Enthalpy change

h = Plank's constant (6.626×10^{-34}. J s)

R = 8.314 J. deg^{-1}. mol^{-1}

The values of enthalpy change of activation $(\Delta H)^{\neq}$, Gibb's free energy change of activation $(\Delta G)^{\neq}$ and entropy change of activation $(\Delta S)^{\neq}$ increases with rise in temperature. (table.1). The negative values are due to the exothermic binding of adsorbate molecules with the active sites of charcoal [30].

b) Equilibrium Studies

The adsorption of Copper on charcoal was studied at six different temperatures from 25^{0}C to 50^{0}C with difference of 5^{0}C.The amount adsorbed "Y"(ug/g) was plotted Vs Equilibrium concentration (ppm) is shown in fig. 2.The equilibrium was found to be established within 20 minutes, gives a straight line, showing the validity of Henry's law. Which is given below.

$$C_a = KC \quad (3)$$

Where C_a = Amount of adsorption layer.

C = Concentration of solution

The values of "K", were determined from the slope of the figure. 2, which show that the Henry's coefficients are independent of concentration but decrease with the increase in temperature. This application of Henry's equation to the data reveals that the surface of charcoal is homogenous and the concentrations of copper in the adsorption layer is uniform.

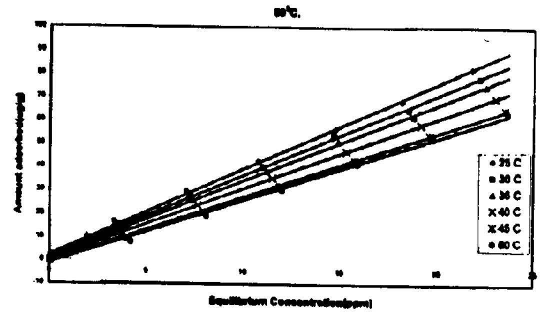

Fig. 2: Utake study of copper on charcoal at temperature, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

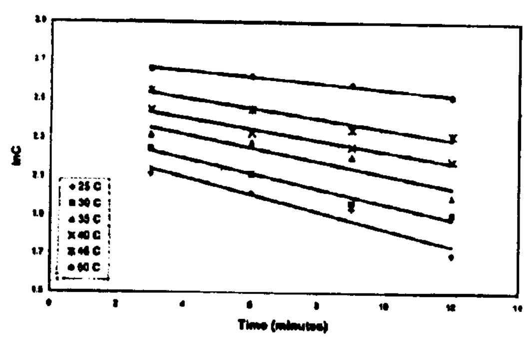

Fig. 3: First order Kinetic studies of copper and charcoal at temperature, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

The equilibrium data for copper at different temperature (25^{0}C, 30^{0}C, 35^{0}C, 40^{0}C, 45^{0}C and 50^{0}C) have been correlated using the linear form of Freundlich adsorption isotherm i.e. $\ln x/m = \ln K + 1/n \ln C$, The results are shown in fig.4. The experimental data obey the straight-line behavior.

The value of "n" given in table 3, show some variation in adsorption with concentration. It is also obvious from the figure that the adsorption is high from concentrated solutions than from dilute solutions. This increase is more pronounced at lower temperatures as compared at high temperature (Table 3). The value of adsorption capacity (K) decreases with increase in temperature from 25°C to 50°C.

Table 2: Henry's co-efficient for copper adsorption on charcoal at different temperature.

Temperature(°C)	Henry's co-efficient(K)
25	3.6710
30	3.4575
35	3.2832
40	3.0219
45	2.7625
50	2.6885

The linear form of Langmuir isotherm $c/x = 1/ab + c/b$ was used to plot the adsorption data of Copper, Fig. 5. Langmuir constant "b" determined from the slope of the graph (table.4), is the mono-layer adsorption capacity. The values of "b" indicate that the amount of adsorption increases as the temperature decreases. The plots thus show a good agreement of the data to the Langmuir adsorption.

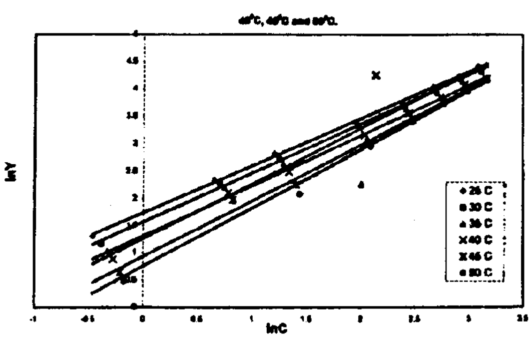

Fig. 4: Freundlich's adsorption isotherms for copper on charcoal at temperature, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

Table: 3. Freundlich's Constants for the adsorption of Copper on Charcoal at different temperatures.

Shaking temp. °C	Slope 1/n	K (ug/g)	n
25	0.8598	1.7400	1.163
30	0.8965	1.5697	1.1154
35	0.9191	1.3103	1.0880
40	1.0100	1.2597	0.9909
45	1.0256	0.9287	0.9750
50	1.0706	0.7507	0.9340

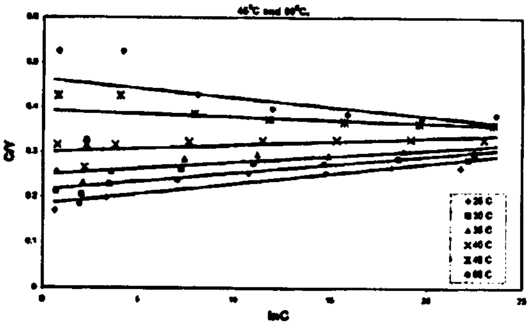

Fig. 5: Langmuir's adsorption isotherms for copper on charcoal at temperature, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

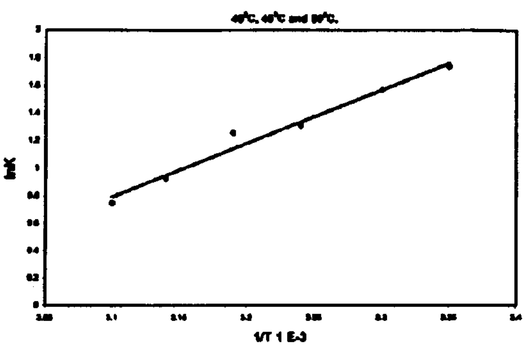

Fig. 6: Plot of lnK vs 1/T for the adsorption isotherms for copper on charcoal at temperature, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C

Table 4: Langmuir's Constants for the adsorption of copper on charcoal at different temperatures.

Shaking temp. °C	Slope 1/b	b (umol/g)	Intercept (1/ab)
25	0.0045	222.22	0.185
30	0.0037	270.07	0.2164
35	0.0037	270.27	0.2164
40	0.0015	666.66	0.3009
45	-0.0014	-714.28	0.3928
50	-0.0042	-380.09	0.4634

Experimental

Materials

Commercial grade charcoal in powder phase was used for the adsorption of copper from copper chloride ($CuCl_2$) solution in the present study.

Measurement of Surface Area

The surface area of powder activated charcoal was determined by C.W. Snow's iodine adsorption method [35].

One gram of charcoal sample was taken and placed in conical flask with 5 ml of Iodine solution, closed the flask air tightly. The mixture was stirred periodically for two hours. After two hours, 45ml of distilled water (double) was added and left for one hour. 20ml clear supernatant solution was titrated with 0.0394 N $Na_2S_2O_3.5H_2O$ solution. The surface area was determined, using the formula i.e. 12.5(24 - V), where V is the volume of titrant used. The experiment was performed in triplicate.

Kinetic Studies

One grams of charcoal sample and 50 cm^3 of copper solution was taken separately in conical flasks and stoppered tightly. These flasks were then placed on shaker for different time periods (3, 6, 9, 12, 24, 48 and 60 minutes) and at different temperatures (25°C, 30°C, 35°C, 40°C, 45°C and 50°C). Filtered the slurry and the amount of metal in filtrate was determined by titration with standard EDTA solution (0.001M). The amount of metal adsorbed was then calculated using the following formula.

$$\text{Amount adsorbed (ug/g)} = (V_1 - V_2)\ \frac{\text{M (at. wt. of copper) 1000}}{\text{Wt. of charcoal taken in grams}} \quad (4)$$

M = Molarity of E.D.T.A =0.001 M

V_1 = Volume of EDTA solution used for 50 ml of blank metal solution

V_2 = Volume of EDTA solution used for 50 ml of blank metal solution containing charcoal simple.

It was concluded through the series of experiments that 20 minutes was enough time in order to attain the adsorption equilibrium.

Uptake Study at Different Temperatures:

One gram of charcoal with 50 cm^3 of aqueous solution of Copper at different concentrations i.e. 1, 3, 5, 10, 15, 20, 25 and 30 ppm were incubated for 20 minutes at different temperatures i.e. 25, 30,35,40,45 and 50°C on an electric shaker. After incubation the slurry was filtered and concentration of copper in the filtrate was determined by titration with standard EDTA solution (0.001M). The amount of metal adsorbed (ug/g) was calculated, using the formula given above.

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