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Research Article

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Adsorption of Cu(II) by Used Aqua Guard Carbon(UAC)

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ABSTRACT

Used Aquaguard Carbon(UAC) was used to remove Cu(II) from aqueous solution. The influence of contact time, suspension pH, temperature, UAC/ Cu(II) dosage on Cu(II) removal were investigated in a series of batch adsorption experiments. Adsorption data was found to follow Langmuir isotherm and pseudo second order kinetics. Thermodynamic parameters were evaluated from temperature experiments. Activation energy was found to be 77.4 kJ/mol. Adsorption data was interpreted kinetically and was found to be controlled both by physio-soption as well as intra particle diffusion. The Cu(II) uptake was found to be suppressed in presence of Co-ions and follows a trend Ni>Zn>Co.

Key Words: Intraparticle diffusion, Langmuir isotherm, Pseudo second order kinetics, Separation parameter, Used Aquaguard Carbon (UAC).

INTRODUCTION

Cu salts are used in water supply system for controlling biological growths in reservoirs and distribution pipes. The corrosion of Cu containing alloys in pipe fittings may introduce measurable amounts of Cu into the water. Although Cu is essential to humans, it should be limited upto 2.0 mg daily. Since like other heavy metals, Cu(II) has high affinity for ligands containing nitrogen and sulphur donors, enzymes and nucleic acids present in the human body are greatly affected and lead to haemolysis, damage of lever and kidney and fever with influenza[1].

So, the removal of the excess of copper from the drinking water by a simple and cost effective method is very much essential to protect human and environmental health. Reverse osmosis, electro-dialysis, liquid extraction and precipitation are the so called conventional methods, which are generally used for the sequestration of Cu(II) from the aqueous solution. But these methods are not economically viable when the concentration of the metals in the solution are low[2,3]. Therefore, adsorption process is considered to be a better technique for the removal of Cu(II) by using low cost adsorbents. Various low cost adsorbents being used are natural bentonite, natural clay, kaolinite, montmorillonite, steel making slag, peat, fly ash and carbonaceous substrates[4-13]. Although activated carbon has also very good adsorption capacity towards most of the heavy metals, however it is not cost effective for the removal of Cu(II) under consideration because of its high price and expensive regeneration[14]. Now a days, silver impregnated activated carbon has been used in the domestic water filter and it has been discarded after six months use.

In order to check the maximum reusability of used aqua guard carbon, in the present paper an attempt has been made to remove Cu(II) from the drinking water system by using Used Aqua Guard Carbon. The aim of this study is to investigate the kinetics and mechanism of Cu(II) adsorption on Used Aqua Guard Carbon(UAC).

EXPERIMENTAL SECTION

Adsorbent

Bacteriostatic silver impregnated granular activated carbon specially packed for Eureka Forbes limited was used as adsorbent after 6 months use in the domestic aqua guard. It is manufactured by Active Carbon India Pvt. ltd., Banzara Hill Pvt.Ltd. It has Item code GWTMST20000055 and granular size 8X20 ASTM. After 6 months use, the charcoal was washed several times and finally with de-ionised water and dried in the oven overnight at 100^0C.

Adsorbate

Stock solution of 1000mg/dm^3 Cu(II) ion was prepared dissolving copper sulphate pentahydrate ($CuSO_{4,}$ $5H_2O$) purchased from MERK India Ltd. in deionised water. It was diluted to desired level to perform different experiments.

Adsorption studies

Batch kinetic experiments were carried out using a magnetic stirrer. A fixed amount of UAC was placed in stoppered conical flasks to which 100mL of Cu(II) solution of various concentrations were added. The mixture was stirred for 150 minutes. The initial pH of the solution was adjusted by dilute H_2SO_4 / NaOH. For temperature variations, the adsorption studies were carried out in a thermostat where the variation in temperature was only ± 0.5^0C. Samples were collected at regular time intervals and equal volume of the original solution was replaced in order to maintain the volume constant. Due corrections were made during interpretation of results. Each experiment was repeated two times and the mean values were taken into consideration. The loading (q) was calculated according to the equation-1

$$q = \frac{(C_o - C_e)V}{M} \qquad (1)$$

Where,
q = Adsorbent phase concentration after equilibrium, mg adsobate /g adsorbent or loading
C_o = Initial concentration of Cu(II),mg/dm^3
C_e = Equilibrium concentration of Cu(II), mg/dm^3
V= Volume of the liquid in the reactor , dm^3
M= Mass of the adsorbent, g.

$$\text{Sorption}(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

Analysis

The Cu(II) ions in the solution were analyzed using ELICO SL 176 double beam Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Effect of contact time

Each adsorption experiment was carried out for 150 minutes. Maximum Cu(II) adsorption was observed within the first 30 minutes. After that no further uptake of Cu(II) was observed. Because, as long as the residual or unbalanced sites are present on the adsorbent UAC, there is an increase in the % of Cu uptake. When all the sites present on UAC get satisfied, there is no further increase in the % of Cu(II) uptake. Decrease of removal with increasing time may also be due to intra particle diffusion process dominating over adsorption[15]. The % of Cu uptake by UAC was compared with the unused silver impregnated aqua guard carbon. The % of Cu(II) uptake by used(UAC) and unused aqua guard carbon were found to be 78 and 100 respectively in the first 30 minutes as shown in Figure

1(Condition : Metal concentration – 10 mg/dm^3, w/v(%) – 2). It indicates that the UAC can be used further for the removal of Cu(II).

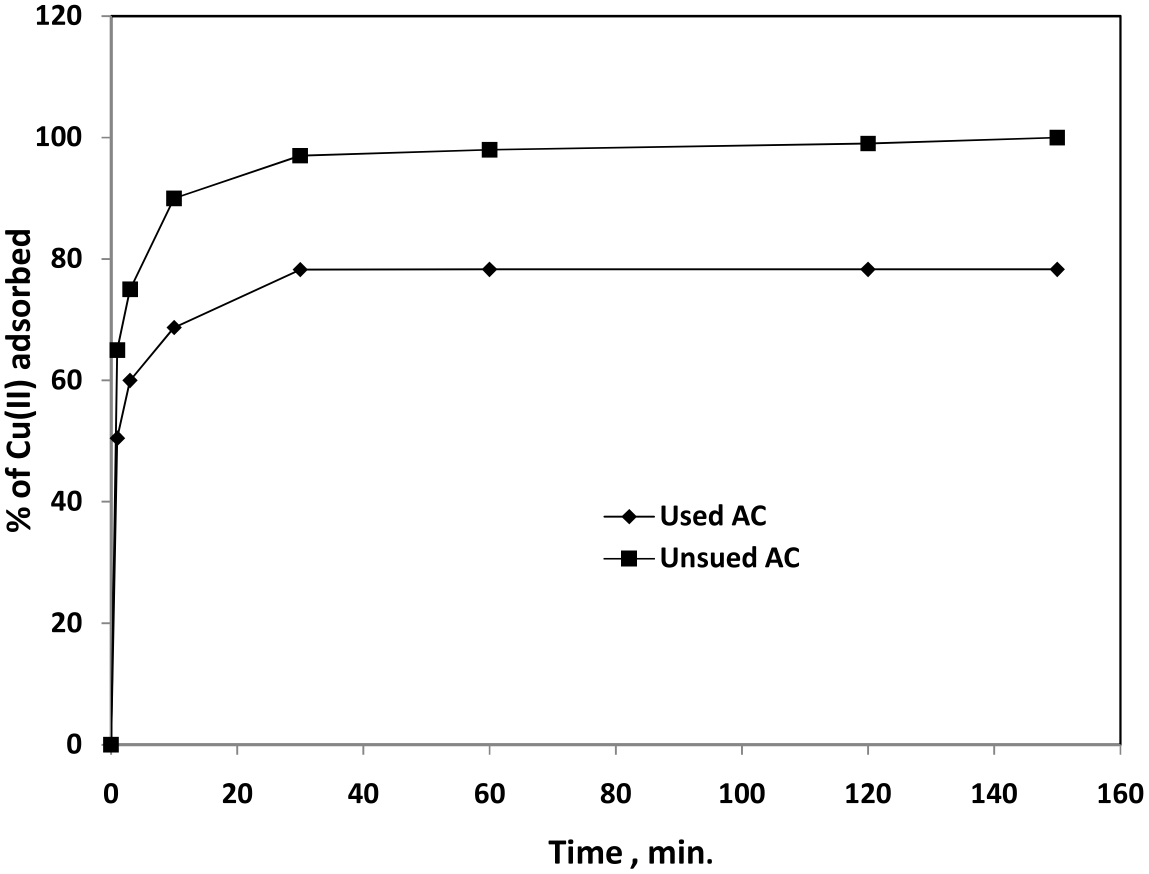

Figure 1 : Comparison of Cu(II) adsorption between used and unused Aquaguard Carbon(AC)

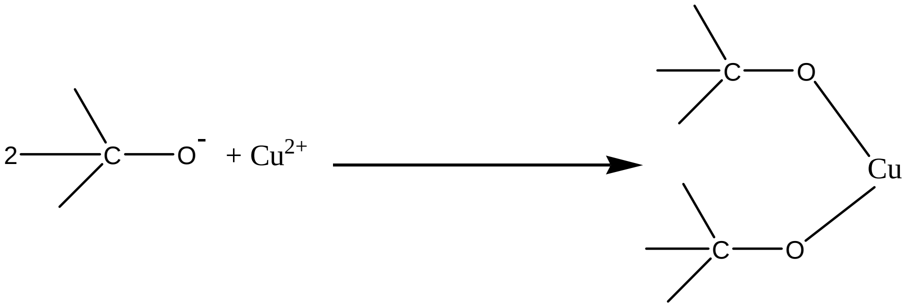

Figure 2: Adsorption of Cu(II) ion on UAC

Effect of pH

The surface charge of most of the carbons become positive at low pH[16]. Therefore, the uptake of positively charged Cu(II) ion is less at low pH . Similarly, at higher pH there is a possibility of Cu(II) precipitation. So, the pH of the solution was varied from 2-7. It was observed that maximum Cu(II) removal was achieved at pH 5.0. X-Ray Photoelectron Spectroscopy (XPS) shows that the functional groups present on surfaces of the various types of carbons are hydroxyl (C-O$^-$), Carbonyls (C=O) and carboxylic acids or, esters (O-C=O). Out of these, the C-O$^-$ functional state contributes 60-70% of the total % of oxygen containing states[17]. Therefore, adsorption of Cu(II) on UAC may follow the following mechanism as shown in Figure 2.

Cu(II) ions may also hydrolyse in aqueous solution and adsorb in a hydrolysed form according to the following reaction.

$$Cu^{2+} + H_2O \rightarrow Cu^{(n-1)+}OH + H^+ \text{ (Hydrolysis)}$$

Effect of Cu(II) and UAC concentration

With the increase in Cu(II) concentration from 4 to 20 mg/dm^3, the % of Cu uptake decreased from 66 to 53, whereas loading increased from 0.15 to 0.58 mg/g. Earlier report indicates that the removal of Cu(II) is dependent on Cu(II) concentration[18]. Similarly, with the increase in UAC concentration from 20 to 50 g/dm^3, the loading decreased from 0.36 to 0.15 mg/g, whereas % of Cu(II) uptake increased from 78 to 85 mg/g. It shows that adsorbent/adsorbate doses and removal efficiency are greatly influenced by the number of adsorption sites present on the adsorbent surface exposed to adsorbate. Once equilibrium was achieved, there was no effect of change of adsorbent/adsorbate dose. With the increase of UAC concentration, the functional groups present on adsorbent which are responsible for adsorption are increased and therefore adsorption also increased. Similarly, with the increase in Cu(II) concentration, the competition between the sorbate increases for the limited number of sorbent. Therefore, % of adsorption is decreased.

Effect of Temperature

Effect of temperature on adsorption of Cu(II) was studied by conducting different sets of experiments at different temperatures i.e. 30, 40, 50 and 63°C. It was observed that adsorption of Cu(II) ion increased when the temperature increased from 30 to 40°C and then it decreased. The negative effect of temperature is due to exothermic nature of the reaction and the greater degree of hydrolysis of the functional groups present on the charcoal surface.

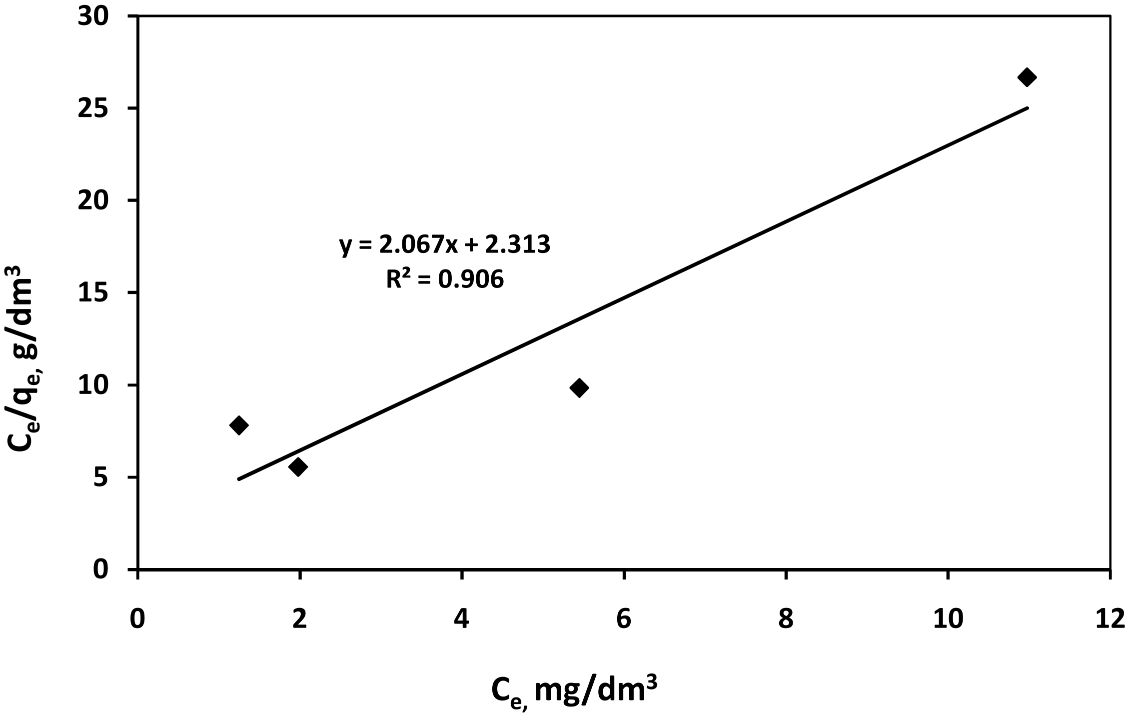

Figure 3 : Langmuir Plot

Adsorption isotherms

The adsorption of Cu(II) on UAC was fitted with two well known models given by Freundlich and Langmuir. These two isotherms were studied by using initial Cu(II) concentration between 4 and 20 mg/dm^3 at an adsorbent dose of 20 g/dm^3.

The Langmuir adsorption isotherm is

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (3)$$

Where, constants b and q_m relates to the energy of adsorption and adsorption capacity and their values were obtained from the intercept and slope of the plot of C_e/q_e versus C_e as shown in Figure 3. The linear nature of the plot showed that the adsorption follows Langmuir isotherm.

The obtained q_m value can be compared with the other reported results [14,19]. The values of b which is a measure of heat of adsorption was utilized to calculate a dimensionless constant i.e., separation parameter R_L[20].

$$R_L = \frac{1}{1 + bC_0} \qquad (4)$$

Where,C_0=Initial concentration of Cu(II). According to McKay et al.[21] ,$R_L>1$ ⇨ unfavorable, R_L =1 ⇨ Linear ,$0 < R_L<1$ ⇨ Favorable, R_L =0⇨ Irreversible adsorption. R_L values = 0.05 to 0.22 indicated the sorption of Cu(II) on UAC is favorable in nature.

The adsorption data obtained was also fitted with Freundlich isotherm. Freundlich isotherm actually gives the relationship between loading and equilibrium concentration.

The equation is

$$\log q_e = \log K + \frac{1}{n} \log C_e \qquad (5)$$

Where, K and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity respectively. The slope (1/n) and intercept (log K) can be obtained from the graph plotted between log q_e versus log C_e. The results showed that Langmuir isotherm is a good fit for the experimental data as is evidenced from R^2 values shown in Table I.

Table I Freundlich and Langmuir isotherm constants

Isotherm model	Various Constants		
Langmuir	R^2	q_m(mg/g)	b
	0.91	0.48	0.89
Freundlich	R^2	K(mg/g)	n
	0.57	0.20	2.44

Activation energy was determined from the slope of Arrhenius plot i.e. a plot between ln(reaction rate constant) versus reciprocal of temperature(K). The equation is

$$k = A e^{-E/RT} \qquad (6)$$

The low activation energy i.e. 77.4 kJ/mol indicated the ease of sorption reaction. These values are comparable to the other reported data[22].

The values of ΔH and ΔS were calculated from the slopes and intercepts of the plot of $\ln K_D$ versus 1/T [23] as shown in Figure 4 by using the relation.

$\ln K_D = \Delta S/R - \Delta H/RT$ (7)

Where,
K_D = Distribution coefficient
T = Temperature, K
ΔS = Entropy change
ΔH = Enthalpy change
R = Universal gas constant

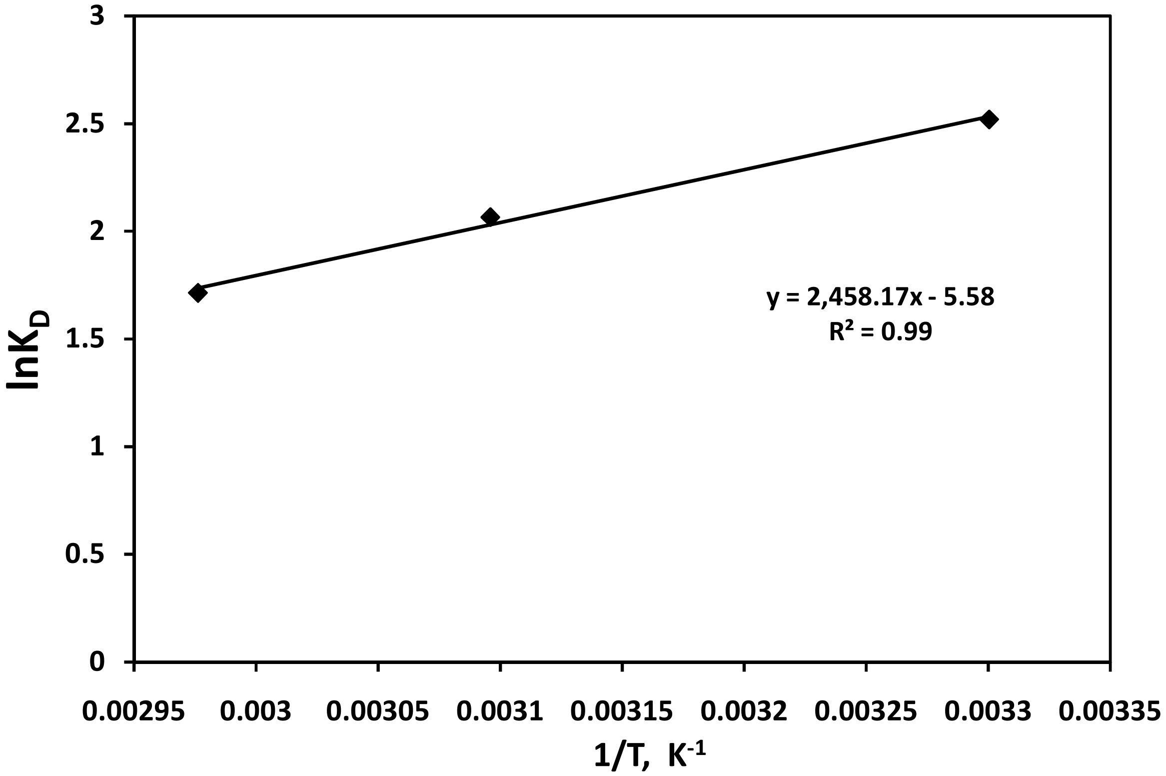

Figure 4 : A plot of $\ln K_D$ versus 1/T to determine thermodynamic parameters

The free energy of specific adsorption ΔG was calculated from the following relation

$\Delta G = \Delta H - T\Delta S$

The ΔG , ΔH and ΔS values are shown in Table - II. The negative values of the enthalpy change suggested the reaction to be exothermic in nature. The negative values of the free energy change ΔG indicated the spontaneity of the adsorption process.

Table II Thermodynamic Parameters

Temp(K)	ΔE kJ/mol	ΔH kJ/mol	ΔS kJ/mol	ΔG kJ/mol
303	77.39	-20.4	-0.046	-6.38
323				-5.45
336				-4.85

Adsorption Kinetics

A number of models have been developed to describe kinetics of metal adsorption in batch experiments. Conformity between the experimental data and the model predicted values are expressed by correlation coefficients ($R^2 \approx 1$). Relatively high R^2 values for all the models tested indicated that the model successfully described kinetics of Cu(II) adsorption on UAC.

Lagergren's equation (pseudo 1st order)

It is expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (8)$$

Where,
q_e and q_t (mg/g) are the adsorption capacity at equilibrium and at time t respectively.
k_1 = Rate constant for pseudo 1st order adsorption process.

After integration and applying initial conditions ($t=0$ to $t=t$ at $q_t=0$ to $q_t= q_1$), integrated form of the above equation becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (9)$$

Plot of log (q_e- q_t) versus t should give a linear relationship from which k_1 and q_e can be determined from slope and intercept of the plot respectively[24]. The data was fitted to the above equation and k_1 and R^2(the correlation coefficient) values for the experiments are shown in Table III.

Ho and McKay Equation(Pseudo 2nd order)

The sorption kinetic model by Ho and McKay equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (10)$$

Where, k_2 =rate constant of Ho and Mc Kay equation (g/mg/min). For boundary condition ($t=0$ to $t=t$ at $q_t=0$ to $q_t= q_1$), integrated form of the above equation becomes

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (11)$$

This is integrated rate law for a pseudo 2nd order reaction. The above equation can be rearranged as :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \qquad (12)$$

The initial adsorption rate h(mg/g/min) is $h= k_2 q_e^2$. Then equation 12 becomes

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}(t) \qquad (13)$$

Plot by (t/q_t) and t will give a straight line from which q_e and k_2 can be determined from slope and intercepts respectively[25]. Cu(II) adsorption on UAC obeys pseudo second order kinetics in comparison to pseudo first order kinetics and is evidenced from R^2 values which is listed in Table III.

Table III Comparison of different constants (rate constants for pseudo 1st order kinetics and pseudo 2nd order kinetics, Morris-Weber equation and D.R. Isotherms) along with the R^2 values for different initial metal ion concentration and adsorbent concentration at pH 5.0 and temperature 30^0C.

Sl. No	Cu(II) a)	UAC b)	L-k_1 c)	L-R^2 d)	H-k_2 e)	H-R^2 f)	M-R_{id} g)	M-R^2 h)	D-R ln X'_m i)	D-R K′ j)	D-R R^2 k)	E kJ/mol l)
1	4	20	0.0184	0.84	1.973	0.996	0.005	0.99	-2.127	-0.094	0.71	2.3
2	10	20	0.1266	0.96	-1.784	0.995	0.030	0.93	-1.545	-0.527	0.90	0.8
3	15	20	0.0690	0.60	-1.328	0.997	0.103	0.84	-1.044	-2.268	0.83	0.5
4	20	20	0.0667	0.98	0.979	0.998	0.018	0.89	-1.978	-21.78	0.99	0.2
5	10	20	0.1266	0.96	-1.784	0.995	0.030	0.93	-1.545	-0.527	0.87	0.8
6	10	30	0.0253	0.96	1.049	0.997	0.013	0.93	-1.655	-0.115	0.62	2.1
7	10	40	0.0322	0.97	1.503	0.997	0.009	0.88	-2.406	-0.351	0.87	1.2
8	10	50	0.0644	0.98	2.828	0.998	0.003	0.80	-2.304	-0.139	0.84	1.9

a) Initial Cu(II) concentration , mg/dm^3
b) UAC, g/dm^3
c) Lagergren's equation (Pseudo 1st order kinetics), k_1 ,/min
d) Lagergren's equation (Pseudo 1st order kinetics) , R^2.
e) Ho & Mc-Kay equation (Pseudo 2nd order kinetics), k_2 , g./mg./ min
f) Ho & Mc-Kay equation (Pseudo 2nd order kinetics), R^2.
g) Morris- Weber equation, R_{id}
h) Morris- Weber equation , R^2
i) Dubinin-Radushkevich(D.R.) isotherm, ln X'_m , mg/g .
j) Dubinin-Radushkevich(D.R.) isotherm , K′, mol^2 k/J^2.
k) Dubinin-Radushkevich(D.R.) isotherm , R^2.
l) Dubinin-Radushkevich(D.R.) isotherm , E, kJ /mol.

Morris-Weber Equation

Intraparticle diffusion model and sorption kinetics of Cu(II) was examined by using Morris-Weber equation[26] as

$$q_t = R_{id}\, t^{1/2} \qquad (14)$$

Where, q_t = Sorbed concentration at time t; R_{id} = Rate constant of intraparticle transport, t= Time. R_{id} can be obtained from the slope of a graph plotted between q_t and $t^{1/2}$.The R_{id} for each experiments are shown in Table III. High R^2 value led to the conclusion that the intraparticle diffusion process is the rate limiting step. Higher R_{id} values indicate the higher rate of adsorption and better adsorption mechanism.

The Dubinin-Radushkevich(D.R.) isotherm

It assumes a heterogeneous surface and is expressed as

$$q_e = X'_m \exp(-K' \epsilon^2) \qquad (15)$$

Where,
ϵ= Polanyi potential =RT ln (1+ 1/C_e)
q_e= Amount of Cu(II) ions adsorbed per unit weight of adsorbent (mg./g)
X'_m = Adsorption capacity of the adsorbents (mg./g)
C_e = Equilibrium concentration of metal ions in solution (mg./dm^3)
K' = Constant related to adsorption energy (mol^2k/J^2)
R= Gas constant (kJ./K /mol)
T = Temperature (K)

In linear form, D.R. isotherm can be expressed as

$$\ln q_e = \ln X'_m - K'\epsilon^2 \quad (16)$$

A straight line would be obtained if $\ln q_e$ would be plotted against ϵ^2. Slope and intercept would give K' and X'_m values for different experiments, which are listed in Table III.

The mean adsorption energy (E, kJ/mol) can be obtained from K' values of the D.R. isotherm using the following equation.

$$E = (-2\,K')^{-1/2} \quad (17)$$

Adsorption energies were found to be within the range 0-2.5 kJ/ mol, suggested that physio sorption dominates the sorption mechanism[27].

Co-Ion effect

Other metal ions like Co, Ni, Zn, Pb, Cd may be present along with Cu in the drinking water. Therefore, co-ion effect was studied by adding different cations separately to the solution containing Cu to find out the influence of other metal ions over its sorption. These ions were considered as they are quite likely to be present in the waste water. The sorption reactions were carried out under the following conditions, metal ion concentration – 10 mg/dm^3(each), pH -5.0, adsorbent amount 20 g/ dm^3, solution volume – 0.1 dm^3, temperature 30^0C and time 60 minutes. It was observed that in presence of co-ions, % of Cu uptake on UAC decreased. % suppression in Cu(II) uptake was maximum in presence of Ni and follows a trend Ni > Zn > Co as shown in Figure 5. If x = % sorption of Cu(II) in absence of any other metal ions and y= % sorption of Cu(II) in presence of co ions. Then % suppression in sorption = 100-100(y/x).This may be due to the fact that Cu adsorbing sites present on UAC matches more with the Ni adsorbing sites and Cu adsorbing sites present on UAC are different from that of Co.

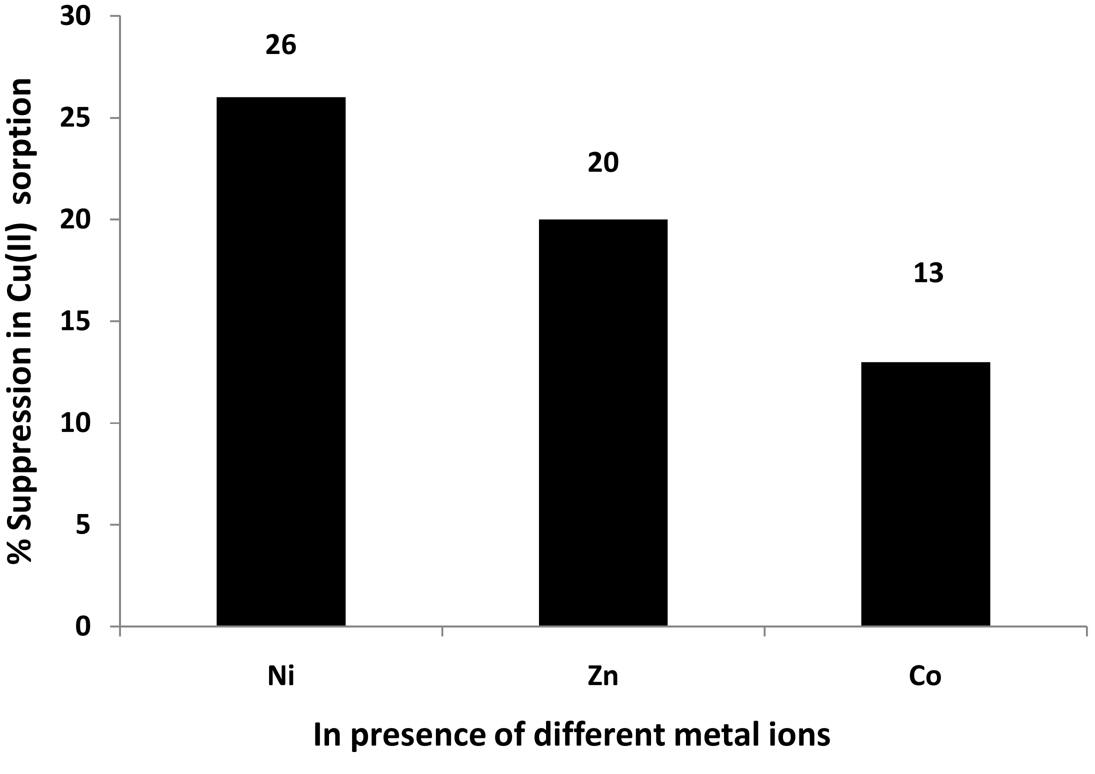

Figure 5 : % suppression in Cu(II) uptake in presence of co-ions

CONCLUSION

1. The optimum condition of Cu(II) uptake on UAC was found to be Time – 30 minutes, pH-5.0, Temperature - 40^0C.
2. The value of separation parameter (R_L) lies between 0.05 to 0.22 indicated the sorption to be favorable in nature.
3. The low activation energy (77.4 kJ/mol) indicated the ease of sorption reaction.
4. The negative values of enthalpy and free energy change suggested adsorption to be exothermic and spontaneous in nature.
5. The order of the reaction was found to be pseudo 2nd order in nature.
6. The adsorption kinetics was found to be controlled both by physio sorption as well as intraparticle diffusion.
7. The Cu(II) uptake was found to be suppressed in presence of Co-ions and follows a trend Ni>Zn>Co.

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REFERENCES

[1] J Aaseth; T Norseth. Hand book on the toxicity of metals , Vol. 101 , Elsevier, New York,**1986** ; 233.
[2] A Blanco ; B Sanz ; MJ Llama ; JL Serra. *J of Biotechnology,* **1999**, 69, 227.
[3] HS Lee ; JH Suh . *J.Chem.Eng.* **2000**, 17, 477.
[4] N Karapinar ; R Donat. *Desalination,* **2009**, 249,123.
[5] S Veli ; B Alyuz . *Journal of Hazardous Materials,* **2007**, 149, 226.
[6] K Bhattacharyya ; S Gupta . *Advance in colloid and interface science,* **2008** , 140 , 114.
[7] DH Kim ; MC Shin ; HD Choi ; CI Seo . *Desalination* , **2008**, 223 , 283.
[8] F Barbier ; G Duc ; H Petit-Ramel . *Colloids Surf. A: physiochem., Eng. Aspects* , **2000**, 166, 153.
[9] PA Brown ; SA Gill ; SJ Allen . *Water Res.* **2000**, 34 , 3907.
[10] PK Baskaran; BR Venkatraman; M Hema; S Arivoli. *J. Chem. Pharm. Res*. **2010**, 2(5), 642.
[11] R Prabakaran; S Arivoli; M Hema; C Kamatchi. *J. Chem. Pharm. Res*. **2011**, 3(5), 532.
[12] MV Subbaiah; G Yuvaraja; Y Vijaya; A Krishnaiah. *J. Chem. Pharm. Res*. **2011**, 3(2), 365.
[13] V Balakrishnan; S Arivoli; AS Begum; AJ Ahamed. *J. Chem. Pharm. Res*. **2010**, 2(6), 176.
[14] MM Rao; DHKK Reddy; P Venkateswarulu ; K Seshaiah. *J. Environ. Manage,* **2009**, 90, 634.
[15] I Sharma; D Goyal. *Journal of Scientific and Industrial Research,* **2009** , 68 ,640.
[16] http://en.wikipedia.org/wiki/Activated carbon (accessed on 24 October 2011)
[17] GM Burke; DE Wurster ; MJ Berg ; P Veng-Pedersen; DD Schottelius. *Pharmaceutical Research,* **1992**, 9 , 126.
[18] SP Mishra ; GR Chaudhury . *Hydrometallurgy* , **1996**, 40 ,11.
[19] R Malik ; DS Ramteke ; SR Wate. *Waste Management* , **2007** ,27, 1129.
[20] TW Weber ; RK Chakraborti . *J. AIchE.* **1974** , 20, 228.
[21] G McKay ; HS Blair. *J.Appl.Polymer Sci* , 1982, 27 ,3043.
[22] SP Mishra ; GR Chaudhury. *Int. J. Env. Studies,* **1996**, 50 , 117.
[23] J Berrueta ; JM Freige; G Adrio ; J Coca . *J. Solvent Extraction Ion exchange* , **1990**, 8, 817.
[24] C Namasivayam ; RT Yamuna . *Chemosphere,* **1995** , 30 , 561.
[25] TG Chuah ; A Jurmasiah; I Azni ; S Katayon . *Desalination,* **2005**, 175, 305.
[26] WJ Weber ; JC Morris . *Journal of Sanit. Eng,* Div(ASCE), **1963**, 89 , 31.
[27] BP Bering ; MM Dubinin; VV Serpinisky . *J. Colloid Interface Sci.,* **1972** , 38,185.