

PREPARATION OF CARBON SUPPORTED NICKEL CATALYST AND ITS ADSORPTION BEHAVIOUR FOR COPPER FROM AQUEOUS SOLUTIONS

T. YAMIN, *R. AHMED¹, M.S. ANSARI and M.M. CHAUDHRY²

Department of Chemistry, Quaid-e-Azam University, Islamabad, Pakistan

¹Fuel Cell Group, Chemistry Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan

²Pakistan Institute of Engineering and Applied Sciences, P.O. Nilore, Islamabad, Pakistan

Nickel catalysts have numerous industrial applications in hydrocarbon chemistry, hydrogenation of oil, fuel cells and many other areas. Addition of nickel to platinum supported on carbon increases the catalytic activity of platinum significantly for fuel cells. Graphite carbon of 100-mesh size was used for the preparation of nickel catalyst. Graphite was given acid treatments and dried. Nickel solution was added under an inert atmosphere, heated at 200°C and dried under vacuum at 100°C overnight. Method for the preparation of the catalyst is described. Copper is a pollutant and is also used in catalysts. Its adsorption on catalyst can be used for the evaluation of catalytic activity of catalyst and also for removal purposes. Adsorption behaviour of copper on the nickel catalysts was studied. Effect of pH, shaking time, loading capacity and adsorbent weight was investigated. The data was tested for Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms. The monolayer sorption capacity and adsorption constant related to the Langmuir isotherm are $(65 \pm 2) \times 10^{-5}$ mol g⁻¹ and $(12.3 \pm 0.6) \times 10^4$ L. mol⁻¹. The Freundlich constant 1/n and C_m are found to be 0.32 ± 0.2 and 0.12 ± 0.02 mmol g⁻¹ respectively. The mean free energy of copper adsorption on catalyst is 14.7 ± 0.3 kJ mol⁻¹ which indicates chemical sorption. The effect of temperature was studied and thermodynamic parameters ΔH, ΔS and ΔG were evaluated and found to be 34 ± 1 kJ mol⁻¹, 123 ± 3 J mol⁻¹ K⁻¹ and -2.7 ± 0.1 kJ mol⁻¹ for the adsorption of copper on nickel catalyst. The positive values of enthalpy (ΔH) and entropy (ΔS) and negative value of Gibbs free energy (ΔG) indicate the endothermic, entropy driven and spontaneous nature of sorption. Coating of nickel on graphite increases its catalytic activity significantly.

Keywords: Ni/C catalyst, Adsorption, Cu (II) ions, Kinetics, Thermodynamics.

1. Introduction

Nickel catalysts are being extensively used in energy and food industry. It has been used in hydrocarbon processing [1] including tar cracking, methane reforming and hydrogenation of oil [2]. It is also being used for the production of carbon nanotubes [3] and carbon fibers [4] by the decomposition of methane on the catalyst. Now it has been reported that addition of nickel to platinum can improve the activity of catalysts [5] for fuel cells by many times which can help in the commercialization of fuel cells. Fuel cell catalysts are prepared by depositing platinum, nickel and other metals on carbon supports. Copper is also being added to platinum for methanol fuel cells. Copper is essential element but becomes toxic at more than 1.0 mg/L levels [6]. Monitoring and speciation of copper in environmental samples is also important [7,8].

Studies about sorption of Cu have been done

* Corresponding author : riaz_ecfc@yahoo.com

on different materials including, soil [9] and on different types of adsorbents [10-12]. Any small change in physical characteristic of carbon will change the adsorption properties. Naturally available carbon powders are mostly of graphite type. Graphite carbon powders coated with catalyst metals are being used as catalysts in fuel cells [13]. Adsorption of some constituents on catalysts can change their efficiency. Thus it is useful to study the adsorption of copper on graphite coated with nickel which is a catalyst metal.

In this work the nickel coated graphite catalyst has been prepared and studies have been done for the sorption of copper (II) ions from aqueous solutions. Different adsorption isotherms, kinetics and thermodynamic parameters have been evaluated. Effect of Nickel coating on the adsorption properties of carbon has been investigated.

2. Experimental Details

2.1. Reagents

Chemicals and reagents used were of analytical grade or equivalent. Buffer solutions of pH 1-10 with ionic strength of 0.1M solutions of HCl, KCl, CH₃COOH, CH₃COONa, H₃BO₃ and NaOH for pH of 1-3, 4-6 and 7-10 were used respectively.

Carbon powder was prepared from commercially available graphite blocks. Graphite was of high purity. These were ball milled to get fine powders of 100 mesh size. The BET surface area of graphite was measured to be 11.35m²g⁻¹. The graphitic carbon powder was treated with Ni(NO₃)₂ · 6 H₂O to get it impregnated with Nickel [14]. Three percent Nickel was deposited on graphite.

2.2. Equipments

Polarographic analyzer 174A from Princeton applied research (PAR), New Jersey, USA, with an X-Y recorder model RE 0089 from Houston instruments was used for voltammetric measurements. The pH was adjusted using a pH-meter 605 from Metrohm, Switzerland. A hanging mercury drop electrode 303A from PAR was used with Ag/AgCl as a reference electrode and platinum wire as a counter electrode.

An atomic absorption spectrophotometer from Varian Model SpectrAA 300/400 Australia was also used. Wavelength selected was 324.7 nm with 0.5 nm slit width.

2.3. Analytical measurements

For Voltammetric measurement, the background electrolyte was 0.02 M HClO₄, initial potential -0.9V and deposition time 2.0 minutes. Modulation amplitude was 50mV, voltage range of 1.5V and scan rate of 10 mV/ sec were used. After deaeration and deposition for two minutes, stirring was stopped and after 20 sec. waiting time the potential was scanned in the positive direction. The copper peak appeared at -0.01 volts.

Atomic absorption spectrophotometer (Varian spectra AA300/400) was also used.

2.4. Sorption measurements

A known volume of solution (10ml) was taken in the tube and a known concentration of Cu (II) was

added and mixed thoroughly for voltammetric and atomic absorption measurements. The uptake of copper ions by graphite and nickel coated graphite was studied using batch techniques. Details of adsorption procedure employed were similar to those described elsewhere [16-17]. All experiments were performed at least in triplicate at 25± 2.°C or at a temperature specified otherwise. The percentage sorption and distribution coefficient (R_d) were calculated as

$$\% \text{Adsorption} = \frac{A_0 - A_e}{A_0} \times 100 \quad (1)$$

A₀ is the initial concentration and A_e after equilibration.

$$R_d = \frac{\text{Amount of metal on adsorbent}}{\text{Amount of metal in solution}} \times \frac{\text{Volume of solution (V)}}{\text{Weight of dry adsorbent (w)}} \text{ cm}^3/\text{g} \quad (2)$$

The percent sorption and R_d may be co-related using the following relationship.

$$\% \text{Sorption} = \frac{100R_d}{R_d + V/w} \quad (3)$$

The linear regression analysis was carried out on the statistical data for slope and intercept evaluation. The results are the average of at least triplicate independent measurements and precision in most cases is ± 5%.

3. Results and Discussion

Nickel supported on carbon catalyst was prepared. Sorption of copper ions on graphite carbon and the same carbon coated with nickel was investigated by optimizing different parameters including shaking time, pH, amount of adsorbent and concentration of adsorbate.

3.1. Preparation of nickel coated carbon catalyst

For the coating 10g commercially available carbon of mesh size ≤100 was first of all washed with a mixture comprising equal volumes of concentrated HCl and HF solutions followed by drying between 103 and 105 °C for 24 hours.

A 727 mg Ni(NO₃)₂ · 6H₂O solution in 75 mL H₂O was added to 5.00 g of the above treated carbon; Ni content in Ni(NO₃)₂ · 6H₂O as established by AAS and ICP technique was better than 92%.

Table 1. Effect of acids on the sorption of Cu(II) onto 100mg uncoated and coated graphite.

Sorptive medium	Conc. of Sorptive medium (N)	Carbon K_d ($\text{cm}^3 \text{g}^{-1}$)	Ni/ Carbon K_d ($\text{cm}^3 \text{g}^{-1}$)
HCl	0.001	158.5±1.4	196.5±1.4
	0.01	98.4±0.8	175.4±1.3
	0.1	60.2±0.5	112.2±1.1
HNO ₃	0.001	218.6±1.5	258.6±2.5
	0.01	187.5±0.9	227.5±2.9
	0.1	105.6±0.7	195.6±1.7
HClO ₄	0.001	267.4±2.4	269.4±2.4
	0.01	182.5±0.9	252.5±2.9
	0.1	92.6±0.7	212.6±2.7
Deionized water	----	219.8± 0.9	244.9± 2.9

The flask used in the above process was connected to an argon purged distillation set up wherein the contents were kept for 30 minutes under the argon flow. Later on water was distilled under continuous supply of argon in a temperature bath maintained between 175 and 180 °C.

After accomplishment of distillation, the flask was kept at temperature range between 180 - 210 °C for an additional 15 minutes. Upon cooling to ambient temperature, the black solid was twice washed with about 50 mL water under argon.

After vacuum drying at room temperature the contents were subsequently dried under low pressure at 100 °C for 18 hours.

According to the above procedure and employing the given amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, total nickel could be impregnated on 5g of carbon used as support (corresponding to 0.552 mmol Ni per g carbon or 3.2 weight percent Ni on the carbon).

3.2. Effect of acids

The sorption of copper (II) ions onto catalyst and carbon was investigated in deionized water, HCl, HNO₃ and HClO₄. The concentration ranges of acids are 0.001 to 0.1M and results are shown in Table 1. It is clear from the results that sorption increased with the decrease in acid concentration in all the three mineral acids. The sorption is more in deionized water. The sorption is more on coated graphite than graphite alone. Sorption of Cu (II) increased in oxidizing acids with maximum in HClO₄. It may be due to the creation of additional sites for sorption.

3.3. Effect of pH

The sorption of copper (II) ions on the catalyst and carbon was investigated using buffer solutions of pH 1-10. The parameters selected were $[\text{Cu}(\text{II})] = 4.82 \times 10^{-5} \text{ M}$, 100mg of adsorbents and shaking time 30 minutes. The results are shown in Figure 1. Maximum sorption takes place at pH 6 on uncoated carbon and at pH 4 for the nickel coated carbon.

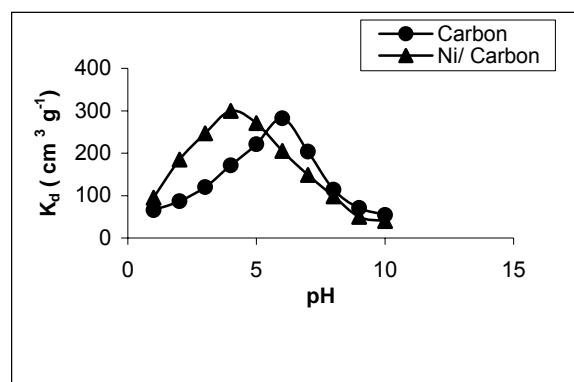


Figure 1. Effect of sorptive medium's pH on the sorption of Cu (II)

3.4. Influence of the amount of sorbent

The amount of sorbent affects the sorption, therefore, sorption of cadmium $4.82 \times 10^{-5} \text{ M}$ ions was monitored in the range of 20-300 mg/ 10ml of sorbents with shaking time of 30 minutes, the results are shown in Figure 2. The percent sorption increases with the increasing amount of the sorbent and the distribution co-efficient R_d decreases with an increase in the amount of the sorbent. Decrease in R_d with an increase in sorbent concentration is expected as the concentration of sorbent is in the denominator for the calculation of R_d value. After 100mg weight of sorbent no change was observed therefore, it was used for further studies.

3.5. Influence of equilibration time

Effect of shaking time was studied and plots of shaking time vs. distribution co-efficient are shown in Figure 3. It shows the variation of distribution co-efficient of ions onto Ni/C and graphite with shaking time using de-ionized water as a sorptive medium. This was done with 100 mg of Ni/C graphite for different intervals of time ranging from 1 to 60 minutes. It is evident from the plots that fifteen minutes shaking time is enough to obtain

maximum sorption and beyond fifteen minutes no further increase in sorption was observed. This data was used to study the kinetic behavior of sorption of Cu (II) ions.

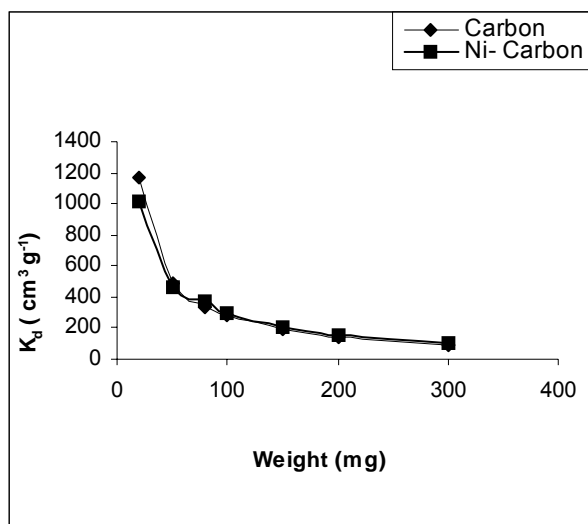


Figure 2. Effect of amount of adsorbent on the sorption of Cu (II).

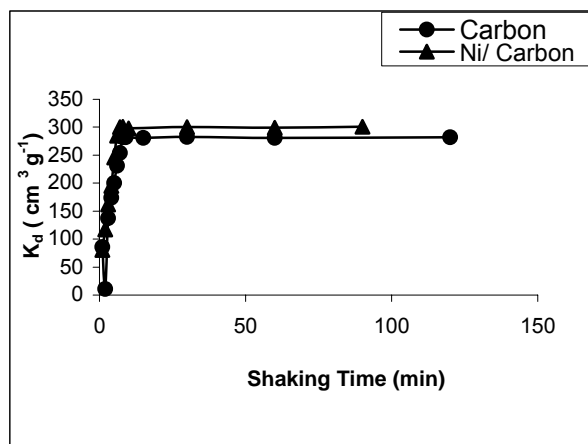


Figure 3. Effect of shaking time on the sorption of Cu (II).

3.6. Kinetic studies

The kinetic behavior was studied using different equations. The Morris–Weber equation was applied to see the kinetic behavior [18].

$$q_t = k_i \sqrt{t} \tag{4}$$

Where q_t is the amount of ion sorbed onto sorbate (mol g^{-1}) at time interval t and k_i is the rate of intraparticle diffusion in $\text{cm}^3 \text{g}^{-1} \text{min}^{-1/2}$. Linear plots were obtained.

To verify the intraparticle diffusion process the Reichenberg equation [19] was also applied

$$F = (1 - 6/\pi^2) e^{-Bt} \text{ or} \tag{5}$$

$$Bt = 0.4977 - \ln(1 - F) \tag{6}$$

$F = q_t / q_e$, where q_e is the sorbed concentration of sorbate at equilibrium

A plot of Bt vs. time for Cu (II) is shown in Figure 5. It is clear that intraparticle diffusion is the rate controlling step. Now in both cases of Morris–Webber and Reichenberg, the lines do not pass through origin. This shows that partial film diffusion is also occurring along with intraparticle diffusion.

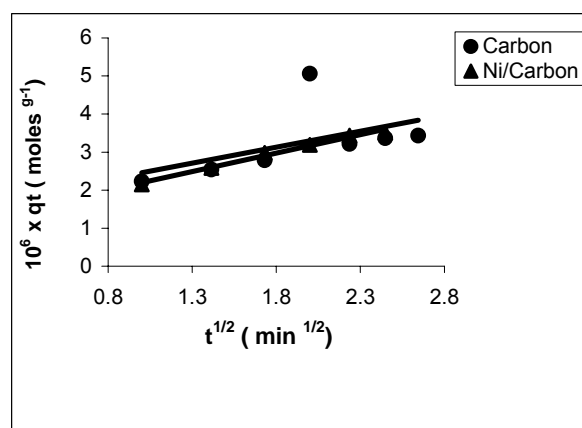


Figure 4. Plot of q_t vs. $(\text{time})^{1/2}$ for the sorption of Cu (II).

The kinetic data can also be interpreted by mass action phenomena. In this case the uptake of the solute by the sorbent follows the mass action process which assumes that sorption of the solute on the surface of the particle of sorbent is a first order reaction and can be verified by applying the Lagergren [20] equation.

$$\log(1 - q_t / q_e) = -k_1 t / 2.303 \tag{7}$$

or

$$\ln(1 - F) = -k_1 t \tag{8}$$

Where k_1 is the rate constant of the sorption process. The plot of $\ln(1 - F)$ vs. t for Cu(II) metal ions is shown in Figure 5. It is linear with correlation factors of 0.998 and 0.993 for both the adsorbents. This means that adsorption is a first order reaction with respect to the adsorbate concentration. The rate constants for adsorption of

Cu (II) from the slope of the lines of plots are 0.43 ± 0.02 and $0.53 \pm 0.04 \text{ min}^{-1}$ for graphite and coated graphite.

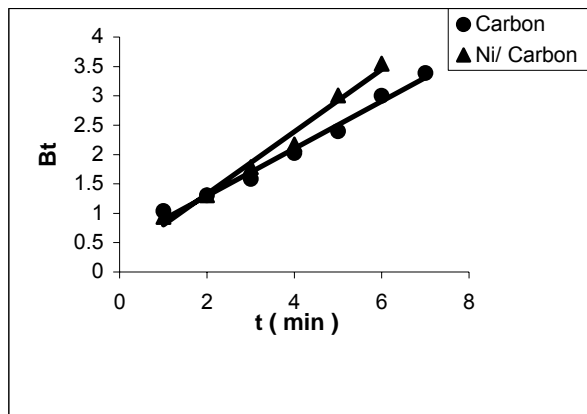


Figure 5. Plot of Bt vs time for the sorption of Cu (II).

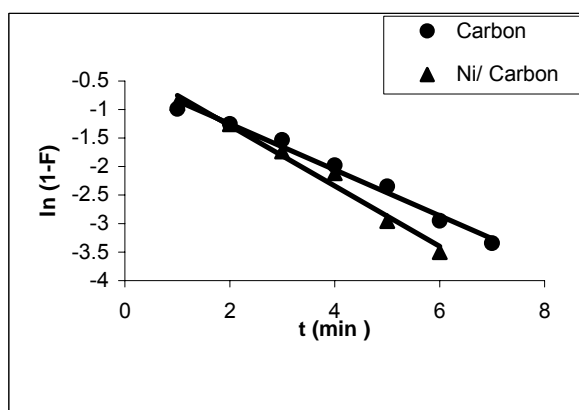


Figure 6. Plot of $\ln(1-F)$ vs. time for the sorption of Cu (II).

3.7. Effect of adsorbate concentration

The influence of ion concentration has been studied with 20 minutes shaking time on the adsorbents. The R_d vs. Cu (II) ion concentration curves are shown in Fig.7. These show a gradual decrease in sorption of Cu (II) with increase in metal ion concentration. The decrease of Cu (II) ions sorption with concentration may be due to the saturation of the active sites and availability of a lesser number of active sites. The sorption data was subjected to different isotherms.

The Freundlich isotherm suggests that sorption is not restricted to one specific class of sites and assumes surface heterogeneity. It does not predict saturation of the surface of sorbent by sorbate and thus infinite surface coverage is predicted

mathematically. The linear form of Freundlich isotherm [21] is shown as:

$$\log C_{\text{ads}} = \log C_m + 1/n \log C_e \quad (9)$$

Where C_{ads} and C_e are the amount of solute adsorbed (mol/ g) and in aqueous solution (mol L⁻¹) and C_m and $1/n$ are constants. Plots of $\log C_{\text{ads}}$ vs. $\log C_e$ are shown in Figure 7 which are linear. The values of $1/n$ and C_m are computed from the slope and intercept of the plot. The value of $1/n$ shows the heterogeneous nature of sorbent surface, the higher the fractional value the higher is the heterogeneity of the surface. The value of C_m represents the adsorbent capacity of the sorbent. The values of $1/n$ and C_m for graphite and coated graphite are 0.37 ± 0.02 , 0.32 ± 0.02 and 0.22 ± 0.04 , 0.12 ± 0.02 mmoles/ g. The adsorption capacity of catalyst is considerably higher.

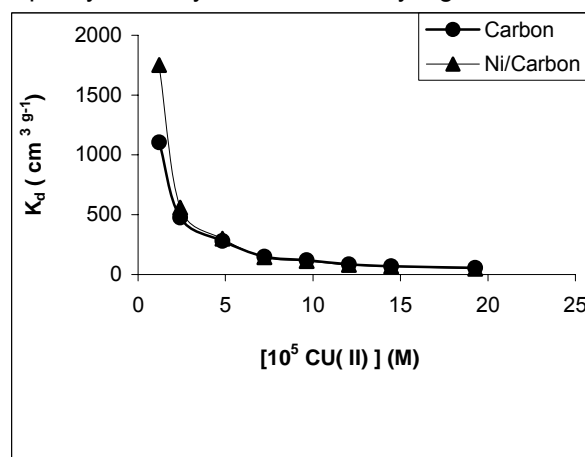


Figure 7. Variation of distribution coefficient with Cu (II) conc. For its sorption.

The Langmuir isotherm was applied to see whether the adsorption is monolayer or multilayer. The isotherm in the linear form [22] was applied.

$$C_e / C_{\text{ads}} = 1/M b + C_e / M \quad (10)$$

C_{ads} is the amount of cadmium ion adsorbed on the sorbates (mol g⁻¹), C_e is equilibrium metal ion concentration in solution (mol L⁻¹) M is constant related to the maximum amount of solute adsorbed and b is the constant related to the binding energy of the solute.

The graphs of C_e / C_{ads} vs. C_e are given in Figure-9 which are linear for graphite and coated graphite showing a reasonable presentation of the sorption isotherm. The numerical values of

constants M and b evaluated from the slope and intercept respectively for graphite and coated graphite are $74 \pm 2 \times 10^{-5}$, $65 \pm 2 \times 10^{-5}$ mole g^{-1} and $(8.1 \pm 0.8) \times 10^4$, $(12.3 \pm 0.6) 10^4$ L mol^{-1} . M is the value of saturation capacity and corresponds to the monolayer coverage and is therefore substantially independent of temperature. The adsorption capacity b is related to the enthalpy (ΔH) and should vary with temperature.

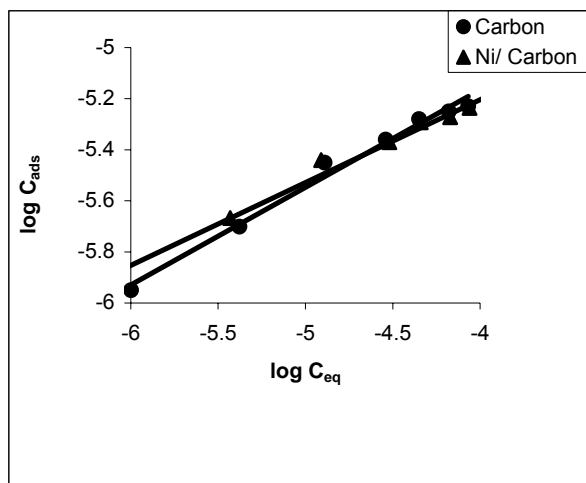


Figure 8. Freundlich's isotherm for the sorption of Cu(II).

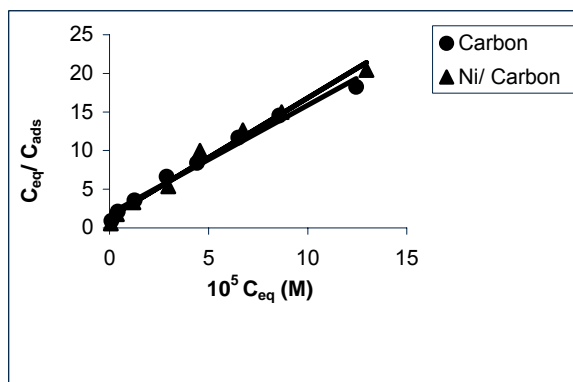


Figure 9. Langmuir's isotherm for the sorption of CU(II).

The D-R isotherm was applied to distinguish between physical and chemical sorption. It assumes that there are very small subregions of the sorption surface that are uniform in structure and energetically homogeneous. The linearized form of equation is [23].

$$\ln C_{ads} = \ln X_m - B\epsilon^2 \quad (11)$$

Where C_{ads} is the amount of metal ions adsorbed per unit mass of sorbent (mole g^{-1}) X_m is the maximum sorption capacity of sorbent (mole g^{-1}). B

is the constant with the dimension of energy mole² kJ^{-2} and ϵ is the polanyi potential given as

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

R is the gas constant in $kJ \text{ mole}^{-1}$, T is the absolute temperature in Kelvin and C_e is the equilibrium concentration of sorbate in solution (mole L^{-1}). The plots of $\ln C_{ads}$ vs ϵ^2 are shown in Figure 10 which are straight lines with a correlation factors of 0.994 and 0.996 for graphite and coated graphite.

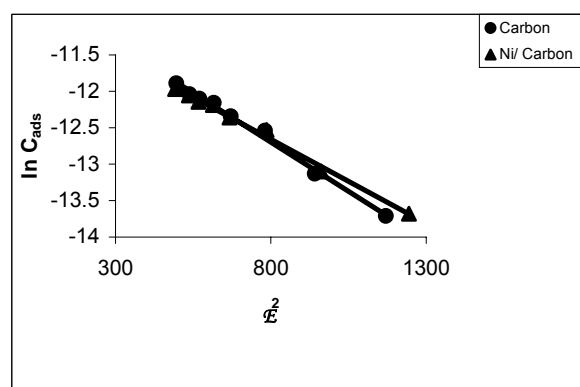


Figure 10. The D-R isotherm for the sorption of Cu(II).

It can be seen that the D-R isotherm is obeyed by graphite and coated graphite. The values of $D - R$ constants B and X_m were calculated from the slope and intercept of the graph. If the surface of the sorbent is heterogeneous in nature and a very small sub region of the sorption surface is assumed to be uniform in structure and energetically homogeneous, and an approximation to the Langmuir isotherm is chosen as the local isotherm then the quantity B can be related to the mean sorption energy E as

$$E = \frac{1}{\sqrt{-2B}} \quad (13)$$

Sorption energy E may be regarded as the free energy of transfer of one mole of solute from infinity (in solution) to the surface of sorbent. The numerical values of mean sorption energy E in the range of 1 to 8 $kJ \text{ mol}^{-1}$ show the physical adsorption and more than 8 as chemical adsorption respectively.

The values of B , X_m and E were calculated for graphite and coated graphite adsorbents and are -0.0027 ± 0.0001 , $-0.0023 \pm 0.0001 \text{ mole}^2 \text{ kJ}^{-2}$, 27 ± 2 , $20 \pm 1 \mu\text{mole s}^{-1}$ and 14.2 ± 2 , $14.7 \pm 0.3 \text{ kJ mole}^{-1}$.

The values of E show that cadmium metal ions are adsorbed predominantly by chemisorption. The values of E are higher for Ni/C followed by graphite which shows the better activity of catalyst.

The Freundlich adsorption isotherm gives maximum sorption capacity for both mono and multi layer coverage. The value of $1/n$ shows the percentage of similar active sites for the sorption of solute. The Langmuir isotherm shows the sorption capacity to the monolayer coverage and is lower than Freundlich. The D-R sorption capacity based on polanyi potential theory of solution is near to the Langmuir isotherm.

3.8 Thermodynamic studies

The influence of temperature on the sorption of Cu(II) ions on the sorbents was studied from 283-323 K. Temperature is an important factor for adsorption as it effects the sorption phenomena considerably. It was observed that sorption increases with temperature and is shown in Figure 11. The increase in sorption may be due to the acceleration of sorption steps including creation of more active sites and better transport and diffusion. The following relations may be used for the calculation of ΔG , ΔH and ΔS

$$\Delta G = \Delta H - T\Delta S \quad (14)$$

$$\Delta G = -RT \ln K_c \quad (15)$$

$$\log K_c = -\Delta H / 2.303 RT + \Delta S / 2.303 R \quad (16)$$

Where ΔH , ΔS , ΔG , K_c and T are the enthalpy, entropy, Gibbs free energy, adsorption equilibrium constant and temperature in Kelvin and R is gas constant.

A graph of $\log K_c$ vs. $1/T$ is shown in Figure 11 where $K_c = F / (1-F)$ and T is absolute temperature in Kelvin and F represents the fraction sorbed at equilibrium. Straight lines for both the sorbents were obtained. The values of ΔH and ΔS were calculated from the slope and intercept of (Figure 11) and are 35 ± 1 , $34 \pm 1 \text{ kJ mole}^{-1}$ and 125 ± 3 , $123.3 \pm 3 \text{ J mole}^{-1} \text{ K}^{-1}$ for graphite and Ni-graphite respectively. The values of ΔG were

calculated and are -2.56 ± 0.03 and $-2.7 \pm 0.01 \text{ kJ mole}^{-1}$ for graphite and Ni-graphite. The negative values of ΔG and positive value of ΔH show that adsorptions is spontaneous, endothermic and entropy driven.

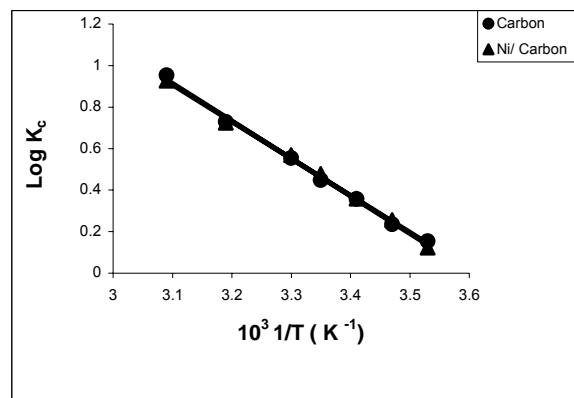


Figure 11. Plot of $\log K_c$ vs. $1/T$ for the sorption of Cu (II).

3.9. Effect of anions / cations on sorption

The influence of common anions, cations and complexing agents on the sorption of cadmium is important because of their competition for the sorption sites, association, dissociation and complex formation.

The effect of different anions on the sorption of Cu(II) ions is shown in Table 2. For cations Cr (III), Pb (II), Cl, and Br increase the sorption (Table 2).

4. Conclusions

Acids decrease sorption. Maximum sorption takes place from deionized water. More sorption takes place on nickel coated graphite than graphite. Adsorption can be used to estimate the catalytic activity of catalysts in aqueous systems. The kinetic studies suggest mostly intraparticle diffusion for both the adsorbents. Sorption of Cu (II) on coated and uncoated graphite follows Langmuir, Freundlich and D-R isotherms. Calculated values of adsorption energy confirm chemisorption for coated and uncoated graphite. The temperature variation has been used to calculate the values of ΔG , ΔH and ΔS . The negative values of ΔG and positive values of ΔH indicate spontaneous and endothermic nature of adsorption respectively. Ni/C can be used more effectively for the removal of copper from water. Influences of different anions and cations on adsorption have been studied.

Table 2. Effect of various ions on the sorption of Cu (II).

Other Ions present	Carbon $K_d(\text{cm}^3 \text{g}^{-1})$	Ni/ Carbon $K_d(\text{cm}^3 \text{g}^{-1})$
Sodium (Na^{1+})	285.36±2.25	295.36±2.15
Potassium (K^{1+})	283.45±2.15	293.45±2.05
Zinc (Zn^{2+})	487.5±4.85	459.7±4.78
Cadmium (Cd^{2+})	315.85±3.85	335.87±3.25
Magnesium (Mg^{2+})	297.58±2.95	287.58±2.25
Calcium (Ca^{2+})	357.60±3.75	327.60±3.65
Lead (Pb^{2+})	468.55±4.35	468.66±4.35
Chromium (Cr^{3+})	326.55±3.45	436.66±4.55
Uranium (U^{3+})	185.87±1.25	295.85±2.25
Selenium (Se^{4+})	128.34±1.55	288.34±1.58
Nitrate (NO_3) ¹⁻	280.35±2.15	305.39±3.35
Bicarbonate (HCO_3) ¹⁻	355.95±3.85	326.94±2.95
Chloride (Cl) ¹⁻	495.55±4.15	465.25±4.25
Bromide (Br) ¹⁻	235.65±2.35	335.68±2.95
Iodide (I) ¹⁻	185.65±1.25	225.67±2.24
Carbonate (CO_3) ²⁻	198.36±1.95	248.36±2.64
Sulphate (SO_4) ²⁻	355.55±3.45	375.54±3.43
Oxalate	255.95±2.45	298.98±2.35
Sulphide (S) ²⁻	270.85±2.50	356.87±3.51

References

- [1] M.A. Gerber, Review of novel catalysts for biomass tar cracking and methane reforming, U.S. Department of Energy Report. No. PNNL-16950 (2007)
- [2] Yan-Hwa Chu and Li-Hur. Lin, J. Am. Oil Chemists Society **68**, No. 9 (1991) 680.
- [3] L.C. Delzeit, V.Nguyen, B.Chen and R. Steven, J. Phys. Chem.B **106** (2002) 5629.
- [4] Y. Ju, F. Li and R. Wei, J. Natural Gas Chemistry **14** (2005) 101.
- [5] V.R. Stanenkovic, B. Fowler, B.S.Mun, G.Wang, P.N.Ross, C.A.Lucas, and N.M.Markovic. Science **315** (2007) 493.
- [6] H. G. Seilor, H. Sigel and A. Sigel, Handbook on Toxicity of Inorganic Compounds, New York: Marcel Dekker, Inc. (1988).
- [7] Viqar-un-Nisa, R. Ahmed and M. Muhammad, Toxicol. Environ. Chem. **87**, No. 1-4, (2005) 67.
- [8] A.S. A.Khan, R. Ahmed and M. L. Mirza Radiochim. Acta **95** (2007) 693.
- [9] J.G. Han Zhu, Y-L Liu, Y. Qian, G. Hu, J. Yan, M. J. Y. Chu, C-D, Wetland, Science **5**, No. 4 (2007) 356.
- [10] M. Ulmanu, E. Maranon, Y. Fernandez, L. Castrillon, I. Anger and D. Dumitriu, Water, Air and Soil Pollution **142** (2003) 357.
- [11] H. Aydin, Y. Bulut and C. Yerlikaya, Journal of Environmental Management **87**, No. 1 (2008) 37.
- [12] S. Kaur, T.P.S Walia, , R.K. Mahajan, Journal of Environmental Engineering and Science **7**, No. 1 (2008) 83.
- [13] G. Hoogers, (Ed.) Fuel Cell Technology Handbook, London: CRC Press(2003).
- [14] B. H. Lipshutz and S. Tasler, Adv. Synth. Catal. **343**, No. 4 (2001) 327.
- [15] R. Ahmed, T. Yamin, M. S. Ansari and S. M. Hasany, Radiochim. Acta. **94**, 441- 446 (2006).
- [16] R. Ahmed, T. Yamin, M.S. Ansari and S.M. Hasany, Ads. Sci. Technol. **24**, No. 6 (2006) 475.
- [17] M. M. Saeed, S. Z. Bajwa, M. S. Ansari and R. Ahmed, J. Chin. Chem. Soc. **54**, No. 1 (2007) 173.
- [18] W. J. Morris and J.C. Weber, J. Saint. Eng. Div, ASCE **89**, No. SA2 (1963) 31.
- [19] D. Reichenberg, J. Am. Chem. Soc. **75**, (1953) 589.
- [20] S. Lagergren, Theorie der sogenanten adsorption geloster stoffe K. Sven. Vetenskapsakad. Handl. **24** (1889) 1-39.
- [21] H. Freundlich, Colloid and Capillar Chemistry, London: Methuen. (1926) p.397.
- [22] I. Langmuir, J. Am. Chem. Soc. **80** (1918) 1361.