

Adsorption studies of cyanide onto activated carbon and γ -alumina impregnated with cooper ions

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ABSTRACT

In this research, adsorption of cyanide onto catalyst synthesized with activated carbon and γ -alumina used supported and cooper has been studied by means of batch technique. Percentage adsorption was determined for this catalyst in function of pH, adsorbate concentration and temperature. Adsorption data has been interpreted in terms of Freundlich and Langmuir equations. Thermodynamics parameters for the adsorption system have been determined at three different temperatures.

Keywords: Activated carbon; Alumina; Cyanide; Isotherms; Thermodynamic

1. INTRODUCTION

Waste water discharged by industrial activities is often contaminated by a variety of toxic or otherwise harmful substances which have negative effects on the water environment. For example, of metal finishing industry and electroplating units is one of the major sources of heavy metals such as (Zn, Cu, Cr, Pb etc.) and cyanide pollutants which contribute greatly to the pollution load of the receiving water bodies and therefore increase the environmental risk [1-4]. Cyanide present in effluent water of several industries. Cyanidation has dominated the gold mining industry. In view of the toxicity of cyanide, and the fact that cyanide is fatal in small dosages, authorities have been forced to tighten up plant discharge regulations. It is therefore vital to recover as much cyanide as possible, not only to meet standard requirements, but to strive towards obtaining lower levels of free cyanide (CN⁻) in tailing and plant effluent [4-8]. The solubility of gold in cyanide solution was recognized as early as 1783 by Scheel (Sweden) and was studied in the 1840s and 1850s by Elkington and Bagration (Russia), Elsner (German) and Faraday (England) [9]. Elkington also had a patent

for the use of potassium cyanide solutions for electroplating of gold and silver [9]. Cyanide is a singly-charged anion containing unimolar amounts of carbon and nitrogen atoms triply-bounded together. It is a strong ligand, capable of complexing at low concentrations with virtually any heavy metal. Because the health and survival of plants and animals are dependent on the transport of these heavy metals through their tissues, cyanide is very toxic. Several systems have been adopted for the reduction of cyanide in mill discharges. There are SO₂ assisted oxidation, natural degradation, acidification volatilization-reneutralization, oxidation and biological treatment. However, in the first three processes, cyanide reduction does not appear to meet the strict regulatory requirements, and as for the fourth process, it is limited to certain climate conditions. The next best process used, is the oxidation with hydrogen peroxide where the cyanide concentration is reduced to low enough levels, but this process requires an expensive reagent which cannot be reused [10-16]. Activated carbon was used for the removal of free cyanide from solution, but observed that copper-impregnated carbon yielded far better cyanide removal [17]. However, did not test other metal impregnated carbons or different metal loadings on the carbon. The use of a metal impregnated carbon system would therefore be more effective in reducing cyanide concentrations in solution. Due to the problem mentioned above, the study on using activated carbon in the removal of free cyanide is being done in our laboratory [18,19]. The adsorption onto activated carbon has found increasing application in the treatment of wastewater, as well as for the recovery of metals from cyanide leached pulps. Activated carbon has a great potential for cyanide waste treatment both in gold extraction plants and effluent from metal finishing plants and hence, it forms a subject studied in the present work. Characterization of activated carbon shows that surface area has an effect although the reactivity of the surface as a result of oxygenated functional groups, e.g.

carboxylate and phenolate is thought to be significant in the sorption of metal cations. Pore size distribution has been used to describe the internal structures and adsorption capacities of activated carbons [20]. The highly active surface properties of the activated carbon are attributed to the chemical functional groups and the internal surface areas, which typically range from 500 to 3000 m²/g [21]. The effect of copper was studied in the adsorption of cyanide onto activated carbon. It was found that the removal capacity was highly improved by the presence of copper [18-21]. It is the aim of this research to use of activated carbon (obtained from cassava peel) [22,23] and alumina impregnated with copper for obtain catalyst for the removal of cyanide for dilute solutions. The pertinent parameters that influence adsorption such as initial cyanide (CN⁻) concentration, agitation time, pH and temperature were investigated. Adsorption isotherms at three different temperatures (*i.e.* 283 K, 313 K, 323 K) have been studied. The adsorption data have been interpreted using Freundlich and Langmuir isotherms. Various thermodynamic parameters including the mean energy of adsorption have been calculated.

2. EXPERIMENTAL

All reagents used in the experimental work were of analytical grade (E.MERCK)® Argentmetric (largely AgNO₃) titrations were employed for CN⁻ determination [8]. Stock solution of cyanide (1000 mg.L⁻¹) was prepared by dissolving Sodium cyanide in distilled water. The concentration range of cyanide prepared from stock solution varied between 10 to 80 mg.L⁻¹.

2.1. Preparation of Catalysts

The activated carbon used in this study was prepared for by pyrolysis of cassava peel in presence of chloride zinc (chemical activities) by our research group. Cassava peel from Colombian Cassava cultivars were impregnated with aqueous solutions of ZnCl₂ following a variant of the incipient wetness method [22,23] with a specific surface area of 1567 m².g⁻¹.

One of them was obtained commercial (Sasol™) sample of γ -alumina.

2.1.1. Impregnation

Catalysts (activated carbon with copper was labeled Cu-AC and γ -alumina with copper was labeled Cu-A) were formulated using a solution of Cu(NO₃)₂.3H₂O (5 wt.%) Cu) as a precursor of the active agent because of its water solubility, lower cost, and lack of poisonous elements. Activated carbons from cassava peel and γ -alumina were used as supports. There are two well known methods of loading the metal precursor on the support: incipient wetness impregnation and soaking method. In

this case, the second one was used; the activated carbon and γ -alumina were soaked in a copper nitrate solution for 8 days under agitation until the equilibrium was reached. The ratio solid/solution (weight base) was equal to 6. The impregnated solids were filtered and stirred during 24 hours. Then, they were dried at 378 K for 24 hours 12.

2.1.2. Thermal Treatment

The objective of this step is to transform the copper salt (cupric nitrate) in copper oxides, which are the active catalytic agents. The high temperature used decomposes the nitrate releasing nitrogen oxides. The reactor must work in a nitrogen atmosphere to avoid the combustion of the support. The catalysts were treated in the activation reactor, at 830 K for 24 hours. After that, a nitrogen flow was maintained until the reactor reached room temperature 12.

2.2. Characterization

Nitrogen adsorption-desorption isotherms were performed using an Autosorb-3B (Quantachrome) equipment. Samples of 0.100 g were oven-dried at 378 K during 24 hours and outgassed at 473 K under vacuum for 10 hours. The final pressure was less than 10⁻⁴ mbar. Textural parameters were derived from adsorption data. The specific BET surface area was estimated 15. The specific total pore volume (V_T) was determined from the adsorption isotherm at the relative pressure of 0.99, converted to liquid volume assuming a nitrogen density of 0.808 g.cm⁻³. The specific micropore volume (V_{DR}) was determined using the Dubinin-Radushkevich mode 116. The pore size distribution (PSD) was analyzed using the BJH method [17,21-24].

Acidity and basicity determinations of the support were made by titrating the acid sites with a strong basic solution and the basic sites with a strong acid solution, following the protocol detailed by Giraldo *et al.* [22,23].

The point of charge zero (PZC) of the catalyst were determined for a procedure very similar [24], which are described here. In a beaker were added 0.1 g of finely ground catalyst in an agate mortar and 20 mL of a 0.01 M KCl-0.004 M KOH. The solution was kept under constant stirring for 48 h. Then, titration was performed with a 0.1 M HCl solution using a burette and a stream of nitrogen to prevent carbon dioxide from the air is absorbed into the solution and the formation of CO₃⁻² and HCO₃⁻¹. The titrant solution was added slowly 0.1 mL and was recorded by adding the aggregate volume and pH of the solution. Furthermore, the evaluation was carried 0.01 M solution of KCl-0004 KOH under the same conditions but without catalyst. The PCC of the catalyst was determined by plotting the pH of the solution against the volume of titrant solution to the solution without

catalyst and the catalyst solution, the pH where these two curves intersect corresponds to the PZC. Another way interpret experimental data is to calculate the burden of surface of the catalyst using the equations reported in literature [24], in this case the pH at which the burden of surface is zero corresponds to the PZC.

Studies of X ray diffraction (XRD) patterns were recorded at room temperature using a Rigaku diffractometer operated at 30 kV and 20 mA, employing Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm). The crystalline phases were identified employing standard spectra software.

2.3. Adsorption Studies

The adsorption of CN⁻ on activated carbon and γ -Alumina impregnated with Cu was studied by batch-technique [9]. The general method used for these studies is described below: A known weight (*i.e.*, 0.5 g of the Cu-AC or Cu-A) was equilibrated with 25 cm³ of the spiked cyanide solution of known concentrations in Pyrex glass flasks at a fixed temperature in a thermostated shaker water bath for a known period of time (*i.e.* 30 minutes). After equilibrium the suspension was centrifuged in a stoppered tube for 5 minutes at 4500 rpm, was then filtered through Whatman 41 filter paper. All adsorption experiments except where the pH was varied were done at pH 7.20, which was obtained naturally at solution to adsorbent ratio of 50:1. To study the effect of pH, in one set of experiments the pH of the suspensions was adjusted by using NaOH/NH₄OH and HNO₃. The pH of solutions was in the range of 3.0-12. The amount of cyanide adsorbed, "X" and the equilibrium cyanide concentration in the solution, "C_e" was always determined volumetrically with standard silver Nitrate solution. Adsorption of cyanide on Cu-AC and Cu-A was determined in terms of percentage extraction. Amount adsorbed per unit weight of the Cu-AC or Cu-A, X/m was calculated from the initial and final concentration of the solution, Adsorption capacity for the adsorption of cyanide species has been evaluated from the Freundlich and Langmuir adsorption isotherms were studied at three different temperatures (*i.e.* 283 K, 313 K, 323 K). The cyanide concentration studied was in the range of 10 ppm to 80 ppm for 50:1 solution to the catalyst.

3. RESULTS AND DISCUSSIONS

3.1. Characterization

Nitrogen adsorption-desorption isotherms for the supports and catalysts are shown in **Figures 1** and **2**. The textural parameters modeled from the adsorption data are summarized in **Table 1**.

Both catalysts present lower surface area and pore vo-

lume compared to that of the corresponding support. This is mainly due to a pore blocking effect, especially micropores, which is evident from the analysis of the uptake at low relative pressures in the adsorption-desorption isotherms for the catalysts compared to the supports. The micropore volume and surface area using activated carbon is higher than that obtained from γ -alumina, as the total pore volume for both materials.

The isotherms corresponding to both catalysts present

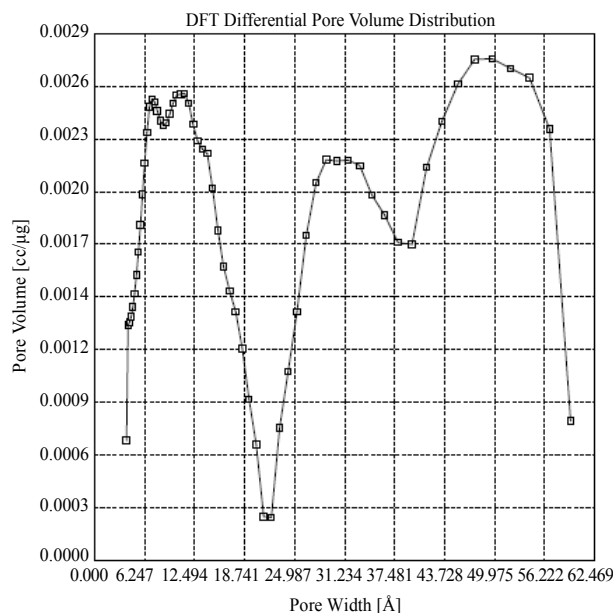


Figure 1. Pore distribution for Cu-AC.

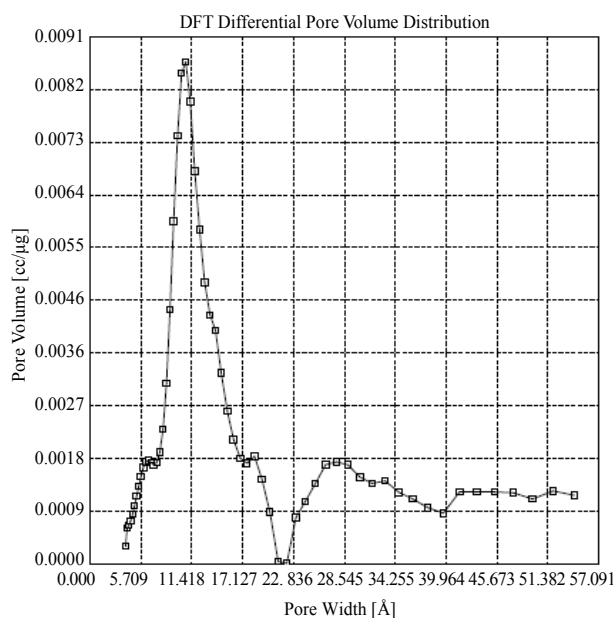


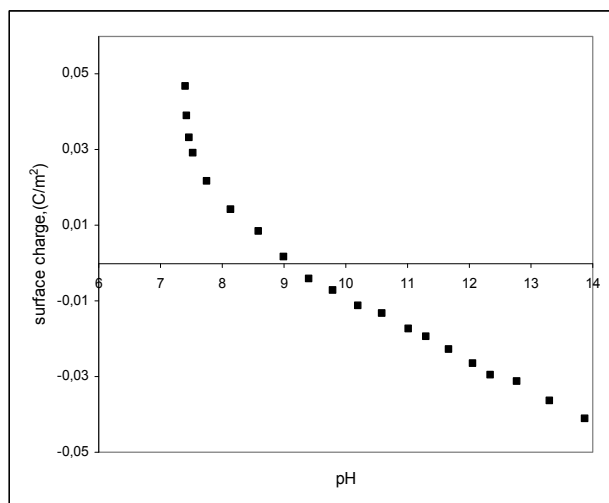
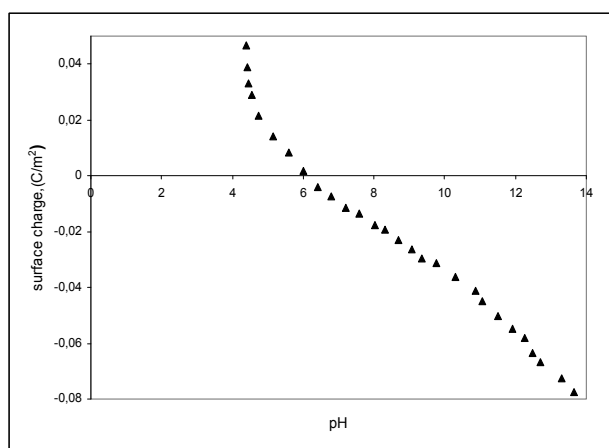
Figure 2. Pore distribution for Cu-A.

Table 1. Textural parameters of catalyst.

Sample	BET surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume (V_T) ($\text{cm}^3 \cdot \text{g}^{-1}$)	Specific micropore volume (V_{DR}) ($\text{cm}^3 \cdot \text{g}^{-1}$)
AC	1567	0.6641	0.6245
Cu-AC	1245	0.5478	0.6042
γ -Alúmina	245	0.2454	-
Cu-A	207	0.2087	-

a hysteresis loop. The uptake at high pressure rises significantly for Cu-A, which indicates a considerable presence of mesoporous. The BJH pore size distribution (**Figures 1 and 2**) shows important mesoporosity in the range of 40-90 Å for both catalysts, especially in Cu-AC, in agreement with its hysteresis loop.

Figures 3 and 4 show the curves obtained in the point of zero charge determinations using the mass titration method. All these results, pH, acidity, basicity and pzc,

**Figure 3.** PZC for Cu-A catalyst.**Figure 4.** PZC for Cu-AC catalyst.

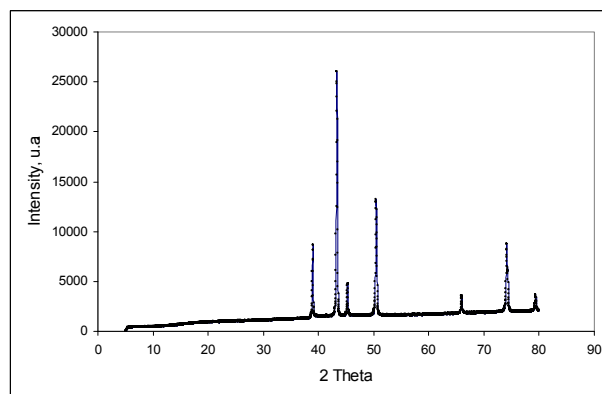
demonstrate that the surface of both supports are strongly basic (**Table 2**).

The X Ray diffraction patterns for both catalysts, Cu-AC and Cu-A respectively are shown in **Figures 5 and 6**. The profiles obtained show that the main oxidized metal compound corresponds to CuO. The signals of Cu_2O and Cu are also present in the spectra, specially the last one. The presence of CuO was expected because the metal appears as divalent ion in the precursor salt. The reduced species (Cu^+ and Cu) could be produced by the reducing action of the carbon surface during the thermal treatment at high temperatures.

The adsorption of cyanide on the catalyst Cu-AC and Cu-A were studied as a function of shaking time in water Bath shaker (Labconco 3535 US), pH, adsorbate concentration and temperature for known cyanide concentration at 313 K. The results are interpreted in terms of percentage adsorption. The variation of % adsorption with different intervals of time ranging from 2 minutes to 48 hours is illustrated by **Figure 7** which shows that the adsorption of cyanide at 25 ppm as well as 50 ppm concentration on Cu-AC and Cu-A is rapid at 313 K and equilibrium reached instantaneously after mixing cya-

Table 2. Physicochemical characteristics of the catalyst.

Support	pH	Acidity ($\text{mmol} \cdot \text{g}^{-1}$)	Basicity ($\text{mmol} \cdot \text{g}^{-1}$)	pH_{PZC}
Cu-AC	8.6	0.27	0.81	9.0
Cu-A	5.8	0.20	0.45	6.0

**Figure 5.** DRX for Cu-AC catalyst.

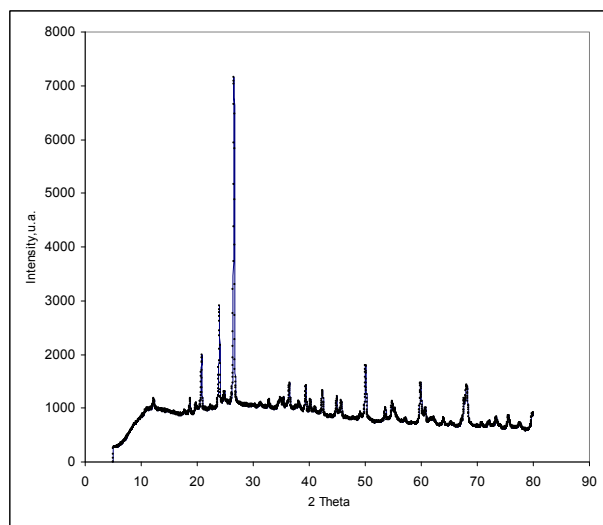


Figure 6. DRX Cu-A catalyst.

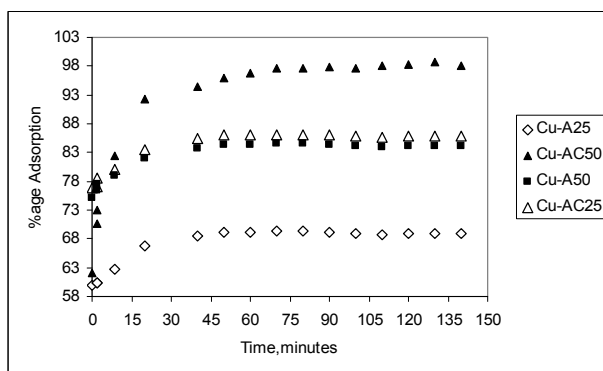


Figure 7. Effect of shaking time % age Adsorption at 25 ppm and 50 ppm for the synthesized catalyst.

nide solution with the catalyst. However, an equilibrium is reached faster with the catalyst of Cu-AC than with Cu-A; that is associated with the greatest amount of copper that is achieved on the activated carbon adsorb taking into account their surface properties and specific chemical the PZC allowing CN ions adsorb more rapidly on the catalyst surface Cu-AC on the Cu-A.

No significant change in % adsorption values was observed up to 48 hours, which indicates that surface precipitation as well as ion exchange may be the possible adsorption mechanism. Therefore, equilibrium time of 20 minutes was selected for all further studies. The adsorption is pH dependent, a much greater adsorptive capacity for cyanide was observed in neutral solution for both catalyst; moreover it is more higher adsorption capacity for Cu-AC, *i.e.*, pH 7- 8.0 (Table 3 and Table 4).

Because when the pH is reduced, surface charge of the particles becomes increasingly positive and because of the competition of the hydrogen ions for the binding sites,

Table 3. Dependence of absorbance concentration relative to CN⁻ on Cu-A catalyst at 293 K.

pH	Amount of CN ⁻ in taken (ppm)	Amount of CN ⁻ in sol. At equilibrium (ppm)	Amount of CN ⁻ Adsorbed (ppm)	Adsorption (%)
2,06	20	6,48	13,52	67,60
4,57	20	5,44	14,56	72,80
6,54	20	4,11	15,89	79,45
7,28	20	2,13	17,87	89,35
9,14	20	4,11	15,89	79,45
11,34	20	6,55	13,45	67,45
12,75	20	7,76	12,24	61,20

Table 4. Dependence of absorbance concentration relative to CN⁻ on Cu-AC catalyst at 293 K.

pH	Amount of CN ⁻ in taken (ppm)	Amount of CN ⁻ in sol. At equilibrium (ppm)	Amount of CN ⁻ Adsorbed (ppm)	Adsorption (%)
2,06	20	5,35	14,65	73,25
4,57	20	3,34	16,66	83,30
6,54	20	1,23	18,77	93,85
7,28	20	0,99	19,01	95,05
9,14	20	2,02	17,98	89,90
11,34	20	4,66	15,34	75,70
12,75	20	5,55	14,45	72,25

metal ions tend to desorb at low pH region, as well a small decrease in cyanide adsorption was observed at pH higher than 9.0. This behavior may be due to the formation of soluble cyanide complexes, which remain in solution as dissolved component. Similarly adsorption of cyanide as a function of its concentration was studied by varying the metal concentration from 10ppm to 80 ppm, % age adsorption values decreases with increasing metal concentration (Table 5), which suggest that at least two types of phenomena (*i.e.* adsorption as well ion-exchange) taking place in the range of metal concentration studied, in addition less favorable lattice positions or exchange sites become involved with increasing metal concentration.

The adsorption in aqueous solutions and adsorption isotherms at three different temperatures (*i.e.* 278 K, 298 K, 323 K) were obtained by plotting the amount of cya-

Table 5. Dependence of adsorbate concentration relative to CN⁻ on Cu-AC (this catalyst present major adsorption).

Amount of Adsorbent CN ⁻ in taken (mg)	Amount of CN ⁻ taken (ppm)	Amount of CN ⁻ in soln. at Equilibrium (ppm)	Amount of CN ⁻ Adsorbed (ppm)	Adsorption (%)
500	5,00	2,42	2,58	51,60
500	10,00	3,12	6,88	68,00
500	20,00	1,41	18,52	92,60
500	40,00	15,65	30,35	75,88
500	60,00	37,98	38,44	64,06
500	80,00	41,09	38,91	48,63
500	100,00	54,58	45,42	45,42

nide adsorbed on Cu-A and Cu-AC (mg/g) against metal at equilibrium concentration “Ce” (mg/l). Adsorption of cyanide decreases with increasing temperature. Two models, Langmuir and Freundlich equations, were used to describe experimental data for adsorption isotherms.

The linear form of the Freundlich isotherm model is given by the following relation:

$$\log x / m = \log K_F + 1 / n \log C_e \quad (1)$$

where x / m is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), and K_F and $1 / n$ are the Freundlich constants related to adsorption capacity and adsorption intensity respectively, of the sorbent. The values of K_F and $1/n$ can be obtained from the intercept and slope respectively, of the linear plot of experimental data of $\log X / m$ versus $\log C_e$. The linear form of the Langmuir isotherm model can be represented by the following relation:

$$C_e / x / m = 1 / K_L V_m + C_e / V_m \quad (2)$$

where V_m and K_L are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and slope of the linear plot of experimental data of $C_e / X / m$ versus C_e . The Freundlich and Langmuir adsorption isotherms are shown in **Figure 3** and **Figure 4** (the isotherms linearized not shown here). The related parameters of Langmuir and Freundlich models are summarized in **Table 6**. The results reveal that both the Langmuir isotherm model adequately describes better the adsorption data (See **Figure 8**).

Calculations of thermodynamic parameters:

Thermodynamic parameters such as Gibbs free energy ΔG° (kJ/mol), change in enthalpy ΔH° (kJ/mol) and change in entropy ΔS° ($J \cdot K^{-1} \cdot mol^{-1}$) for cyanide adsorption were calculated from the distribution constant K [10] by using the following relations:

$$\Delta G^\circ = -RT \ln K \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - \quad (4)$$

and

$$K = -\Delta H^\circ / RT + \text{Constant} \quad (5)$$

Tables 7 and **8** show the values of thermodynamics parameters ΔH° , ΔS° , ΔG° for Cu-AC and Cu-A catalyst synthesized. The positive value of $\Delta H^\circ = 6.234$ kJ/mole for Cu-AC and 4.897 kJ/mole, which is calculated from **Eq.5** and **Figure 5**, confirms the endothermic nature of the overall adsorption process. The positive value of ΔS° suggests increased randomness at the solid/solution interface with some structural change in the adsorbate and adsorbent and also affinity of the Cu-AC and Cu-A towards CN^- ; the values more highest of entropy indicate spontaneous process. A negative value of ΔG° indicates

Table 6. Parameters of Langmuir and Freundlich for adsorption of cyanide.

	Langmuir			Freundlich		
	Q_0	K	R^2	K_f	n	R^2
Alumina	221,9725	0,018648	0,99835	7,431714	1,477998	0,99653
Activated Carbon	226,7673	0,029620	0,99781	11,98697	1,628459	0,99330
Cu-A	317,2252	0,041956	0,99700	22,77397	1,759936	0,98713
Cu-AC	297,2679	0,164927	0,99646	58,15241	2,573350	0,97419

Table 7. Values of thermodynamic data for Adsorption of CN-on Cu-AC.

Temperature K	ΔH° kJ/mol	ΔG° kJ/mol	ΔS° J/K.mol
278	6.234	-8.856	0.0543
298	6.234	-6.636	0.0432
323	6.234	-12.666	0.0585

Table 8. Values of thermodynamic data for Adsorption of CN-on Cu-A.

Temperature K	ΔH° kJ/mol	ΔG° kJ/mol	ΔS° J/K.mol
278	4.897	-6.863	0.0423
298	4.897	-6.963	0.0398
323	4.897	-10.183	0.0467

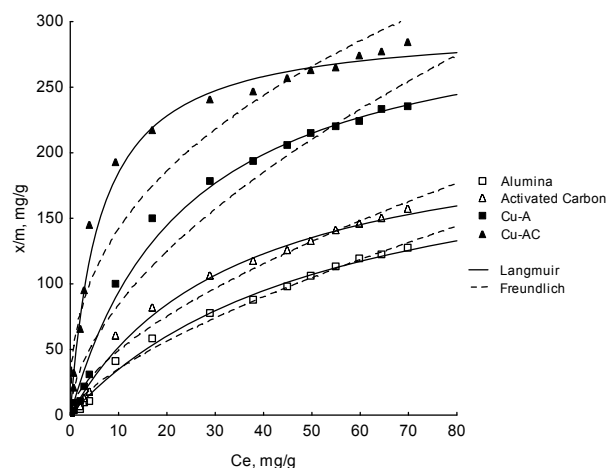


Figure 8. Langmuir and Freundlich models adjustment at 298 K.

the feasibility and spontaneity of the adsorption process, where higher negative value reflects a more energetically favorable adsorption process. The process of adsorption Cu-AC is more favorable.

4. CONCLUSIONS

Keeping the adsorptive nature of Cu-AC and Cu-A in view it is felt desirable to select batch adsorption process for removal of Cyanide from the industrial wastewater using activated carbon and γ -alumina. The main advantages of the procedure are:

- 1) The cost of starting materials for obtaining the catalyst is low and easily available in country.
- 2) Ease and simplicity of preparation of the catalyst due to non-corrosive and non-poisonous nature of activated carbon and alumina.
- 3) Rapid attainment of phase equilibration and good enrichment as well fitting of adsorption data with Langmuir isotherms.
- 4) The positive value of ΔH° and negative values of ΔG° indicate the endothermic and spontaneous nature of the adsorption process.

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