REMOVAL OF CYANIDE FROM AQUEOUS MEDIA BY ADSORPTION USING AL-ACTIVATED CARBON: PARAMETRIC EXPERIMENTS, EQUILIBRIUM, KINETICS, AND THERMODYNAMIC ANALYSIS

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ABSTRACT

The isotherm modelling study on adsorption of cyanide onto Al-AC was carried out by accompanying batch experiments at an initial concentration of 10–100 mg/l. The effect of dose, pH Time, Temperature of solution, and the initial concentrations of cyanide on adsorption performance was examined. Five equilibrium isotherm models for adsorption studies were measured. The experimental data are better fitted by Redlich-Peterson and Fritz-Schlunder model. It was also found that three parameter model indicate a better fit than two parameter model. Kinetic models comprising pseudo-first order, pseudo-second order and intraparticle diffusion were confirmed to fit the kinetic data. Pseudo-second order was found to be reliable with the experimental data and surface diffusion was found rate limiting step for cyanide adsorption. Thermodynamic studies indicated that the cyanide adsorption onto Al-AC as spontaneous and endothermic in nature.

Keywords: Cyanide, Isotherm Modelling, Kinetic Modelling, Process Parameters, Thermodynamic Modelling.

I. INTRODUCTION

All form of cyanide are categorized as toxic materials with chronic and/or acute features of poisonousness [1-3]. The waste water produced in metal finishing processes and gold and silver leaching mainly contain cyanides and cyanide-related complexes at several levels [4-6]. These compounds are the stringently controlled compounds widespread since of their great toxicity. Cyanide is produced as effluent from industries like, paint and ink formulation, coke plant, , explosive manufacturing, petroleum refining case hardening, pesticides industries ,chemicals, and synthetic, fiber manufacture units, etc. [7-10]. Treatment of cyanide, earlier to discharge, is essential to come across environmental limits. The permissible limit of cyanide in effluent according to United States (U.S.) health service cites is 0.2mg/L as [7]. For cyanide, Central Pollution Control Board (CPCB),India has fixed a minimal national standard (MINAS) limit in effluent as 0.2 mg/L and U.S. Environmental Protection Agency (USEPA) standard for drinking waters about total cyanide are 200 ppb[10-12]. Numerous treatment methods such as: chemical and biological oxidation and precipitation have been used for the removal of cyanide levels in effluents in acquiescence with environmental guidelines advantages [9,13,14]. Each of the overhead treatment methods has their specific and limitations. Treatment of cyanide from waste waters by adsorption onto

granular activated carbon has established great consideration [15].The adsorptive characteristics of activated carbons outcome from their great degree of surface reactivity and more surface area. The high surface area comparative to the actual particle size of activated carbon creates it easy to eliminate great amounts of toxic elements from liquid solutions [15-17]. Moreover, granular activated carbon has no drawbacks of further treatment technologies such as complexity of monitoring process, hazardous reagents and consuming expensive and generating harmful residues [15].The important step to optimize and design an adsorption process is finding an suitable isotherm for demonstrating the equilibrium condition of an adsorption process. Similarly, adsorption kinetics is also very applicable because it provides useful facts in the reaction pathway, adsorption mechanism of adsorbate and rate of adsorption [18-19].

In this current study, the potential of aluminium impregnated granular activated carbon for the elimination of cyanide from aqueous solutions was calculated. The effects of pH, adsorbent dosage, time, temp, and initial concentration of cyanide were observed. Since their major significance for the proposal of an adsorption process, equilibrium, kinetics and thermodynamic parameters for the elimination of cyanide were also determined.

II. MATERIALS

All chemicals used in this study were of (AR) analytical grade and obtained from Himedia Laboratories Pvt. Ltd. Mumbai India. 100mg/l Stock solution of cyanide was prepared by dissolving NaCN in millipore water (Q-H2O, Millipore Corp. with resistivity of 18.2 MX-cm) whose pH was pre-adjusted to 10 using 1N NaOH.

2.1 Preparation of Metal-Impregnated Activated Carbons

Earlier to the use in the experimentations, the granular activated carbon was wash away with double distilled water and treated with acid (1% HCL) For treatment of acid, the adsorbent was carefully washed with water prior to heat treatment in an oven for 30 min maintained at 600 °C. Subsequent activated carbon was impregnated with aluminium by using the succeeding procedure. The aluminum impregnation of adsorbent samples was achieved by 100 g of oven dried sample is treated with aluminum sulphate solution comprising 3% Al^{+3} in 1:3 proportion of solid to liquid. The aluminum impregnation was accomplished at 60 ^{0}C. The pH of solution was maintained at 5 because precipitation was found above pH 5 until the comprehensive evaporation was detected followed by drying at 110 ^{0}C for 24 h. The dried adsorbent was washed several time with Millipore water until the liquid was free from Al ions and then dried to constant weight. The final dried product was used to carry out for further batch experimentation.

2.2 Batch Experiment

The stock solution of cyanide with 100 mg/ L was prepared by dissolving anhydrous NaCN in 1 liter of distilled water. Experimental test solution of 30 mg/l cyanide concentration was prepared from dilution of stock solution. All batch adsorption experiments were carried out 250 mL round bottom flasks at 125 rpm in an incubator cum orbital shaker (Metrex,MO-250, India) with 100mL synthetic cyanide aqueous solution. At the end of preferred contact time, the flasks were detached from the shaker, and permitted to stand for 10 min to settle out adsorbent. Then, samples were filtered using Whatman filter paper Cat No. 1001 125 and filtrate was analyzed for cyanide concentration by colorimetric picric acid, described in the Standard Methods of Examination of Water and Wastewater [20]. Batch study was accompanied to define the optimum conditions. The effects of pH, adsorbent

dose, contact time, temp., and initial cyanide concentration on adsorption were calculated by changing pH, dose, contact time, temp, and concentration, respectively. The experimental conditions are shown in Table 1. The effect of pH on cyanide was calculated by regulating the pH of solution using 0.1 N NaOH or 0.1 N HCl on fixed amount of adsorbent.

All experiments were accompanied in duplicate and average results were reported. The Percentage removal and uptake at time t and equilibrium sorption capacity of phenol and cyanide were determined by the following equations (1-3):

$$Percent\ Rmeoval = (C_i - C_f)/C_i \times 100 \quad (1)$$

$$Q_t = (C_i - C_t)V/M \quad (2)$$

$$Q_{eq} = (C_i - C_{eq})V/M \quad (3)$$

Where: Q_{eq} is the amounts of phenol and cyanide adsorbed on to the per unit mass of adsorbent at equilibrium(mg/g), Q_t is the uptake of phenol and cyanide at time t (mg/g),C_t is the liquid phase concentration of phenol and cyanide at time t (min).C_i is the initial pollutant concentration (mg/l),C_f is final concentration of pollutant (mg/l),C_{eq} is the concentration of adsorbate at equilibrium (mg/l),V is the volume of the solution (lit) and M is the weight of the adsorbent (gm).

Table:1 Experimental Conditions for Adsorption of Cyanide on to Al-AC

Effect of parameters	Operating Conditions				
	pH	Dose g/l	Initial conc.mg/l	Time, hr	Temp ^{0}C
Effect of pH	2-12	20	30	50	30^{0}C
Effect of Dose	9	5-60	30	50	30^{0}C
Effect of Time	9	20	30	2-50	30^{0}C
Effect of temp.	9	20	30	32	20-40^{0}C
Effect of initial conc	9	20	10-100	32	30^{0}C
Equilibrium Isotherm	9	20	10-100	32	30^{0}C

III. RESULTS AND DISCUSSION

3.1Effect of pH

The effect of pH on removal of cyanide was calculated in the pH range of 4.0-10.0 and results are demonstrated in Fig. 1. pH played a foremost role in cyanide adsorption on to biosorbent. Numerous researchers reported that biosorption process is dependent on the functional groups on the adsorbent, and the aqueous phase pH, and their ionic states (at specific pH) [21-23]. In this study, the maximum biosorption were detected at above pH 9, where

the surface charges on the adsorbent surface may be negative[15]. .Maximum cyanide adsorption at pH 9 can be described by seeing the fact that the pH of the solution affects both the cyanide in the solution and the surface charge of the adsorbent. According to results of this study, the pH of 9 was designated as the optimum pH when using Al-AC as adsorbents. The pKa of cyanide is 9.0, M.A. Barakat,2005, suggesting that cyanide is totally dissociated to CN− at a solution pH of 9. Cyanide is a nucleophilic ion, when it comes in contact with negatively charged adsorbent, it fixes with the anionic functional groups existing on the adsorbent surface and thus increases adsorption [15]. Furthermore, some removal may occur through chemical reactions with surface sites and surface precipitations, physical adsorption and complexation of cyanide with functional groups. [25].Some researchers have correspondingly reported achieving maximum cyanide adsorption onto dissimilar adsorbents in the pH range of 9–11(Table 1).

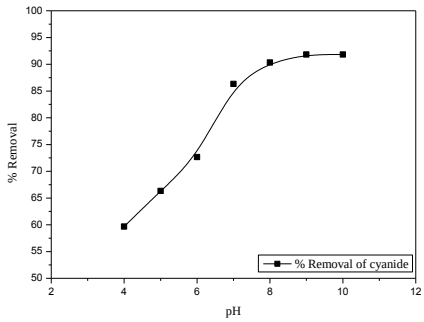


Fig 1 Effect of pH on % Removal

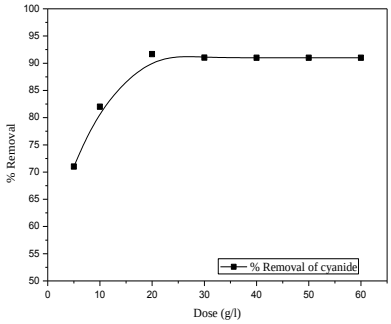


Fig 2 Effect of Dose on % Removal

3.2 Effect of Adsorbent Dose

Adsorption is generally a surface phenomenon , therefore the mass of adsorbent can considerably affect efficiency of adsorption. Therefore, the effect of adsorbent dose on adsorption of cyanide at pH of 9 and contact time of 32 hr for the measured adsorbent was studied. Fig 2 signifies the percentages removal of cyanide as a function Al-AC dosage. As demonstrated in Fig. 2, the cyanide removal at a dose of 5 g/L was 71.01%; removal enhanced to 91.67% when the AC dosage was increased to 1.5 g/L and remained almost unchanged thereafter, dose of 20 g/L was therefore designated as an optimum value for the further experiments. Accomplishment of maximum cyanide percentage removal at low adsorbent dose specifies the suitability of Al-AC and high affinity for removal of cyanide from wastewater. It has been detected that up to assured level of higher doses of adsorbents resulted maximum removal of cyanide. This might be because of greater obtainability of pore volume and surface at higher doses[26]. Though, it can be observed from Fig. 2 that after dosage of 20 g/l , there was no major change in percentage removal of cyanide. It was due to the coinciding of active sites at higher dose, thus decreasing of the surface area available for adsorption [15].

3.3 Effect of Time

Fig. 3 represents the effect of contact time on percentage removal of cyanide. An increasing in the contact time led to enhanced removal percentages for cyanide concentrations, which achieved equilibrium times of 32 hr. The increase in percentage removal at initial portion showed the maximum sorption uptake of the cyanide on to adsorbents. Thereafter the slow uptake of cyanide indicates the consumption of available active sites onto adsorbent surface and accomplishment of equilibrium stage. Initially high sorption was maybe due to contribution of active surface sites onto adsorbent surface and specific functional groups [27]. A reduction in removal efficiency was found with increasing initial concentration. The reduction of percentage removal of

cyanide as a function of time can be described by the limitation of existing free sites for adsorption of cyanide with increased cyanide initial concentration in solution for a fixed amount of adsorbent, as well as by the rise in intraparticle diffusion. The equilibrium removal percentage of cyanide at concentration of 30mg/l was 92.56%.

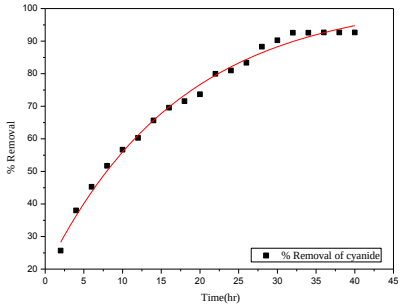


Fig 3 Effect of Time on % Removal

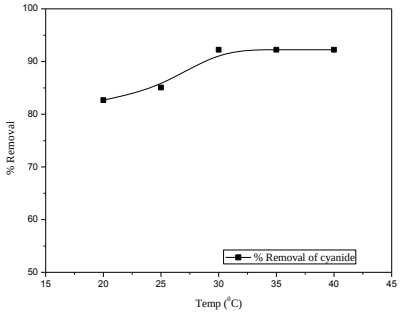


Fig 4 Effect of Temp. on % Removal

3.4 Effect of Temperature

The effect of temperature were carried out at 20, 25, 30, 35,and 40 ^{0}C for Al-AC and shown in Fig 4. The rate of uptake of cyanide onto Al-AC was observed to increase with increase temperature, thus demonstrating the process to be endothermic in nature. Though, the increase in removal percentage was maximum at temperature changed from 20 ^{0}C to 30 ^{0}C and turn out to be more slow on further increasing the temperature. This is maybe due to increase in temperature leads to reduce in viscosity of solution and therefore increase in rate of diffusion of adsorbate inside the pores [28].

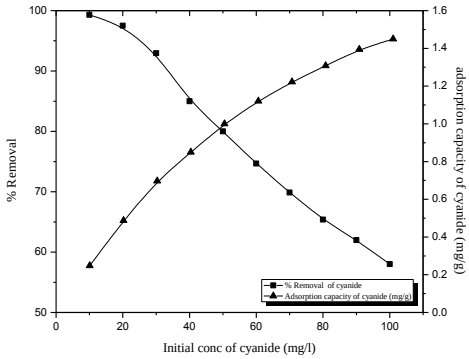


Fig 5 Effect of Initial conc. on % Removal

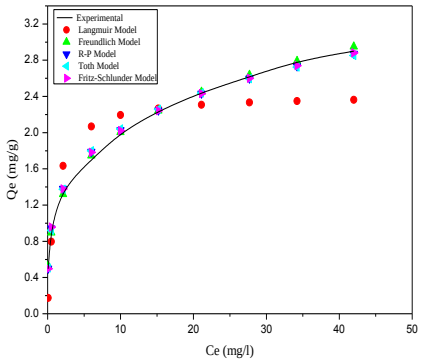


Fig 6 Comparison of Isotherm models

3.5 Effect of Initial Concentration

Fig. 5 indicates the relation between cyanide adsorption capacity and percentage removal at varies initial cyanide concentrations of 10-100 mg/l. The graph showed a decrease in percentage removal and increase in adsorption capacity with increase initial concentration of cyanide. This is perhaps due to sufficient vacant sites are existing and a high concentration gradient occurs between the solid phases and adsorbate in aqueous solution. The adsorbent capacity gets exhausted with the increase in initial cyanide concentration. This was also owing to the fact that for a fixed adsorbent dose, the total existing adsorption sites were limited, which converted saturated at higher cyanide concentration. The percentage removal of cyanide reduced from 99.3 % to 58.01% as cyanide initial concentrations increased from 10 to 100 mg/l. Thus, the adsorption of cyanide by Al-AC has a strongly depends on the initial concentration.

3.6 Adsorption Isotherm Modelling

Adsorption equilibrium isotherms offer significant information for the implementation and design of adsorption processes. Therefore, to better understand the adsorption process, numerous isotherm models that define adsorption equilibrium data were applied to the experimental data, comprising the Langmuir, Freundlich, Redlich-Peterson, Toth and Fritz-Schlunder [29—30]. Fig. 6 indicates the plotted models, with the fitted models and the isotherm parameters along with HYBRID value are consolidated in Table 2. Statistical indices of cyanide for the isotherm models are also tabulated in table 3.

Referring to Fig. 6 and Table 2, it is observed that the HYBRID of the R-P Model and Fritz-Schlunder model is lower the others, signifying that the equilibrium adsorption of cyanide onto Al-AC could be best defined with the R-P Model and Fritz-Schlunder. Among two parameter models Freundlich model indicate better fit than Langmuir Model. The Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces.

In this study, values of Kf and n were found to be 1.078 and 3.715 for Al-AC adsorption data close-fitting in Non-Linear form of model equation which specified the suitability of the model. The favourability of the Langmuir model was measured using the dimensionless equilibrium parameter, R_L, written as

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

In this study, the value of R_L was found less than 1, demonstrating a favourable adsorption process of cyanide onto Al;AC. For high concentration of cyanide, R_L values are lower and adsorption Process is consequently more favorable [31]. Furthermore, the constant n in Freundlich model is greater than unity (between 1 and 10), indicates Al-AC is an suitable and favourable adsorbent for cyanide [32]. The maximum adsorption capacity of Al-AC for adsorbing cyanide was found to be 2.42 mg/g. Cyanide adsorption by different adsorbents stated in the literature (Table 4).The three-parameter Model Redlich–Peterson equation comprises of both Langmuir and Freundlich isotherm models features [33]. The value of constant *b* in Redlich–Peterson isotherm model lies between 0 and 1 [30]. Though the notable similarity is detected in the four adsorption models, Freundlich, Redlich–Peterson, Toth and Fritz–Schlunder signify data closely for adsorption on Al-AC whereas Redlich-Peterson and Fritz–Schlunder are more suitable isotherm models for Al-AC. These results indicate the fact that three and four parameter models minimize the error detected in two parameter models and therefore give better demonstration of data.

In order to calculate the goodness of the fit of experimental data and accuracy of the isotherm models applied in the present work, the resulting statistical indices are employed for the mono component system [34-35].

$$B_{Fac} = 10\left(\sum \log_{10}(Q_{e,cal}/Q_{e,\exp})/N\right) \quad (5)$$

$$NSD = \sqrt{\frac{\sum\left(1-Q_{e,cal}/Q_{e,\exp}\right)^2}{N}} \times 100 \quad (6)$$

$$RMSE = \sqrt{\frac{\sum\left(Q_{e,\exp}-Q_{e,cal}\right)^2}{N}} \quad (7)$$

Hybrid error function (HYBRID) was used to measure the goodness-of-fit. To define the best isotherm model, Hybrid error function (HYBRID) may be produced as follows [36]:

$$HYBRID = \frac{100}{N-P}\sum_{i=1}^{N}\left[\frac{(Q_{e,\exp}-Q_{e,cal})^2}{Q_{e,\exp}}\right] \quad (8)$$

where $Q_{e,\exp}$ is the observed from the experiment , $Q_{e,cal}$ is the approximation from the isotherm model for equivalent $Q_{e,\exp}$, N is the number of observations in the experimental equilibrium isotherm and P is the number of parameters in the regression model. The smaller value of HYBRID shows more exact estimation of Q_e value [36].

Table 2 List of Model Parameters

Single component isotherm Models	Non-Linear Form of Model	Values of model parameters	
Langmuir	$q_e = (Q_0 b C_e)/(1+bC_e)$	Q_o	2.42
		b	0.979
		HYBRID	27.73
Freundlich	$q_e = K_F C_e^{1/n}$	K_F	1.078
		n	3.715
		HYBRID	4.256
Redlich-Peterson	$q_e = \frac{K_{RP}.C_{eq}}{1+a_{RP}.C_{eq}^{\beta}}$	K_{RP}	36.565
		a_{RP}	31.122
		β	0.7603
		HYBRID	2.4424
Toth	$q_e = \frac{q_e^{\infty}.C_{eq}}{(a+C_{eq}^{n})^{1/n}}$	q_{to}	70.04
		a	0.385
		n	0.0787
		HYBRID	3.238
Fritz-Schlunder	$q_e = \frac{\alpha_1.C_{eq}^{\beta_1}}{1+\alpha_2 C_{eq}^{\beta_2}}$	a1	398.464
		a2	347.645
		b1	1.837
		b2	1.591
		HYBRID	2.054

Table 3 Values of Statistical Indices for Cyanide

S.No	Models	Cyanide		
		Bf	NSD	RMSE
1	Langmuir Model	0.874569	24.80328	0.30804
2	Freundlich Model	0.997812	3.806589	0.042366
3	Redlich–Peterson Model	0.999275	2.184534	0.038174
4	Toth Model	0.99812	2.897044	0.047464
5	Fritz Schlunder Model	0.999487	1.837762	0.033563

Table:4 Summary of Published Literature on Cyanide Removal by Adsorption

Adsorbent	pH	Fitted isotherm model	Kinetic model	Adsorption capacity (mg/g)	Reference
Activated Carbon	11	-	-	3.516	37
Cu Impregnated AC	10.5-11	Langmuir	Pseudo second order	19.7	38
Ag impregnated AC	10.5-11	Langmuir	Pseudo-second order	22.4	38
Ni-Impregnated Carbon	>11	-	-	15.4	39
Plain AC	>11	-	-	7	39

3.7 Kinetic Modelling

To estimate the effectiveness of cyanide mass transfer onto Al-AC, the kinetics of adsorption process were calculated based on experimental data (Table 5) by using Lagergren's pseudo-first and Pseudo-second order models. Non-Linear forms of models are given in equation (9) and (10). Also, to determine intraparticle diffusion for cyanide adsorption onto Al-AC, the experimental data were close-fitted to the Weber–Morriss model shown as Eq. (11).

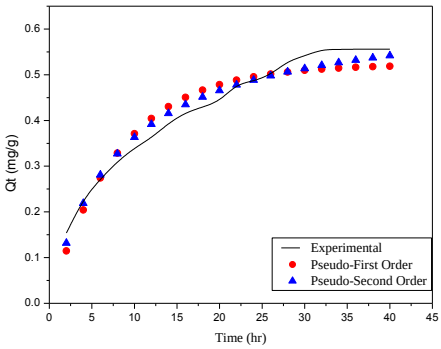
Lagergren's Pseudo-first order : = $q_t = q_e(1-\exp(-K_1 t))$ (9)

Pseudo second order= $q_t = k_2 q_e^2 t/(1+q_e K_2 t)$ (10)

Weber-Morriss equation : $q_t = K_{id} \times t^{0.5} + c$ (11)

The kinetic information acquired is given in Table 5. The comparison of kinetic model are given in fig 7.It was observed from table that ARE value is more for Pseudo first order than pseudo-second order. So, cyanide adsorption onto Al-AC is favored by pseudo-second order model. The validity of the kinetic models was measured by computing the average relative error (ARE) between experimental adsorption and model-predicted data.

$$ARE = 100/n \sqrt{\sum_{i=1}^{p} \left(\frac{Q_{e,i}^{\exp} - Q_{e,i}^{cal}}{Q_{e,i}^{\exp}} \right)^2} \quad (12)$$



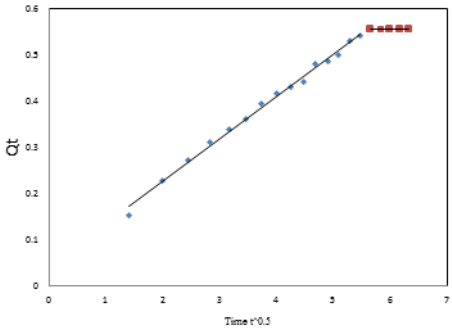


Fig 7 Comparison of Kinetic Models Fig 8 Intraparticle Diffusion Model

The adsorption process generally takes place through numerous following steps: film diffusion, bulk solution transport, pore diffusion, and adsorption onto the pores of adsorbent surface [40]. The slowest step limits the overall rate of adsorption. According to the literature, diffusion into particle pores (intraparticle diffusion) and film diffusion often control a process. To classify the step probably controlling the adsorption process of cyanide onto Al-AC under the certain conditions, the data were fitted with the Weber–Morriss equation [40].

Table 5 List of Kinetic Model Parameters

	Al-AC	
Model	Parameters	Phenol
Pseudo First Order	Qtcal	0.5223
	Kt1	0.124
	ARE	2.018
Pseudo Second order	Qtcal	0.6479
	Kt2	0.1967
	ARE	1.262
Intraparticle	K_{id1}	0.1042
	R^2	0.99
	K_{id2}	0.0926
	R^2	0.76

The existence of intra-particle diffusion was established by plotting the graph between square root of time and amount of cyanide adsorbed (Fig. 8). The dual nature of plot may be described as: the initial portion of curve was recognized to boundary layer diffusion, whereas the second portion was owing to intra-particle diffusion effect. Better fit of experimental data in first region (R_2>R_1)from Table 5) shows the rate limiting step is surface diffusion for cyanide adsorption.

3.8 Thermodynamic Modelling

Thermodynamic parameters for the adsorption of cyanide onto Al-AC was calculated using the following equations and the values are given in Table 6:

$$\ln k = \frac{\Delta s}{R} - \frac{\Delta h}{RT} \quad (9)$$

$$\Delta G^0 = -RT \ln k \quad (10)$$

where R is gas constant = 8.314×10^{-3} kJ/mole/K, ΔG^0 is kJ/mole, T = temperature in °K, Δs^0 is kJ/mol K, Δh^0 is the kJ/mole, and k is the equilibrium constant (amount on adsorbent/amount in solution). ΔG^0 , change in enthalpy Δh^0 and change in entropy Δs^0 . The Δh^0 and Δs^0 values can be calculated from the intercept and slope of the plot of ln k vs1/T, respectively. The free energy changes ΔG^0 were negative, representing the spontaneity and feasibility of the adsorption process The positive value of Δh^0 approves the endothermic nature of process of cyanide over Al-AC [41]. The positive value of Δs^0 demonstrates the increased uncertainty at adsorbent interface and better affinity of Al-AC towards cyanide (Table-6).

Table;6 List of Thermodynamic Parameters

		Al-AC		
Adsorbate	Temp. ^{0}C	ΔG_0	Δh_0	Δs_0
Cyanide	20	-98.4073	35.116	0.1538
	25	-103.841		
	30	-122.242		
	35	-124.258		
	40	-126.274		

IV. CONCLUSIONS

Removal of cyanide from aqueous solutions by batch adsorption process have been carried out using Al-Activate Carbon. Maximum cyanide removal efficiency was found as 99.3 % onto Al-AC. The adsorption isotherm studies indicated that Redlich-Peterson and Fritz-Schlunder adsorption isotherm model satisfactorily defined the adsorption of cyanide. The maximum adsorption efficiency was found to be 2.42 mg/g . It was revealed from kinetic study that the pseudo-second order kinetic model better defined the adsorption kinetics with lower ARE value (1.262). The thermodynamic modelling indicated a endothermic and spontaneous adsorption. it may be concluded that Al-AC could be a promising adsorbent for the removal of cyanide from aqueous solution.

V. ACKNOWLEDGEMENT

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