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# Kinetics and Thermodynamic Studies of Dextrin Adsorption on Modified Coal Surface

Nwoko Christopher Ikpe Amadi[1,a*], Okoji Josephine Nkechi[2,b]

[1,2,]Department of Chemistry, School of Physical Sciences, Federal University of Technology, Owerri, Nigeria

[a]*nwokochristopher@yahoo.com*, [b]*lajoe4real@yahoo*

***Abstract:-*** The present paper deals with the adsorption kinetics of dextrin from an aqueous solution onto modified coal surface. The study explored the feasibility of improving coal surface with aluminium ion for easy adhering of dextrin as an adsorbate on coal under different experimental conditions. The rate constants for the adsorption of dextrin were determined using Lagergren kinetics rate equations and Intraparticle diffusion rate equation. From the kinetic models comparison applied to the adsorption of dextrin on coal samples, the experimental data fitted very well to pseudo second-order kinetic model and also followed by intraparticle diffusion, diffusion is not only the rate-controlling step. The results show that the sorption capacity increases with an increase in solution contact time from 30 to 150 minutes and temperature from 30 to 70 $^{o}$C. The thermodynamic parameters were evaluated. The negative value of free energy change ($\Delta G^{o}$) reflects a more energetically favorable adsorption process (0.554-8.726 kJmol$^{-1}$). $\Delta H^{o}$ (57.32 kJmol$^{-1}$) indicated that the adsorption of dextrin onto aluminium coated bituminous coal (ACB) was endothermic, which result was supported by the increasing adsorption of dextrin with temperature. The negative values of entropy ( $\Delta S^{o}$) confirmed a decrease in randomness of the adsorption process at the solid or solution interface (-187.23 kJmol$^{-1}$) The results have established good potentiality for the modification of coal surface with aluminium sulfate for easy adsorption of dextrin on coal during processing.

***Key words:*** *Dextrin, Coal, Adsorption, Lagergren, Intraparticle, Thermodynamics.*

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## 1.0 Introduction

The treatment of fine particles for the recovery of mineral value is a problem in view of the decrease in size of mineral reserves and finer dispersion of value in the remaining ores [1]. Application of synthetic polymeric flocculants, particularly in coal preparation improves the efficiency of the separation. This brings dispersed particles together and increased the effective particle size of the solid phase. The stability of the suspension is broken and the liquid phase is released. The surface characteristics of coal may be altered significantly by the adsorption of a surface active agent on the coal surface such as dextrin [2]. The kinetic study has the important practical task to determine the degree of utilization of the adsorption capacity as a function of the time of contact between the liquid and the solid. Different models are used to fit the obtained kinetic curves in order to define the rate parameters and explain the mechanism of mass transfer between the adsorption of dextrin on coal. Improving the coal surface with a cation ($Al^{3+}$) or anion ($NO_3^-$) will help dextrin to easily adsorb to the coal surface and enable dextrin to bring out its unique qualities which are: stable paste characteristics, high strength films, excellent heat resistance, slow curing rate which allows sample assembly time and excellent adhesive properties [2].

## 2.0 Materials and Method

### 2.1 Materials

A mineral sample of lignite coal was obtained from Iyiokwu spring at Okuekpe village in Ebenese Iheoma Orlu, Imo State and Bituminous coal was obtained from Onyeama mine, Enugu State, Nigeria. The samples were first crushed in a jaw crusher and subjected to dry grinding in a ball mill. The ground sample was sieved through laboratory test sieve of 212 µm mesh size.

Fresh cassava tubers were bought in Ihiagwa market, Imo State, Nigeria and prepared into dextrin starch according to standard procedures proposed by Adeboye [3].The material was dried and blended to obtain a homogenous powder. The

sample was stored in a dry plastic container and covered until used.

**2.2 Preparation of dextrin**

300 grams of cassava tuber was sun dried until a constant weight was obtained. It was ground in a grinder. 50 grams were weighed into a beaker, sprayed with 0.3 mL of HCl and vigorously stirred. This was allowed to age for 24 hours then heated for 1 hour at a temperature of 60 $^{o}$C while stirring and later cooled in a water-bath at room temperature [3].

**2.3 Preparation of modified coal**

Preparation of Aluminum coated and nitrate coated coal samples were carried out by the method of Liu and Ho [4, 5].

The coal used in the study was subjected to different surface modifications so as to obtain the hydrophilic or hydrophobic characters of the coal sample. The coal types were treated with $Al_2(SO_4)_3$ and $NaNO_3$ for three hours:

i) Coating with $Al^{3+}$ (AC)
ii) Coating with $NO_3^{2-}$ (NC)

The modified coal surface is designated in this study as:

ACB - Aluminium coated bituminous coal

ACL - Aluminium coated lignite coal

NCB - Nitrate coated bituminous coal

NCL - Nitrate coated lignite coal

The Unmodified coal surface is designated as:

UCB - Untreated bituminous coal

UCL - Untreated lignite coal

**2.4 Preparation of Dextrin solution**

The concentrations of the starch samples in solution were determined by the method developed by Oyelude [1]. Here the dextrin solution was prepared by caustization. In this method 20 mL of distilled water was added to 2 g of dextrin powder to produce a thick paste. The paste was then added to approximately 100 mL of boiling distilled water and mixed thoroughly. The resulting solution was added to 1000 mL volumetric flask. 25 g of KOH was weighed into the volumetric flask and brought to the mark with distilled water. The suspension was shaken, and the resultant solution was homogenised. Dilute starch samples was prepared from the stock solution with 2.5 % of KOH. The solution was then cooled to room temperature prior to making the dilute solutions. Fresh starch solutions were prepared each day to minimize the effect of microbial degradation.

**3.0 Absorption study:**

**3.1 Dextrin concentration analysis**

The concentration of dextrin was measured prior to checking the initial concentration and following the adsorption test (determination of residual concentration) by means of a spectrophotometer, at wavelength of maximum absorbance of 490 nm

**3.2 Absorbance test**

The batch biosorption test on the adsorption of dextrin by coal was studied, at known concentration of 25 – 200 mg/L. Concentration of the starch in solution was determined by the method developed by Oyelude [1]. The stock solution was diluted as required to obtain different concentrations of dextrin solution. Here dilute dextrin samples were prepared from the stock solution of 3 % causticised dextrin as required. 2 ml of each of these known concentrations above was pipetted into a test tube and 0.75 mL of 80 % (w/w) phenol diluted with distilled water was added. 5mL of concentrated tetraoxosulphate (VI) acid was added rapidly, the stream of the acid being directed against the liquid surface in the test tube to obtain good mixing. The test tubes were allowed to stand for 10 minutes after which they were shaken and placed in a cold water bath to cool. The absorbance of the solution in each test tube was measured using UV-Visible spectrophotometer at a wavelength of 490 nm. Calibration curves of absorbance against dextrin

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concentration in mg/L were prepared to obtain a standardization curve. A blank solution was prepared by treating 2 mL of distilled water with 0.75 mL of 5 % phenol and 5ml of concentrated tetraoxosulphate (VI) acid. The absorbance was measured using UV-visible spectrophotometer [1].

### 3.3 Adsorption Kinetic Study

Adsorption kinetic study is important in determining the efficiency of adsorption. Kinetic models have been exploited to test the experimental data and to determine the mechanism of adsorption and its potential rate-controlling step that include mass transfer and chemical reaction. Adsorption kinetics expressed as the solute removal rate that controls the residence time of the sorbate in solid-solution interface. These models include pseudo-first order and pseudo-second order models, and particle diffusion.

## 4.0 Results and Discussion

### 4.1 Adsorption Kinetic Study

Adsorption kinetic study is important in determining the efficiency of adsorption. Kinetic models have been exploited to test the experimental data and to determine the mechanism of adsorption and its potential rate-controlling step that include mass transfer and chemical reaction. Adsorption kinetics expressed as the solute removal rate that controls the residence time of the sorbate in solid-solution interface. These models include pseudo-first order and pseudo-second order models, and particle diffusion.

### 4.2 Pseudo-first order model

Lagergren proposed a pseudo-first-order kinetic model; this model was successfully applied to describe the kinetics of many adsorption systems. The integral form of the model equation expressed as follows [4]:

$$\log\ (q_e - q_t) = \ \log - \frac{\mathrm{K}}{2.303}\ \mathrm{t} \qquad (1)$$

Where, $q_e$ (mg/g) are the amount of dextrin that was adsorbed at the equilibrium is time (minutes), and $q_t$ (1/min) is rate constant. The values were calculated from the slopes and intercepts of log ($q_e$ – $q_t$) against the plots and were presented in Table 1. The pseudo first order plots of dextrin adsorption on ACB, ACL, NCB, NCL, UCB and UCL are shown in Figures 1 and 2. The lower correlation coefficients obtained suggest that the adsorption of dextrin on prepared coal samples does not follow the pseudo first order kinetics. Pseudo-first order kinetic model does not comply with the kinetic data which can be attributed to the control of boundary layer over dextrin adsorption at the initial stages [6].

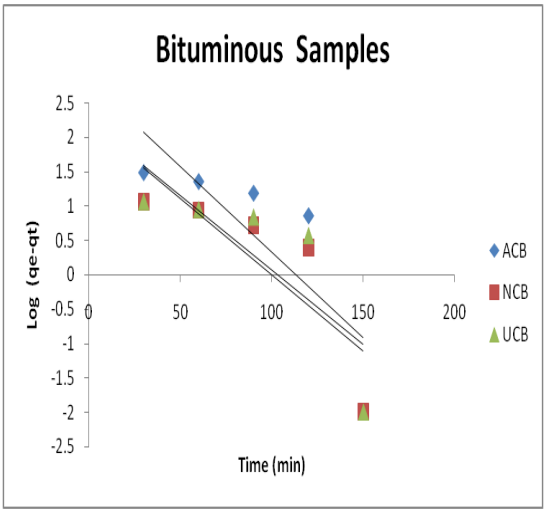


**Figure 1: Pseudo-first order kinetic for adsorption of dextrin on ACB,NCB and UCB**

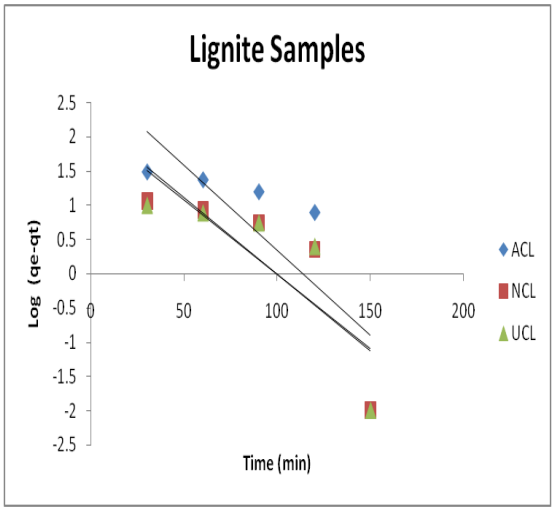


**Figure 2: Pseudo-first order kinetic for adsorption of dextrin on ACL, NCL and UCL**

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### 4.3 Pseudo second order model

The adsorption kinetics was also described by pseudo-second-order kinetic model. The linearized integral form of the model is represented as:

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

Whereqe and qt (mg/g) are the amount of dextrin that was adsorbed at the equilibrium and at time t(min), respectively and$k_2$ is the pseudo-second-order rate constant of adsorption (g/mg min). The initial adsorption rate, h ($k_2qe^2$), has been widely used for evaluation of the adsorption rates [5]. This model is based on the assumption that the rate of occupation of adsorption sites is proportional to the square of number of unoccupied sites [8,9]. From the slopes and intercepts of the linear plots obtained by plotting t/qt versus qe, the values of the pseudo-second-order rate constants $k_2$ and qe were calculated and given in Table 1. The pseudo second order plots of ACB, ACL, NCB, NCL, UCB and UCL were shown in Figures 3 – 4, respectively. For all the types of AC samples the results showed a very good compliance with the pseudo-second-order equation with high regression coefficients. There regression ($R^2$) values obtained are very close to unity and the adequate fitting of the plots confirmed that the adsorption of dextrin by the prepared AC samples followed pseudo second order kinetics. The values of initial adsorption rate, h = ($k_2qe^2$), h followed the trend ACB > ACL > NCB > NCL > UCB > UCL indicating that ACB and ACL adsorbs dextrin more rapidly than NCB, NCL, UCB and UCL.

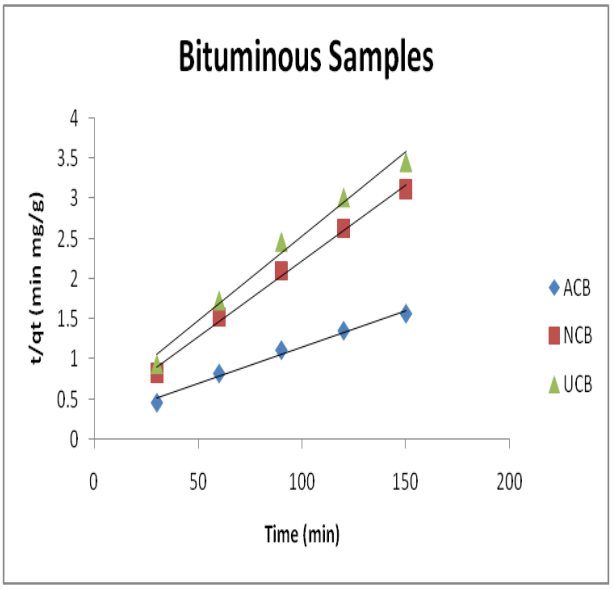


**Figure 3: Pseudo-second order kinetic for adsorption of dextrin on ACB, NCB and UCB**

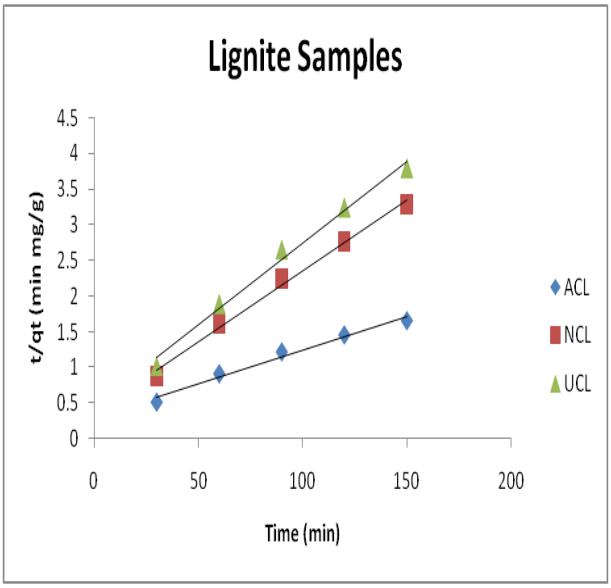


**Figure: 4 Pseudo second order kinetic for adsorption of dextrin on ACL, $NC_L$ and UCL**

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**Table 1: Rate constant for the pseudo-first order, the pseudo-second order and intraparticle diffusion models**

| Sample | First order Kinetic model | | | | Second order Kinetic model | | | | Intraparticle diffusion model | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $q_e$ exp. (mg/g) | $q_e$ cal (mg/g) | $K_1$ | $R^2$ | $q_e$cal (mg/g | $K_f$ (g/mg) | h | $R^2$ | $k_{id}$ (mg/g $min^{1/2}$) | C | $R^2$ |
| ACB | 96.21 | 666.81 | 0.055 | 0.654 | 111.11 | 0.0003 | 4.148 | 0.988 | 4.550 | 39.32 | 0.991 |
| ACL | 89.51 | 654.64 | 0.055 | 0.646 | 111.11 | 0.0002 | 3.370 | 0.984 | 4.440 | 33.54 | 0.988 |
| NCB | 48.26 | 204.17 | 0.050 | 0.692 | 55.55 | 0.0009 | 3.039 | 0.995 | 1.740 | 26.72 | 0.997 |
| NCL | 45.51 | 175.38 | 0.050 | 0.697 | 52.63 | 0.0009 | 2.687 | 0.993 | 1.707 | 24.37 | 0.994 |
| UCB | 43.51 | 175.38 | 0.048 | 0.635 | 47.62 | 0.0010 | 2.290 | 0.986 | 1.654 | 22.10 | 0.957 |
| UCL | 39.51 | 141.91 | 0.048 | 0.670 | 43.48 | 0.0011 | 2.249 | 0.990 | 1.462 | 21.01 | 0.978 |

### 4.4 Adsorption Mechanism

It is always important to predict the rate limiting step in an adsorption process to understand the mechanism associated with the phenomena. For a solid-liquid adsorption process the solute transfer is usually characterized by either external mass transfer or intra-particle diffusion or both.

Generally three types of mechanisms are involved in the adsorption process, mentioned as follows:

1. Metal ion from the bulk liquid to the liquid film or boundary layer surrounding the adsorbent.
2. Transport of solute ions from the boundary film to the external surface of the adsorbent (film diffusion).
3. Transfer of ions from the surface to the intra-particular active sites (particle diffusion).
4. Adsorption of ions by the active sites of adsorbent.

Due to the fact that the first step is not involved with adsorbent and the fourth step is a very rapid process, they do not belong to the rate controlling steps. Therefore, the rate controlling steps mainly depend on either film diffusion or particle diffusion [10].

### 4.5 Intra-Particle Diffusion

Weber and Morris model is a widely used intra-particle diffusion model to predict the rate controlling step [11]. When mass transfer is the controlling step, it is important to identify the diffusion mechanism. According to intra-particle diffusion model, the initial rate of diffusion is given by the following equation:

$$q_t = k_{id} t^{1/2} + C \qquad (3)$$

Where $q_t$ (mg/g) is the amount adsorbed at time t, $k_{id}$ and C are rate constant of intra-particle diffusion,$t^{1/2}$ ($min^{1/2}$) is the square root of time.

The values of $k_{id}$ (mg/g $min^{1/2}$) were determined from the slopes of respective plots of qt versus $t^{1/2}$. The plots of qt against t½ at different contact time values showed multi-linearity characterizations with two steps occurred in the adsorption process and are shown in Figures 5- 6 for ACB, ACL, NCB, NCL, UCB AND UCL respectively. The initial steep portion is due to the instantaneous adsorption on the external surface and the second steep is the gradual adsorption stage, where intra-particle diffusion is rate controlling [11]. The larger slopes of the initial steep sections indicate that the rate of dextrin adsorption is higher in the beginning due to the instantaneous availability of larger surface area and adsorption sites. The lower slopes of the second subdued portions are due to the decreased concentration gradient which makes the diffusion of dextrin

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into the microspores of the adsorbent. The obvious two steps of the process suggested that the intra-particle diffusion is not only the rate controlling step for the adsorption of dextrin [5]. As the contact time increases, the slopes of the plots increased; confirming the higher dextrin adsorption at the interphase. The calculated values of rate constants ($k_{id}$) and regression coefficients ($R^2$) were presented in Table 1. It was observed that the $k_{id}$ values continuously decreased with the increase in time and the maximum values were obtained for ACB at time 150 minutes. The higher values of $K_{id}$ (Table 1) for all samples corresponded to the lower values of $K_2$ (Table 1), indicating that the intra-particle diffusion retards the adsorption process. This also indicates that in all cases, the adsorption of dextrin is rather complex and involves more than one diffusive mechanism [12].

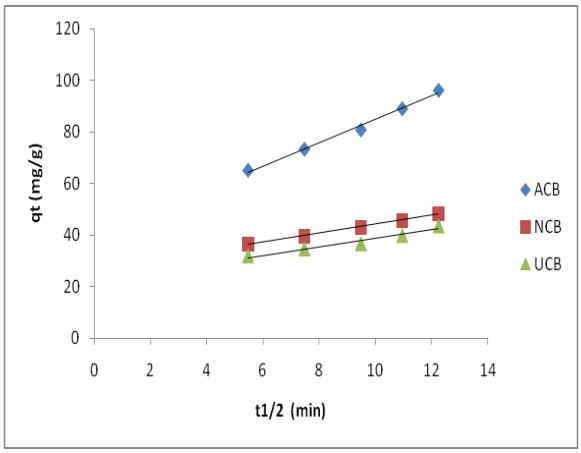


**Figure 5: Intraparticle diffusion plots for dextrin adsorption by ACB, adsorption by NCB and UCB at various Initial concentrations**

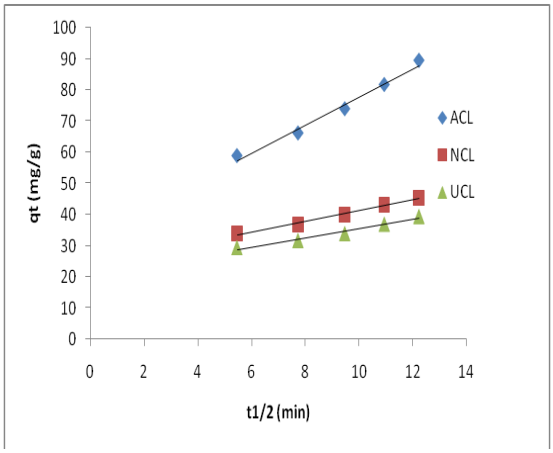


**Figure 6: Intraparticle diffusion plots for dextrin ACL, NCL and UCL at various Initial concentrations**

### 4.6 Thermodynamic of Sample Adsorption

The nature of the adsorption of dextrin on the prepared coal samples was predicted by estimating the thermodynamic parameters. The determination of basic thermodynamic parameters: enthalpy of adsorption, Gibb's free energy and entropy of adsorption is important. It estimates if the process is favourable or not from thermodynamic point of view. It also examines the spontaneity of the system and ascertains the exothermic or endothermic nature of the process. The changes in thermodynamic parameters such as free energy ($\Delta G^o$), enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) were evaluated from the following equations [13, 14].

$$\Delta G^\circ = -\ RT \ln K_c \qquad (4)$$

Where, $K_c$ is the equilibrium constant and is calculated as:

$$k_c = \frac{C_{AC}}{C_e} \qquad (5)$$

$C_{AC} = \left(\frac{mg}{g}\right)$ and $C_e = \left(\frac{mg}{L}\right)$

are the equilibrium concentrations for solute on the adsorbent and inthe solution, respectively. The $K_c$ values were used to determine the $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ expressed in terms of the $\Delta H^o$ (kJ/mol) and $\Delta S^o$ (kJ/mol) as a function of temperature:

$$\ln k_c = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (6)$$

$\Delta H^o$ and $\Delta S^o$ were obtained from the slopes and intercepts of the plots of ln $k_c$ against 1/T shown in Figure 7 and 8. The free energy change ($\Delta G^o$) indicates the degree of spontaneity of the adsorption process and the negative value reflects a more energetically favorable adsorption. The increase in negative value of $\Delta G^o$ with increase of temperature showed that the adsorption of dextrin on prepared ACB and ACL samples increased with the rise in temperature in order of: -0.554 to -8.726 and -0.377 to -5.675 $kJmol^{-1}$ respectively. The positive values of $\Delta H^o$ shown in Table 2 confirmed the endothermic nature of the adsorbents for dextrin adsorption in the studied range 30 – 70 $^oC$. The negative values of $\Delta S^o$ confirmed a decrease in randomness of the adsorption process at the solid or solution interface and it followed the order ACB > ACL > NCB > NCL > UCB > UCL [15].

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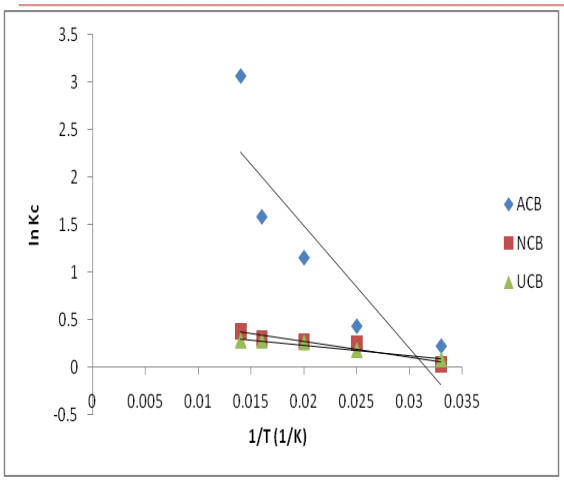


**Figure 7: Plot of ln Kc vs. 1/T for Adsorption of dextrin on prepare ACB, NCB & UCB sample**

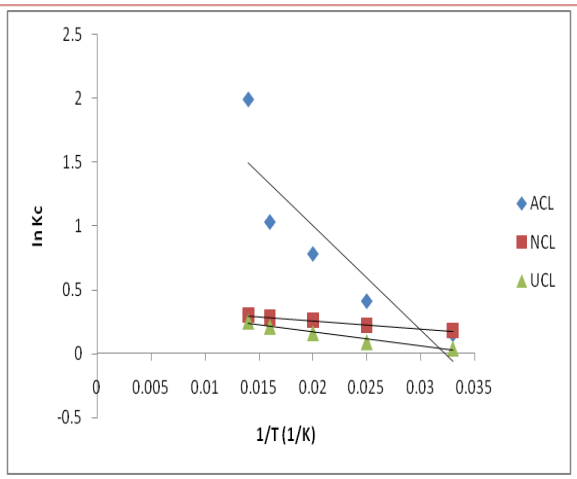


**Figure 8: Plot of ln Kc vs. 1/T for adsorption of dextrin on prepared ACL, NCL & UCL sample**

Table 2: Thermodynamic parameters

| Sample | G△(kJ/mol) 30°C | 40°C | 50 °C | 60°C | 70°C | △H (kJ/mol) | △S (k/mol) |
|---|---|---|---|---|---|---|---|
| ACB | -0.554 | -1.118 | -3.088 | -4.374 | -8.726 | 57.316 | -187.23 |
| ACL | -0.377 | -1.066 | -2.095 | -2.852 | -5.675 | 38.855 | -120.80 |
| NNB | -0.639 | -1.615 | -0.725 | -0.831 | -1.084 | 2.560 | -10.31 |
| NCL | -0.453 | -0.573 | -0.698 | -0.775 | -0.856 | 2.651 | -10.22 |
| UCB | -0.202 | -0.468 | -0.698 | -0.775 | -0.798 | 4.568 | -15.86 |
| UCL | -0.100 | -0.234 | -0.429 | -0.581 | -0.713 | 4.658 | -15.59 |

## CONCLUTION

The adsorption of dextrin from aqueous solution was found to be dependent on contact time and the initial concentration of the adsorbate. The data was found to fit well to Lagergrenand intraparticle equation. All the models fit progressively well with increasing sorbate concentration. The process of adsorption was found to follow second order kinetics. The successful use of a cost-effective adsorbate in the adsorption of coal from aqueous solution is well apparent from the study if the surface is modified with aluminum sulfate. The thermodynamic results showed that the adsorption of dextrin onto aluminium ion modified coal surface was spontaneous, endothermic as well as decrease in entropy during the adsorption studies.

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