Adsorption Properties of Dextrin onto Modified Coal Surface

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Abstract--In this adsorption studies, adsorption properties of dextrin on modified coal surfaces were investigated. Measured quantities such as: pH, initial concentration and temperature were investigated. There was a rapid increase in adsorption of dextrin from a low pH of 2 to a pH of 4. A plateau region was observed from pH 4 to pH 6 for dextrin and the maximum adsorption capacities occurred at pH 6. Adsorption capacity of 61.25 mg/g and 55.00 mg/g was achieved at initial concentration of 200 mg/L for Aluminium coated bituminous coal (ACB) and Aluminium coated lignite coal (ACL) respectively. The equilibrium data have been modelled using Langmuir, Freundlich and Temkin isotherms. The result indicated that the Freundlich isotherm provides the best correlation of the equilibrium data and its equation is found to best represent the equilibrium separation data in the temperature range of 303 -343 K. The maximum adsorption capacity of dextrin onto coal surface was obtained to be 6.71 and 4.42 mg/g for both ACB and ACL respectively. Dextrin from cassava appeared to be more stable adsorbate in solution when the coal surface is modified with Al^{3+} from $AI_2(SO_4)_3$.

Keywords- *Adsorption properties, dextrin, coal, equilibrium data, isotherms.*

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1. Introduction

Crushing and grinding of an ore to liberate the mineral grains from each other is important in mineral processing. This operation leads to loss of some mineral particles which may become too small to be effectively processed by the conventional mineral processing methods. The treatment of fine particles for the recovery of mineral value is, therefore an important problem in view of the dwindling mineral reserves and finer dispersion of value in the remaining ores [1]. The efficiency of solid/liquid separation may be greatly improved by the application of synthetic polymeric flocculants, particularly in coal preparation where sedimentation, filtration and centrifugation processes are extensively used. This improvement is achieved by bringing dispersed particles together increasing the effective particle size of the solid phase. The stability of the suspension is broken and the liquid phase is released. Adsorption is a technique that is used in many different fields. It involves the accumulation of solute molecules at an interface. Reagent usage and type of coal are important factors in coal cleaning processes, coal-liquid mixtures and the dewatering characteristics of slurries. The separation performance and rheological behavior of coal-liquid mixtures are affected by reagent adsorption on the coal particles as well as the nature of solid particles. The degree and extent of adsorption may significantly affect the performance of the process. Dextrin $(C_6H_{10}O_5)_n$ a starch derivative has found many applications in mineral processing operations such as flotation, flocculation and selective flocculation. All these processes involve the initial adsorption of the polymeric substance at the solid-liquid interface [2].

Starch has found many applications in mineral processing operations such as flotation and even dated back to 1931 when Lange patented starch as a selective depressant in the separation of quartz or hematite, salt type mineral.

A polymer can only function as a flocculants only if it is adsorbed on the particle surface, this gives special consideration to the surface chemistry of the mineral [1, 2]. Dextrin is synthetic water-soluble organic polymer of low molecular weight used to bridge flocculants and are strongly adsorbed onto the coal particles, which are capable of spanning the gap between the particles. Charge reduction lessens electrical repulsion and enables coagulation to proceed to a further degree. Charge is neutralized by the addition of reagents giving rise to charged ions opposite in charge to that carried by the particles. In addition of $AI_2(SO_4)_3$ and $NaNO_3$ give rise to NO_3^- and Al^{3+} ions which will improve the surface of the coal types in order to obtain the best adsorption properties of dextrin onto coal samples.

This work is deemed worthwhile because coal is an important mineral worldwide and dextrin can be used as an additive in processing coal. Moreover, improving the coal surface will 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. Materials and Method

2.1. Collection and Preparation of Samples

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 [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.

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 °C while stirring and later cooled in a water-bath at room temperature [3].

Preparation of modified coal

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

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

Preparation of Dextrin solution

The concentrations of the starch samples in solution were determined by the method developed by [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.

2.2. Adsorption study:

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

Adsorbance 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 [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 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.

3. Results and Discussion

Effect of contact time: The effect of contact time on the adsorption of dextrin from aqueous solution by coal is shown in Fig. 1 and 2. The initial concentration of starch in the aqueous solution was 200 mg/L. For a given initial concentration of dextrin, the quantity of dextrin adsorbed at equilibrium increased with time and optimum starch was adsorbed between 120 and 150 minutes for ACB, ACL, NCL, NCB, UCB, UCL samples. A general increase in dextrin adsorption with contact time is observed in the initial stage and has the maximum at 150 minutes. The contact time is essential for the establishment of equilibrium during the adsorption process. From the result of this study, the maximum adsorption capacity of 96.25 and 89.50 were obtained at 150 minutes for ACB and ACL respectively. Therefore all the adsorption experiments were carried out at 150 minutes.

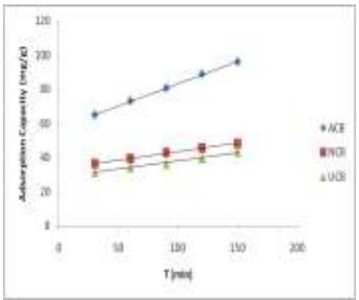

Fig. 1. Effect of contact time on the adsorption of dextrin on ACB, NCB and UCB,

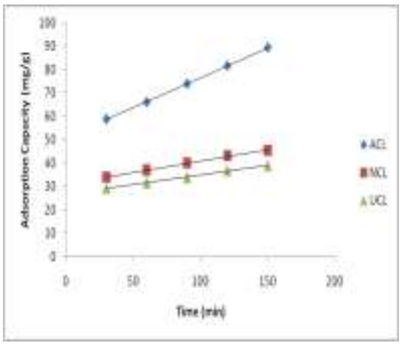

Fig. 2. Effect of contact time on the adsorption of dextrin on ACL, NCL and UCL.

Effect of Initial pH of Pulp

The impact of pH on the uptake of dextrin by coal is shown in Fig. 3 and 4. The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process; the effect of pH on the adsorption of dextrin from aqueous solution by coal is presented in the figures 3 and 4. The initial concentration of the starch used is 200 mg/L .However; there was a rapid increase in adsorption of dextrin from low pH of 2 to a pH of about 4. A plateau region was observed from pH 4 to pH 6 for dextrin. For pH values from 4 to 12, the amount of dextrin adsorbed is independent of pH for each initial concentration of starch. However for pH 6 and above to alkaline side, the quantity of dextrin adsorbed at equilibrium decreased sharply .This could be associated with the formation of dextrin $(OH)_2^-$ and $[(OH)_2^-]_2$ species which might be more attracted to the adsorbent rather than the positively charged dextrin ions. At lower pH, the surface of the adsorbent becomes positively charge as the OH^- and other such groups become protonated. This will result in the increase of electrical repulsion between the adsorbent surface and the species to be adsorbed. At higher pH, the surface of the adsorbent was almost neutral and thus resulting in minimal repulsion between adsorbent and the adsorbate [5]. Following the trend in coal, the negative charge density increases with increases in pH. This observation can be explained in terms of the surface functional groups on coal. It is well known that the surface of low rank coals are dominated by oxygenated surface groups.

Several studies have shown that the surface chemistry of this coal is determined by these groups although inorganic species also play a role. In aqueous and basic environments these acidic groups dissociate and the coal particles acquire negative charges, whereas the surface groups are protonated in acidic medium, reducing the negative charge density and the surface may become positively charged in strongly acidic media [6]. The formation of surface charge on coal is depicted by equations (1-4) for carboxyl (-COOH) and hydroxyl (-OH) functional groups:

$$-COOH_{(S)} \rightarrow OH^- - COO^-_{(S)} + H_2O_{(L)} \quad (1)$$

$$-COH_{(S)} + OH^- \rightarrow -CO_2^+ + H_2O_{(L)} \quad (2)$$

$$-COOH_{(S)} + H^+ - COOH^+_{2(S)} \quad (3)$$

$$-COH_{(S)} + H^- \rightarrow -COH^-_{2\,(S)} \quad (4)$$

Where (s) designate the coal surface

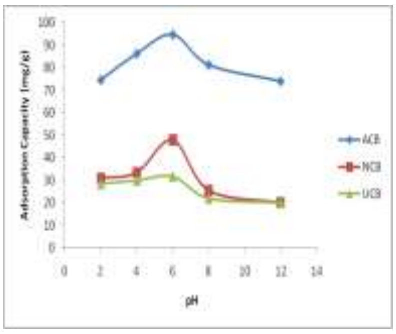

Fig.3. Effect of pH on the adsorption of dextrin on ACB, NCB and UCB.

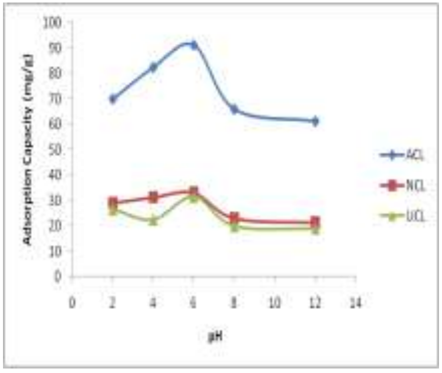

Fig. 4. Effect of pH on the adsorption of dextrin on ACL, NCLand UCL.

Effect of Temperature

The adsorption of dextrin from aqueous solution at different temperatures was investigated. Samples were subjected to temperature treatment which range from 30 °C to 70 °C and can be seen from Fig. 5 and 6. The adsorption of dextrin has been found to increase with an increase in temperature from 30 °C to 70 °C. The increase in adsorption capacity of dextrin with temperature indicates an endothermic process. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or adsorbate adsorbing species and the decrease in the thickness of boundary layer surrounding the adsorbate. At higher temperature the possibility of diffusion of solute within the pore of the adsorbent may be enhanced leading to higher adsorption density since diffusion is an endothermic process, greater adsorption will be observed at high temperature. Thus the diffusion rate of ion in the external mass transport process increases with temperature. The observation of temperature effect of dextrin adsorption on coal therefore confirms that chemical reaction is dominant and this is as a result of fast reaction kinetics of the adsorbate species. This means, particle will travel at a faster rate to the surface to get adsorbed. However, the adsorbed species gain enough energy from temperature of the system and get desorbed at even a faster rate than adsorption rate. From this study, it was observed that ACB and ACL have the highest adsorption capacity of 95.50 and 88.00 respectively as the temperature increased to 70 °C.

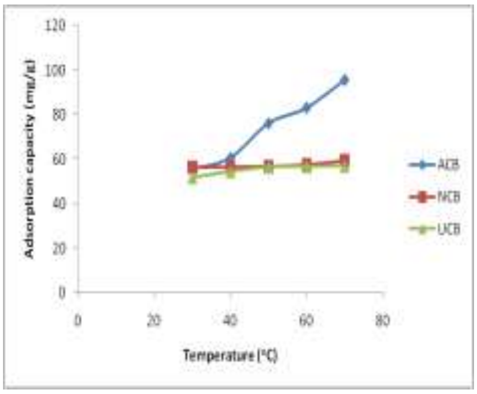

Fig.5. Effect of temperature on the adsorption of dextrin on ACB, NCB and UCB.

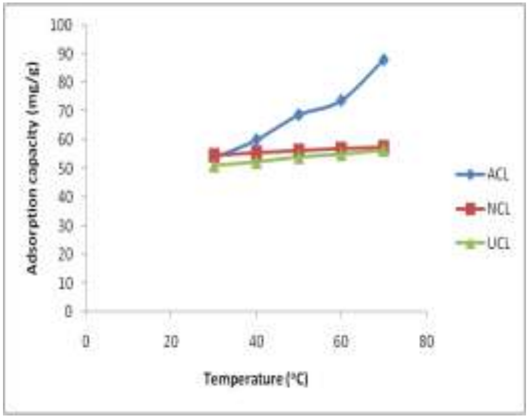

Fig. 6. Effect of temperature on the adsorption of dextrin on ACL, NCB and UCL.

Initial Concentration

The effect of concentration on the adsorption capacity of dextrin on coal is shown in Figure 7 and 8. There is a general increase in adsorption of dextrin up to a concentration of 150 mg/L, thereafter the adsorption levels off, remaining almost constant. This observation can be attributed to the saturation of adsorption active sites. Adsorption capacity of 61.25 and 55.00 mg/g was achieved at initial concentration of 200 mg/L for ACB and ACL respectively and the initial concentration ranged from 25 to 200 mg/L. An amount of 1.0 g of adsorbent with pH 6.6 was used for each adsorption experiment. The adsorption capacity of dextrin depends on the initial concentration of ion which decreases with the increase of initial metal ion concentration. This is due to more adsorption sites available on the adsorbent at low concentrations of the metal ions. The final concentrations remain constant at initial dextrin concentrations of 150 – 200 mg/L. This might be due to the fact that the adsorption sites become more saturated as the initial coal concentration are increased and the amount of adsorbent concentration remained constant.

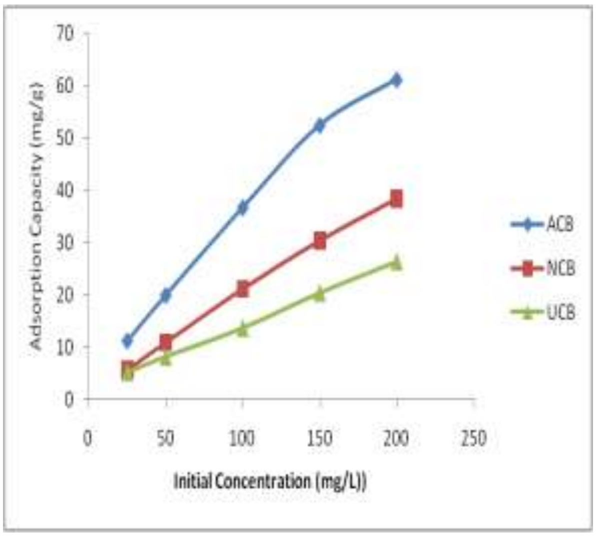

Fig. 7. Effect of initial concentration on the adsorption of dextrin On ACB, NCB and UCB.

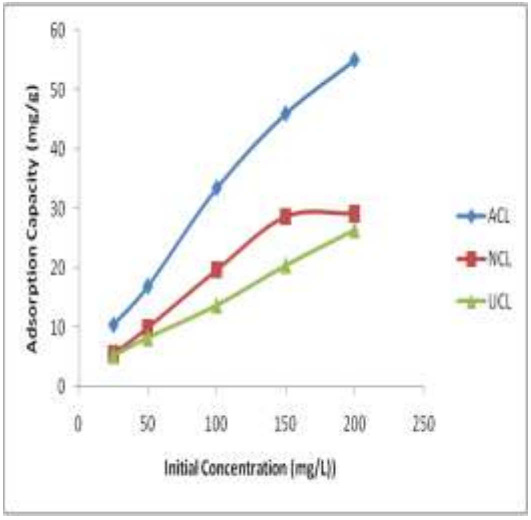

Fig.8. Effect of initial concentration on the adsorption of dextrin on ACL, NCL and UCL.

2.3. Adsorption Equilibrium Study

The successful representation of the dynamic adsorptive separation of solute from solution by an adsorbent depends upon a good description of the equilibrium between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed [7]. Adsorption equilibrium studies provide information about the nature of the physico-chemical interaction involved in the adsorption process. The experiment was conducted at pH 6 and at temperature of 30°C. The adsorption isotherm of dextrin onto coal surface is presented in Table 1. In the present work three isotherms were applied to investigate the adsorption process of dextrin on prepared coal samples at different conditions of process parameters.

Langmuir Isotherm

The Langmuir isotherm is applicable to homogeneous sorption where the sorption of each sorbate molecule on to the surface has equal sorption activation energy and is represented as follows [5]:

$$q_e = 1 + \frac{K_L C_e}{Q_{max}\ C_e} \qquad (5)$$

where qe is the solid phase sorbate concentration at equilibrium, K_L and Q_{max} are the Langmuir isotherm constants.

The linear form of Langmuir equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}\ K_L} + \frac{C_e}{Q_{max}} \qquad (6)$$

The adsorption data were analyzed according to the linear form of Eq. 5. The plots of Ce/qe versus C_e are linear which indicates that the adsorption data fitted to the Langmuir isotherm shown in Table 1. The constants were evaluated from the slope Q_{max} and intercept $1/Q_{max}\ K_L$, where Q_{max} gives the theoretical monolayer saturation capacity Q_0. The Langmuir constants obtained for all the six adsorbents are summarized in Table 1. The high value of Q_{max} obtained for the samples indicate the efficiency of Langmuir model to explain the adsorption process. The adsorption data of AC_B and AC_L samples were well fitted to the Langmuir equation with reasonably higher Q_{max} .

$$R_L = 1 + \frac{1}{K_L C_o} \qquad (7)$$

Where

C_o and K_L are the initial concentration and constant related to the affinity of binding sites with the metal ions, respectively. The value of R_L, a positive number ($0 < R_l < 1$), signifies the feasibility of the adsorption process for developed coal samples.

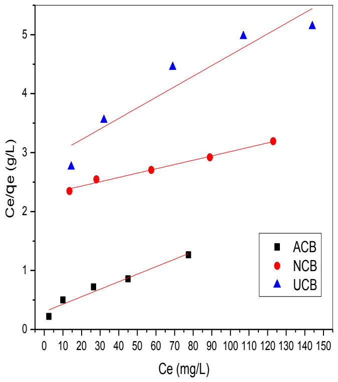

Fig. 9. Langmuir adsorption isotherm of ACB, NCB and UCB.

Freundlich Isotherm

The most important multisite or multilayer adsorption isotherm for heterogeneous surfaces is the Freundlich isotherm which is characterized by the heterogeneity factor 1/*n* and is represented by the equation:

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (8)$$

Where, q_e is the solid phase concentration in equilibrium, C_e is the liquid phase sorbent concentration at equilibrium, K_F is the Freundlich constant and 1/*n* is the heterogeneity factor.

The magnitude of *n* gives an indication on the favorability of adsorption. It is generally stated that the values of *n* in the range 2 – 10 represent good, 1 – 2 moderately good, and less than 1 poor adsorption characteristics. The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies [8]. The linear form of Freundlich equation is:

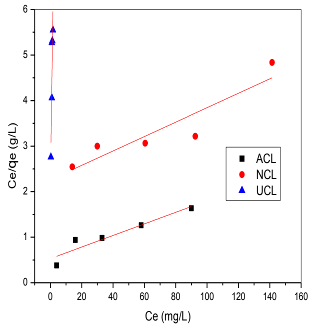

Fig.10. Langmuir isotherm of ACL, NCL and UCL.

$$\text{In}\ q_e = \text{In}\ k_F + \frac{1}{n}\ \text{In}\ C_e \qquad (9)$$

Where, the intercept lnk_F is a measure of adsorption capacity, and the slope 1/n is the adsorption intensity. The values of K_F and n were calculated from the intercept and slope of the plots lnq_e against lnC_e. The Freundlich isotherm describes reversible adsorption and was not restricted to the formation of monolayer. The isotherms were found to be linear as evidenced from correlation coefficients obtained in the range of 0.969 – 0.989 higher than Langmuir model . The Freundlich isotherm showed a better fit to the adsorption data than Langmuir isotherm suggesting heterogeneous adsorption nature of the coal samples. Freundlich sorption isotherm constants were determined for all the samples and are summarized in Table 1. The steepness and curvature of isotherms were obtained from the values of K_F and n. The value of K_F signifies the adsorption intensity and higher K_F value of ACB and lower value of 1/n confirmed the higher adsorption capacity for dextrin as compared to other samples i.e. NCB/L-UCB/L. The obtained K_F and n values of ACB and ACL are 6.714/1.934 and 4.415/1.783 respectively.

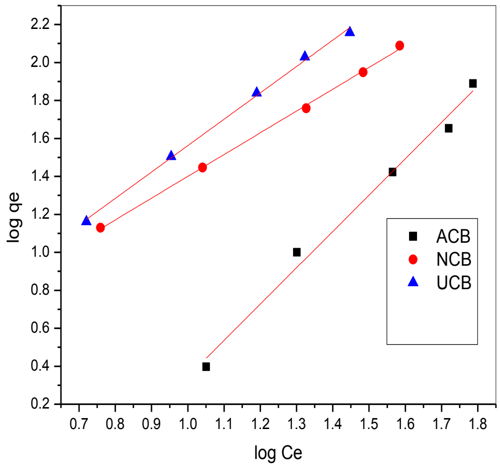

Fig. 11. Freudlich adsorption isotherm of ACB, NCB and UCB

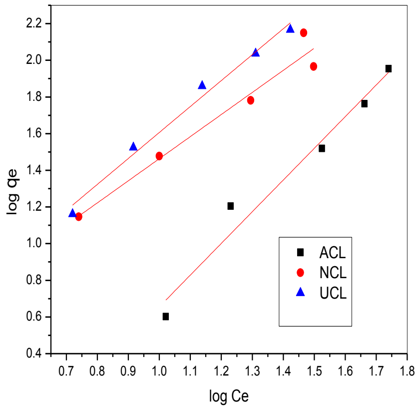

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Fig. 12. Freundlich adsorption isotherm of ACL, NCL and UCL.

Temkin Isotherm

Temkin isotherm model contains a parameter that explicitly accounts for the interaction of adsorbent and adsorbate species. It is based on the assumption that the heat of adsorption of all the molecules in the layer diminishes linearly with coverage which is attributed to adsorbate–adsorbate repulsion of the species. It also assumes that adsorption is due to uniform distribution of the binding energy. Contrary to Freundlich's model, it assumes that fall in heat of adsorption is linear rather than logarithmic. The Temkin equation is given as [9]:

$$q_t = B_T lnA_T + B_T lnc_e \qquad (10)$$

Where $B_T = RT/b$, T (K) is the absolute temperature;

R is the universal gas constant (8.314 J/Kmol);

A_T (L/mg) is the equilibrium binding constant that corresponds to the maximum binding energy; BT is related to the heat of adsorption; and q_e and C_e are the amount of adsorbate adsorbed per unit weight of adsorbent and equilibrium concentration of adsorbate remained in solution, respectively. The Temkin isotherm parameters were obtained by plotting q_e verses C_e. The positive values in Table 1 of adsorption energy (B_T) obtained indicate that the process is exothermic, which is contrary to the obtained results suggesting that the adsorption data does not follow Temkin isotherm [10].

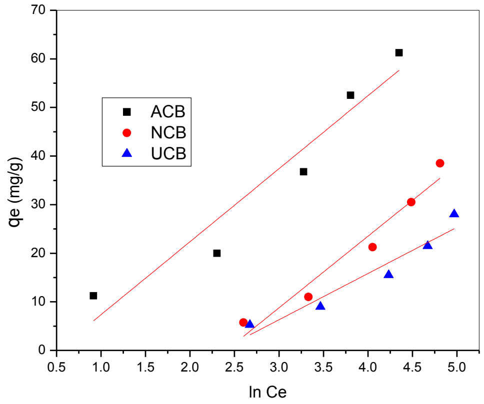

Fig.13. Temkin adsorption isotherm of ACB, NCB and UCB.

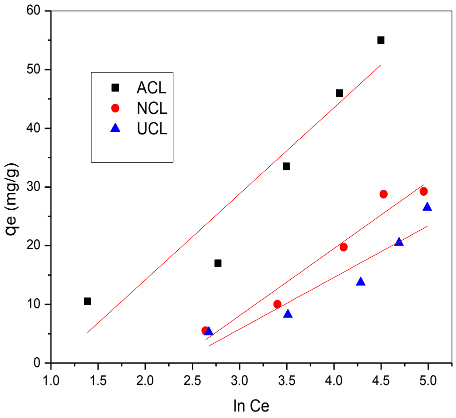

Fig.14. Temkin adsorption isotherm of ACL, NCL and UCL.

Table 1. Langmuir, Freundlish and Temkin Isotherm Constants

	Langmiur			**Freundlich**			**Termkin**		
Sample	**K_L (dm-3/g)**	**Qmax (mg/g)**	**R^2**	**K_F (dm3/g)**	**n**	**R^2**	**B**	**A(dm^3/g)**	**R^2**
ACB	0.0398	83.33	0.959	6.714	1.934	0.989	-7.663	0.6	0.932
ACL	0.0226	83.33	0.898	4.415	1.783	0.969	-15.16	0.355	0.909
NCB	0.0064	76.92	0.992	0.605	1.149	0.998	-35.44	0.09	0.954
NCL	0.0066	66.66	0.847	0.732	1.285	0.97	-26.21	0.1	0.952
UCB	0.0059	58.82	0.903	0.748	1.385	0.998	-22.24	0.1	0.932
UCL	0.006	52.63	0.777	0.76	1.434	0.986	-20.63	0.096	0.898

4. Conclusion

In this work, the ability of dextrin to adsorb on coal surface from aqueous solution was investigated. Studies concerning the adsorption equilibrium are presented and discussed. Experimental results show that dextrin was effective in aqueous solution when coal surface was coated with $Al^{3+.}$ Equilibrium data obtained was modelled using three isotherms: Langmuir, Freundlich and Temkin and the equilibrium isotherm were well described by Freundlich equation. This study proved that dextrin appeared to be more stable adsorbate in solution when the coal surface is modified with Al^{3+} from $AI_2(SO_4)_3$. It provides a means of adsorption onto the particle surface by electrostatic attraction and causes the polymer to extend and uncoil due to charge repulsion along the length of the polymer chain, so that the molecule is more nearly linear and can therefore accommodate more particles.

Since dextrin can be locally prepared and is cheap, the result is expected to be economically viable for the adsorption of dextrin on coal surface from aqueous solution. Therefore, locally prepared dextrin can serve as a replacement for currently expensive adsorbates such as silica gel, gum and zeolite during coal processing.

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