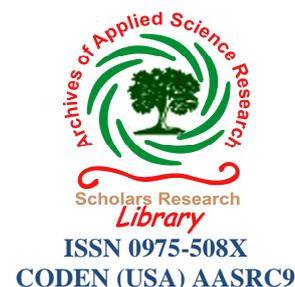




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Kinetics, equilibrium, and thermodynamics studies of colour pigments removal from palm oil using activated ukpor clay

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ABSTRACT

Clay from Ukpor was acid activated (at various concentrations) to improve its adsorptive capacity by increasing the specific surface area. The activated samples were used to adsorb colour pigments from palm oil. To study the adsorption capacity of the activated clay samples, the effects of temperature, contact time, adsorbent dosage and particle size were studied. The experimental data were analyzed using the established kinetic models of Pseudo-first order, Pseudo-second order, Elovich, and intra-particle diffusion. The data fitted very well to the Pseudo-second order kinetic model with a regression coefficient of 0.995. Equilibrium isotherms were analyzed by Langmuir, Freundlich, and Temkin adsorption models. The data conformed to the Freundlich isotherm model with regression coefficient of 0.998. The activation energy was calculated as 18kJ/mol, while the other thermodynamics parameters were determined as $\Delta S = 0.075\text{J/mol}$, $\Delta H = 43.565\text{J/mol}$, and $\Delta G = -74.347\text{kJ/mol}$. These values indicate that the removal of colour pigment from refined palm oil by acid activated Ukpor clay is exothermic and can be attributed to a physico-chemical adsorption process.

Keywords: Kinetics; isotherm; activation; adsorption; colour pigments; thermodynamics

INTRODUCTION

Bleaching involves solely the removal of variety of impurities like fatty acids, gums, trace metals, phosphatides, etc., followed by decolourization. Bleaching of edible oils helps in raising their smoke point and storage durability. Bleaching is achieved by using natural or activated clays and activated carbons. The use of activated clays in bleaching edible oils has been investigated by many authors [1-8]. The bleaching capacity of natural clay materials is greatly increased by acid treatment (activation). The acid treatment of the natural clay materials imparts different physico-chemical properties like surface area, acidity, and cation exchange capacity (CEC), thereby increasing their adsorptive ability.

Kinetics describe the solute uptake rate that controls the residence time of sorbate uptake at the solid-solution interface, and are more important because to design appropriate sorption treatment plants, the rate at which any pollutant is removed from solutions must be predicted [9], [10]. There are few researches on the kinetics of the bleaching process. Topallar [11], studied the kinetics of sunflower seed oil bleaching and proposed a rate formula of $\log (A/A_0) = -k \sqrt{t}$, according to absorbance measurement. Nwankwere et al, [12], investigated the kinetics of B-carotene removal from palm oil using unmodified natural clay, and they concluded that the adsorption followed the

zero order kinetic equation. Al-Zahrani et al, [13], investigated the kinetics of sulphuric acid activation of Saudi bentonite and found out that it followed the zero order kinetic equation.

In this study the adsorption performance of acid-activated Ukpok clay was investigated in bleaching purified palm oil. The kinetics, equilibrium and thermodynamics of the bleaching process were studied to elucidate the mechanism of the process.

MATERIALS AND METHODS

Materials

The clay used in this study was mined at Ukpok (N: 5° 54' 27.5"; E: 6° 56' 3.7"; A: 137m) in Nnewi South local government area, while the palm oil was obtained from a local palm oil mill in Isuofia (N: 6° 1' 60"; E: 7° 2' 60"; A: 361m) in Aguata local government area, both in Anambra state of Nigeria. All the chemicals used were of analytical grade bought from Conraws Nig. Ltd.

Clay preparation and activation

The mined clay was sun-dried for two days and grinded to smaller particles using mortar and pestle. The ground samples were sieved to remove impurities and then oven dried at 105⁰C. The samples were then put in contact with hydrochloric acid in a 250 cm³ flask placed in a regulated water bath. The flask was heated while continuously being stirred. To study the effect of activation variables, the experiment was repeated at various concentrations (1 – 5M), temperatures (50 – 120⁰C), for various contact times (2 – 6h). At the completion of the heating time, the slurry was removed from the bath and allowed to cool. After the cooling, the slurry was filtered via a Buchner funnel and the clay residue was washed several times with distilled water, followed by filtration until the filtrate was neutral to pH indicator paper. The prepared wet sample was then dried in an oven at 120⁰C over night. The lumps of the prepared clays were crushed and sieved again into various particle sizes ranging from 0.045 to 0.408 mm and stored for further use in the bleaching process. The activated clay samples were labeled as follows: UK0, UK1, UK2, UK3, UK4, and UK5, where the numbers denote the acid concentration. The activated clays were then characterized.

Adsorption Experiment

100g of the refined unbleached palm oil was measured out into a 250 ml conical flask and heated on a magnetically-stirred hot plate to 90⁰C while stirring continuously. 2g of the sized activated clay samples was then added to the heated oil and stirred continuously via a magnetic stirrer carefully inserted into the beaker. The whole mixture was heated to a temperature of 130⁰C for 45 minutes. At the completion of the time, the hot oil and clay mixture was filtered under gravity using Whatman filter paper No. 42 (15 cm diameter), before measuring the absorbance. The bleaching/adsorption efficiency of the activated clay samples was then determined by measuring the colour of the bleached oil using UV-VIS Spectrophotometer (Model WFJ 525) at 450 nm. The bleaching efficiency is defined by the following expression in this study:

$$BE (\%) = \frac{A_{\text{unbleached}} - A_{\text{bleached}}}{A_{\text{unbleached}}} \times 100 \quad (1)$$

Where $A_{\text{unbleached}}$ and A_{bleached} are absorbencies of unbleached and bleached palm oil, respectively, at 450 nm, BE is bleaching efficiency.

To study the effect of process variables on the bleaching efficiency of the activated clay samples the above experimental procedure was carried at different values of the parameters. The experiment was performed at different mass of the adsorbent (activated clay) which was varied at 0.5, 1.5, 2.5, 3.5, and 4.5 grams. The temperature and time of heating were also varied at 30, 70, 80, 100, and 120; and 10, 20, 30, 40, 50, 60, and 80 minutes, respectively. The effect of activation parameters on the bleaching efficiency of the clay samples was investigated by using the different samples activated with varying acid concentration in the bleaching process.

RESULTS AND DISCUSSION

Physical characterization

The results of the physical characterization of the raw and activated clays are summarized in Table 1. The results show that the acid activation of the clay caused some modifications in the structure of the clays.

Table 1: Physical properties of raw and activated clay samples [14]

Properties	Clay type					
	UK0	UK1	UK2	UK3	UK4	UK5
Surface area (m ² /g)	96.2	159.5	202.4	226.6	294.3	342.8
Bulk Density (Kg/m ³)	1153.4	874	838.5	753.9	715.8	864.9
Oil Retention (%)	35	41.2	45.8	50.4	53.8	55.8
Acidity	0.02	0.07	0.12	0.13	0.16	0.17
pH	7.6	3.9	1.8	1.7	1.5	1.3
Cation Exchange Capacity (meg/100g)	97	84	68	59	50	48

As can be seen from the table, the surface area of the activated samples increased as the acid concentration used in the activation step increased and also the cation exchange capacity decreased with increasing acid concentration indicating the extent of removal of the octahedral cations (Al³⁺, Fe³⁺, and Mg²⁺) from the clay structure. Comparing Table 1 with Figure 1 shows that the maximum bleaching efficiency does not always coincide to the highest surface area as reported by other authors [15], [16].

Effect of acid concentration on bleaching efficiency

Figure 1 shows the variation of bleaching efficiency with time at different acid concentrations. The figure shows that as the acid concentration increased, the bleaching efficiency increased up to a maximum value of 68.7% at a concentration of 4M HCl. Above this concentration, the bleaching efficiency decreased to 60.4%. This can be attributed to the destruction of the clay crystalline structure by the excess acid.

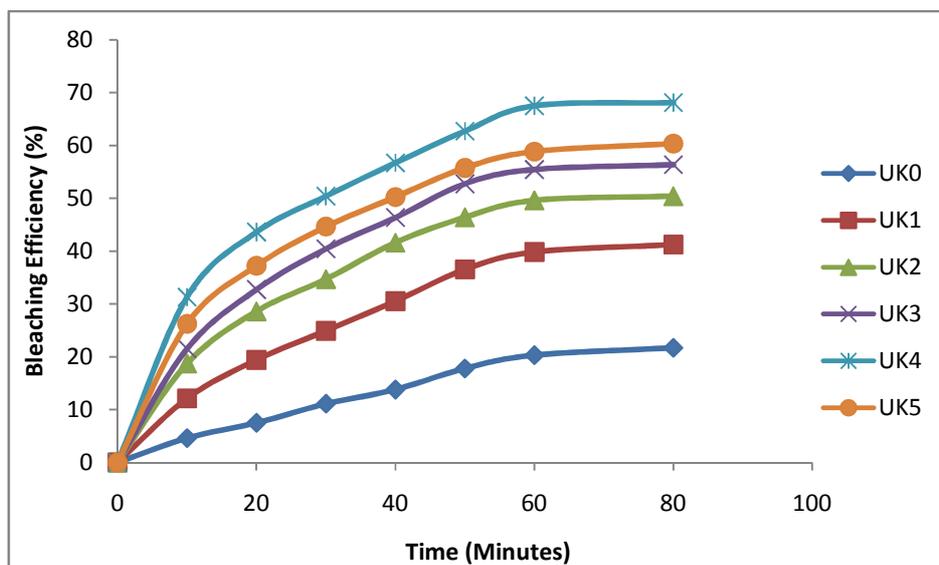


Figure 1: Variation of bleaching efficiency with time at different acid concentration.

Effect of temperature on the bleaching efficiency

The variations of bleaching efficiency with time at different temperatures are shown in Figure 2. The figure shows that the bleaching efficiency increased with increase in temperature up to a temperature of 393K and decreased with further increase in temperature. This is as a result of undesirable structural changes of the oil molecules via oxidative degradation and isomerisation. This situation was also reported by other researchers [17], [18].

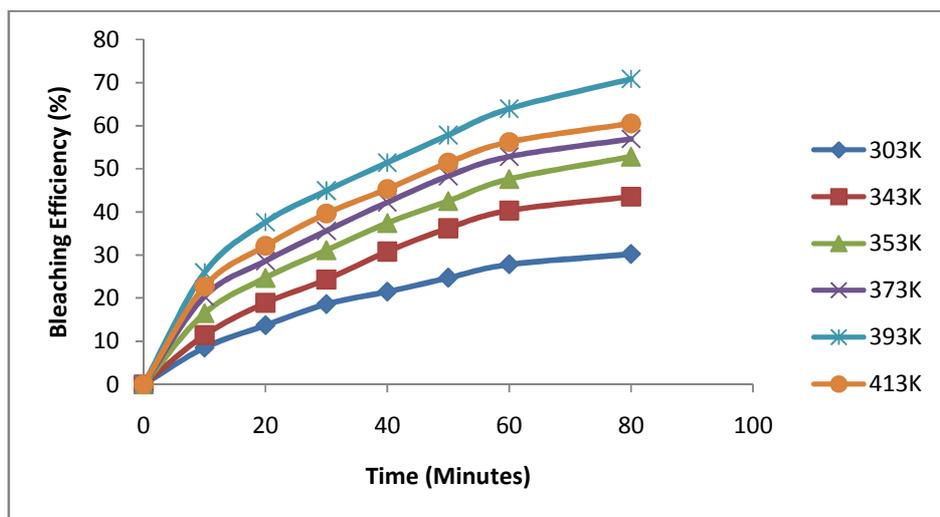


Figure 2: Variation of bleaching efficiency with time at different temperatures.

Effect of particle size on the bleaching efficiency

The effect of varying the particle size of the clay adsorbents on the bleaching efficiency is shown in Figure 3. The figure shows that the bleaching efficiency has an inverse relationship with the particle size. The bleaching efficiency decreases as the particle size increased. This could be attributed to larger surface area available for contact on the surface of the adsorbent resulting to enough active sites for adsorption.

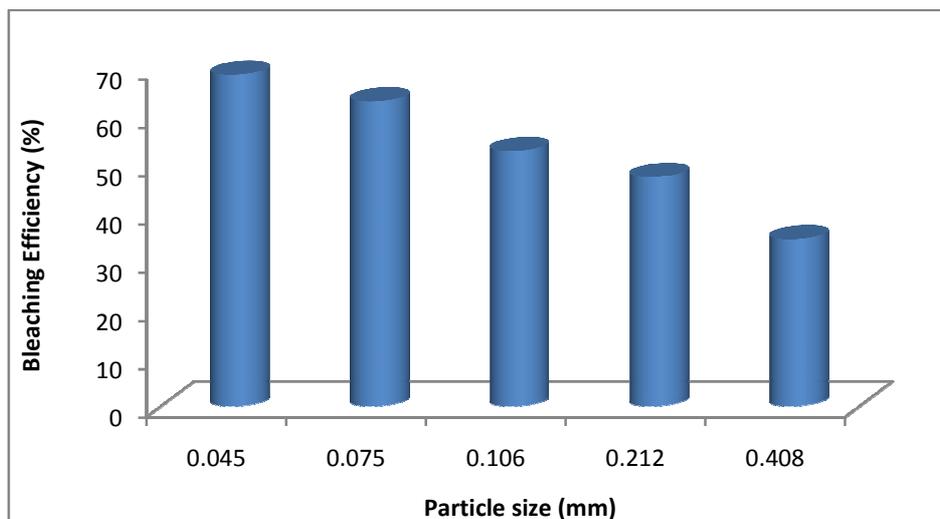


Figure 3: Variation of bleaching efficiency with particle size.

Effect of clay dosage on bleaching efficiency

Figure 4 shows the effect of clay dosage on the bleaching efficiency of the adsorbent prepared from Ukpore clay. The figure shows that as the adsorbent dose increased, the bleaching efficiency increased as well with time. The increase in bleaching efficiency remained constant after 40 minutes for higher doses of 3.5 and 4.5g, but remained constant after 50 minutes at doses below 3.5g. This could be attributed to the complete adsorption of the colour pigments to the available active sites on the adsorbent.

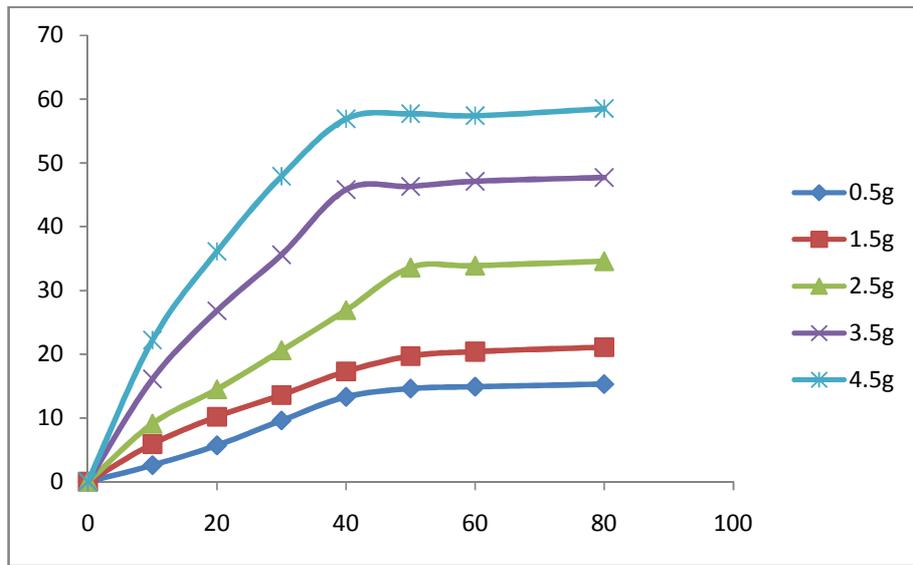


Figure 4: Variation of bleaching efficiency with time at different clay dosage.

Kinetics of bleaching

The effect of temperature on the bleaching efficiency of Ukpor clay activated with 4M hydrochloric acid is reflected in Figure 1. The data were tested with different kinetic models in order to describe the adsorptive interaction between the colour pigment and the activated clay. The kinetic models used in the analysis of the data are as follows: Pseudo-first order, pseudo-second order, Elovich, intra-particle diffusion, and mass transfer kinetic equations. The respective linear forms of the equations are as given below:

- $\log (q_e - q_t) = \log q_e - k_1 t$ (Pseudo-first order model) (2)
- $1/q_t = 1/(k_2 q_e^2) + t/q_e$ (Pseudo-second order model) (3)
- $q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t$ (Elovich model) (4)
- $\log q_t = \log K_{id} + a \log t$ (Intra-particle diffusion model) (5)
- $\ln (C_o - C_t) = \ln D + K_o t$ (Mass transfer equation) (6)

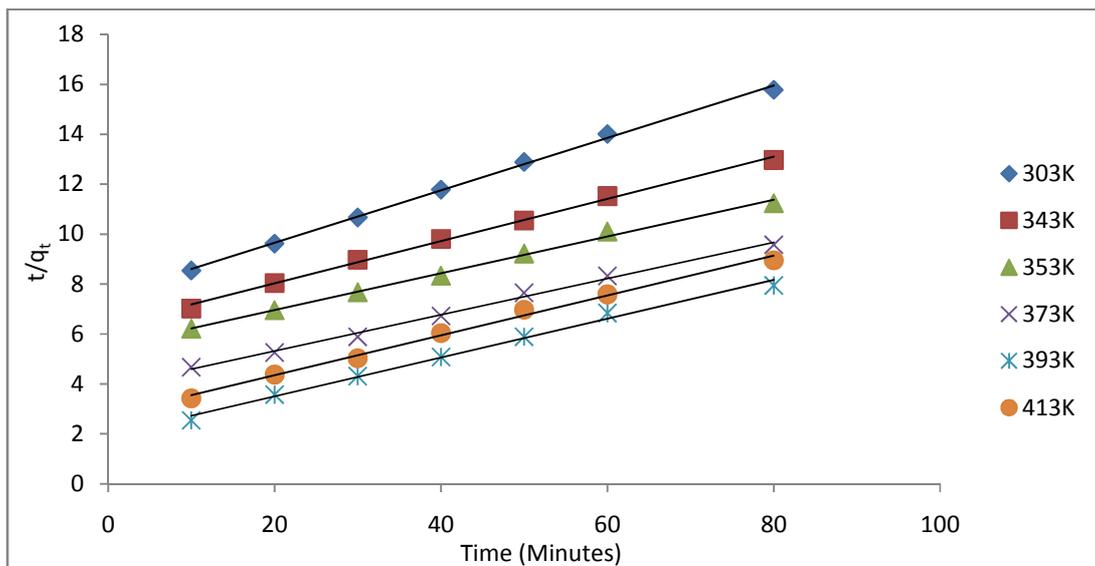


Figure 5: Pseudo-second order kinetic plot for colour pigment removal from palm oil.

Table 2: The kinetic parameters evaluated for colour pigment adsorption onto activated Nteje clay [14].

Kinetic models	Parameters	Temperature (°C)					
		303	343	353	373	393	413
Pseudo-first Order	K_1	0.4×10^{-2}	0.5×10^{-2}	0.6×10^{-2}	0.7×10^{-2}	0.8×10^{-2}	0.7×10^{-2}
	q_e (mg/g)	8.337	10.423	10.520	9.419	11.348	10.982
	R^2	0.976	0.983	0.970	0.960	0.973	0.978
Pseudo second Order	K_2	0.35×10^{-3}	0.34×10^{-3}	1.38×10^{-3}	1.56×10^{-3}	1.78×10^{-2}	1.64×10^{-2}
	q_e (mg/g)	17.54	21.74	15.63	14.93	13.67	12.32
	R^2	0.998	0.997	0.998	0.997	0.997	0.996
Elovich	α (mg/g min)	0.3238	0.4695	0.7896	0.8333	0.9954	0.8943
	β (mg/g min)	0.4980	0.3557	0.3120	0.3494	0.2985	0.3065
	R^2	0.932	0.939	0.980	0.972	0.923	0.947
Intra-Particle Diffusion	K_{id} (mg/gmin)	0.1409	0.2193	0.6295	0.7539	0.8931	0.8043
	a	0.8570	0.835	0.647	0.620	0.438	0.513
	R^2	0.987	0.986	0.984	0.988	0.983	0.986
Mass Transfer	K_0 (min ⁻¹)	0.021	0.020	0.019	0.018	0.016	0.017
	D	0.3091	0.4440	0.5423	0.7712	0.8349	0.7905
	R^2	0.837	0.815	0.826	0.855	0.843	0.837

The associated kinetic parameters have been evaluated from the slopes and intercepts of the respective linear plots of the kinetic equations, and the values are shown in Table 2. Comparison of the analyzed data based on the linear regression coefficient (R^2) values as shown in the table, showed that the experimental data is best described by the pseudo-second order equation (Eq. (3)), which has the most linear fit with correlation coefficient (R^2) > 0.997. Hence, the plot of the linear form of the pseudo-second order kinetic equation is shown in Figure 5.

Adsorption isotherm

It was observed that as the temperature increased the amount adsorbed on the surface of the adsorbent increased. This change occurs as a result of increase in kinetic energy of the colour pigment particles, which increases the frequency of collisions between the adsorbent and the particles and thus enhances adsorption on the surface of the adsorbent.

Two main types of adsorption may usually be distinguished on surfaces. In the first type, the forces are of a physical nature and the adsorption is relatively weak. The forces in this type of adsorption are known as van der Waals forces and this type of adsorption is called van der Waals adsorption, physical adsorption or physisorption. The heat evolved during van der Waals adsorption is usually small, less than 20 kJ/mol. In the second type of adsorption, first considered in 1916 by Langmuir, the adsorbed molecules are held to the surface by covalent forces of the same general type as those occurring between bound atoms in molecules. The heat evolved during this type of adsorption, known as chemisorptions, is usually comparable to that evolved during chemical bonding, namely, 300 – 500 kJ/mol.

Langmuir considered adsorption to distribute molecules over the surface of the adsorbent in the form of a uni-molecular layer and for the dynamic equilibrium between adsorbed and free molecules, he proposed the following relation:

$$P/(X/m) = 1/a + (a/b)P \quad (7)$$

Where P is equilibrium pressure for a given amount of substance adsorbed, X is the amount of substance adsorbed, m is the amount of adsorbent, a and b are constants.

The mathematical expression relating adsorption to residual solute concentration was developed by Freundlich:

$$X/m = K C^n \quad (8)$$

Where C is the amount of residual substance, and K and n are constants.

Since the absorbance measurements are taken in all experiments for the bleaching process, the relative amount of pigment adsorbed (X) and the residual relative amount at equilibrium (X_e) are obtained from Equations 7 and 8:

$$X = (A_0 - A_t) / A_0 \quad (9)$$

$$X_e = A_t / A_0 = 1 - X \quad (10)$$

where A_0 is the absorbance of unbleached (crude) palm oil and A_t is the absorbance of bleached oil at time t .

Thus, by means of Equations 9 and 10, by writing X_e instead of equilibrium pressure P and the residual substance C , Equations 7 and 8 are rearranged as follows (Topallar, 1998):

$$X_e / (X/m) = 1/a + (a/b) X_e \quad (11)$$

$$X / m = K X_e^n \text{ or the linear form}$$

$$\log (X/m) = \log K + n \log X_e \quad (12)$$

To evaluate the nature of adsorption, the experimental data of Figure 2, was analyzed by the established isotherm equations viz; Langmuir, Freundlich, and Temkin.

The Freundlich, Langmuir, and Temkin model parameters and the statistical fits of the adsorption data to these models as calculated from the respective plots (not shown) are presented in Table 3. It was observed that the Freundlich model adequately described the adsorption data with regression coefficient values greater than 0.997.

Table 3: The isotherm parameters obtained from linear analysis of colour pigment adsorption onto Ukpokor clay activated with 4M HCl (Ajemba, 2012)

Isotherm models	Parameters	Temperature (K)					
		303	343	353	373	393	413
Freundlich	K_f	11.94×10^{-3}	19.36×10^{-3}	30.27×10^{-3}	47.42×10^{-3}	56.31×10^{-3}	49.41×10^{-3}
	n	-0.112	-0.117	-0.118	-0.131	-0.168	-0.153
	R^2	0.998	0.998	0.998	0.997	0.997	0.996
Langmuir	K_a	-0.0524	-0.0272	-0.0149	-0.0078	-0.0053	-0.0024
	q_m	-6.1720	-3.4312	-2.2349	-1.4876	-1.0542	-0.8321
	R^2	0.982	0.983	0.987	0.987	0.985	0.984
Temkin	K_T	0.8988	1.0000	1.0515	1.0159	1.1237	1.0935
	b_T	-19.01×10^3	-19.44×10^3	-10.09×10^3	-6.98×10^3	-2.75×10^3	-0.76×10^3
	R^2	0.939	0.941	0.985	0.983	0.964	0.955

Adsorption Thermodynamics

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG° , is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of an adsorption, considering the adsorption equilibrium constant K_f is given by the following equation:

$$\Delta G^\circ = -RT \ln K_f \quad (13)$$

Where ΔG° is the standard free energy change (J/mol), R the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). Considering the relationship between ΔG° and K_f , change in equilibrium constant with temperature can be obtained in the differential form as follows:

$$D \ln K_f / dT = \Delta H^\circ / RT^2 \quad (14)$$

After integration, the integrated form of Eq. (14) becomes:

$$\ln K_f = -(\Delta H^\circ / RT) + Y \quad (15)$$

Where Y is a constant. Eq. (15) can be rearranged to obtain

$$-RT \ln K_f = \Delta H^\circ - TRY \quad (16)$$

Let

$$\Delta S^\circ = RY \quad (17)$$

Substituting in Eq. (16), becomes

$$-RT \ln K_f = \Delta H^\circ - T\Delta S^\circ \quad (18)$$

The above equation can then be written in the following forms:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (19)$$

Or

$$\ln K_f = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \quad (20)$$

The values of ΔH° and ΔS° are calculated from the slope and intercept of the plot of $\ln K_f$ versus $1/T$ (not shown).

The values of the thermodynamic parameters are shown in Table 4. As can be seen from the table, the values of the Gibbs free energy change of adsorption, ΔG° , are all negative and show a decrease in the negative value as the temperature increases. According to Saha and Chowdhury, [19], a decrease in the negative value of ΔG° with an increase in temperature indicates that the adsorption process is more favourable at higher temperatures. This is possible because the mobility of adsorbate ions/molecules in the solution increased with an increase in temperature and that the affinity of adsorbate on the adsorbent is higher at high temperatures. This postulation was confirmed in this study as can be seen in the effect of temperature on the adsorption efficiency. As the temperature of the reaction was increased, the adsorption of the colouring pigments onto the adsorbent increased.

The values of the enthalpy, ΔH° , and entropy, ΔS° , as calculated from the plot of $\ln k_f$ versus $1/T$, are also presented in Table 4. The value of the enthalpy is negative and this implies that the adsorption of colour pigments from palm oil onto locally activated clay is exothermic. The adsorption process in the solid-liquid system is a combination of two processes: (a) the desorption of the solvent molecules previously adsorbed, and (b) the adsorption of the adsorbate species. In an exothermic process, the total energy absorbed in bond breaking is less than the total energy released in bond making between adsorbate and adsorbent, resulting in the release of extra energy in the form of heat. The magnitude of ΔH° gives an idea about the type of sorption. The heat evolved during physical adsorption falls in the range of 2.1 – 20.9kJ/mol while that evolved during chemical sorption is in the range of 80 – 200 kJ/mol. Therefore, as seen from Table 4, it is deduced that the adsorption of colour pigments onto acid activated Nteje clay can be attributed to a physico-chemical adsorption process rather than a pure physical or chemical adsorption process [19].

The value of ΔS° as presented in Table 4 is positive and this reflects the affinity of the adsorbent towards the adsorbate species. A positive value of ΔS° suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of randomness in the system [19].

Table 4: Adsorption thermodynamic parameters

Temp. (K)	$\ln K_f$	$\Delta G^\circ(\text{kJ/mol})$	$\Delta H^\circ(\text{J/mol})$	$\Delta S^\circ(\text{J/mol})$
303	-4.42786	-84.865		
343	-3.94434	-85.827		
353	-3.49763	-86.877	-48.762	0.105
373	-3.04863	-87.927		
393	-2.87688	-88.784		
413	-3.00760	-89.824		

CONCLUSION

The kinetics, equilibrium and thermodynamics studies of the removal of colour pigments from palm oil using acid activated Ukor clay have been successfully investigated. The structure of the activated clay was modified and it led

to increased surface area and adsorption capacity. The removal of the colour pigment increased as the temperature of the process and acid concentration increased. The same trend was observed when the clay dosage and time were varied. The experimental data agreed with the pseudo-second order kinetic equation, while the linear isotherm analyses indicated that the equilibrium data can be described with the Freundlich model. The thermodynamic parameters revealed the spontaneous and exothermic nature of colour pigment adsorption onto activated Ukpokor clay, and the adsorption takes place with increase of entropy.

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