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ADSORPTIVE REMOVAL OF COLOUR PIGMENT FROM PALM OIL USING ACID ACTIVATED NTEJE CLAY. KINETICS, EQUILIBRIUM AND THERMODYNAMICS

Regina O. AJEMBA, Okechukwu D. ONUKWULI

Department of Chemical Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Anambra, Nigeria,
ginaajemba@rocketmail.com

Abstract: The kinetics of colour pigment removal from palm oil using acid activated clay from Nteje has been investigated. To determine the equilibrium adsorption capacity, the effects of temperature, contact time, adsorbent dosage and particle size were studied. The experimental adsorption data were analyzed using pseudo-first order, pseudo-second order, and Elovich kinetic models. The pseudo-second order model fitted very well to the kinetic experimental data. Equilibrium isotherms were analyzed by Langmuir and Freundlich adsorption models. The data was in line with the Freundlich isotherm indicating a monolayer adsorption. The activation energy was calculated as 12 kJ/mol, and other thermodynamic parameters were determined as $\Delta S^\circ = 0.063$ J/mol, $\Delta H^\circ = -34.994$ J/mol, and $\Delta G^\circ = -58.606$ kJ/mol. These values indicate that the adsorption of colour pigment from palm oil onto acid activated clay was exothermic and can be attributed to physico-chemical adsorption process.

Keywords: *adsorption, kinetics, isotherm, activation, colour pigment, palm oil, bleaching*

Introduction

Acid activated clays (bentonite) have been employed as catalysts for a number of reactions of industrial interests (Didi, et al., 2009; Foletto et al., 2003; Breen et al., 1997; Mokaya et al., 1995). Activated clays have also been used in the paper industry, in the chemical industry, for environmental protection and in the foodstuff industry, for sulphur production, forest and water conservation (O'Driscoll, 1988), as well as bleaching of vegetable oils (Kirali and Lacin, 2006; Christidis et al., 1997; Makhoukhi et al., 2009; Selvaraji et al., 2004; Bakhtyar et al., 2011). Bleaching involves solely the removal of variety of impurities like fatty acids, gums, trace metals, phosphatides etc., followed by decolourization. Bentonites are found in nature abundantly. However, most of them should undergo appropriate physical or chemical treatments such as acid activation, ion exchange and heating in order to promote their surface properties (Ros-

si et al., 2003; Rozic et al., 2010; Foletto et al., 2011; James et al., 2008; Taha et al., 2011). Acid activation of clays is one of the most important processes that have been performed to achieve structural modifications in the clays for edible oil bleaching. Activated clays show a much higher bleaching capacity when compared to natural clays. During acid activation, initially interlayer cations are replaced with H^+ ions followed by partial destruction of aluminum octahedral sheets with subsequent dissolution of structural cations. The desired changes in the physicochemical properties of clay occurring as a result of acid activation depend considerably on the condition of acid activation such as acid concentration and the duration and temperature of the activation process (Motlagh et al., 2008, 2011).

There are few researches on the kinetics of the bleaching process. Topallar (1998), 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. (2012) 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. (2000), investigated the kinetics of sulphuric acid activation of Saudi bentonite and found out that it followed the zero order kinetic equation.

In this work, the main objective was to investigate the equilibrium and kinetic parameters of the application of acid activated Nteje clay in the bleaching of palm oil.

Materials and methods

The clay used in this study was mined at Nteje (N: 6° 16' 00"; E: 6° 55' 00"; A: 118 m) in Aniocha 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: 361 m) in Aguata local government area, both in Anambra state of Nigeria. All the chemicals used were analytical grade reagents.

Clay preparation and activation

The mined clay was sun-dried for 24 hours and grinded to smaller particles using mortar and pestle. The ground samples were sieved to remove impurities and then oven dried at 105°C. 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 (0.5–5 mol/dm³), temperatures (50–120°C), for various contact times (2–6 h). 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 120°C 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: NT0.5, NT1, NT2, NT3, NT4 and NT5, where the numbers denote the acid concentration. The activated clays were then characterized.

Adsorption Experiment

A 100 g sample of the refined unbleached palm oil was measured out into a 250 cm³ conical flask and heated on a magnetically-stirred hot plate to 90°C while stirring continuously. A 2 g sample of the sized activated clay 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 130°C 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:

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

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 repeated at different adsorbent dosage (0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 g); reaction temperatures (30, 70, 80, 100, and 120°C); particle size (0.045, 0.075, 0.106, 0.212, and 0.408 mm) and reaction time (20, 40, 60, 80, 100, 120, and 150 min). The effect of activation parameters on the bleaching efficiency of the clay samples was investigated by using the samples activated with different acid concentrations bleach palm oil.

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. With an increase in concentration of hydrochloric acid, the activated samples showed a gradual increase in surface area until treatment with 3 mol/dm³ HCl. In treatment with 4 mol/dm³ HCl, a decrease of surface area was observed in comparison with the surface area of sample treated with 3 mol/dm³ HCl. The increase in the surface area from natural to activated samples is related to the elimination of the exchangeable cations, de-lamination of clays, and the generation of micro-porosity during the activation process (Dias et al., 2003). The

decrease observed at higher acid concentrations could be explained by the process of “passivation” (Pesquera et al., 1992). The octahedral sheet destruction passes the cations into the solution, while the silica generated by the tetrahedral sheet remains in the solids, due to its insolubility. Pesquera et al. (1992) suggest that this free silica generated by the initial destruction of the tetrahedral sheet, is polymerized by the effect of such high acid concentrations and is deposited on the undestroyed silicate fractions, protecting it from further attack and thereby resulting to a decreased surface area. The CEC values of the samples also displayed similar behaviour. With the increase of concentration of HCl, the samples showed a gradual decrease in CEC until treatment with 3 mol/dm³ HCl. In treatment with 4 mol/dm³ HCl, an increase of the CEC was observed in comparison with the CEC of sample treated with 3 mol/dm³ HCl and this could also be explained by the process of passivation.

Table 1. Physical properties of raw and activated clay

Properties	Clay type					
	NT0	NT0.5	NT1	NT3	NT4	NT5
Surface area (m ² /g)	88.4	127.6	186.7	296.3	207.5	199.5
Bulk density (kg/m ³)	1058.9	987.5	964	721.2	853.6	877.3
Oil retention (%)	22	27.4	33.6	54.5	41.8	38.7
Acidity	0.01	0.05	0.09	0.15	0.11	0.08
pH	8.1	6.8	4.4	2.8	3.9	4.1
Cation Exchange Capacity CEC (meg/100g)	89	80	71	50	64	67

Effect of time and acid concentration on the bleaching efficiency

To study the effect of time on the bleaching efficiency of the activated clay samples, the adsorption test was performed at different times ranging from 20–150 minutes. It was observed that adsorption efficiency of the samples increased as time increased

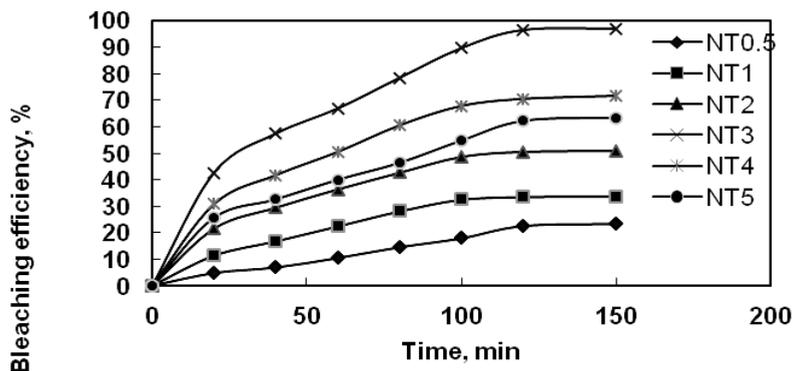


Fig. 1. Effect of bleaching time and acid concentration on bleaching efficiency

with the sample activated with 3 mol/dm^3 HCl (NT3) having the highest efficiency as shown in Fig. 1. Also, the figure shows the effect of varying the concentration of the acid used. It shows that bleaching efficiency increases with increase in acid concentration up to 3 mol/dm^3 above which the efficiency dropped drastically as a result of destruction of the clay structure by the excess acid.

Effect of temperature on bleaching efficiency

Figure 2 shows that the bleaching efficiency is favoured by an increase in reaction temperature. From the figure it is obvious that bleaching does not proceed to any appreciable degree at low temperatures. But as the temperature is increased from 30°C to 120°C , the bleaching efficiency increased showing that temperature promotes access to further adsorption sites in the adsorbent. The bleaching efficiency increased with reaction time at high temperature until it reaches a maximum, then it starts to decrease with increasing reaction time.

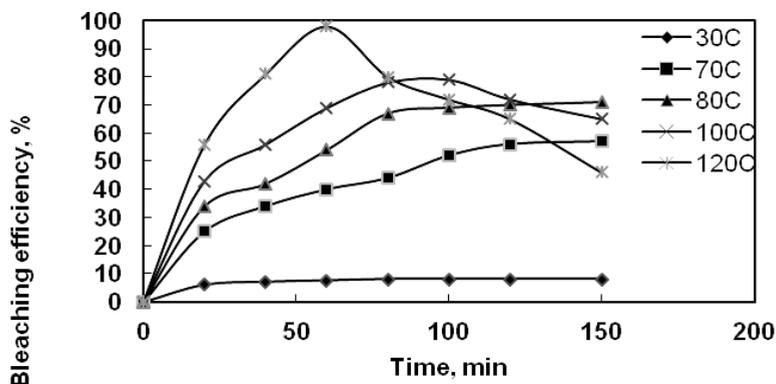


Fig. 2. Variation of bleaching efficiency with time at different temperatures

Effect of adsorbent dosage

Figure 3 represents the plot of bleaching efficiency versus adsorbent dosage. The clay dosage was varied from 0.5 to 4 g. It was observed that increasing the clay dosage increased the bleaching efficiency. The results clearly indicate that the bleaching efficiency increases to an optimum value at adsorbent dosage of 1 g above which further increase in adsorbent dosage has no significant effect on it, but the value remains constant. This could be explained by the fact that adsorption equilibrium has been reached between the adsorbent/oil mixtures, thereby, preventing further pigment removal by the excess adsorbent dosage.

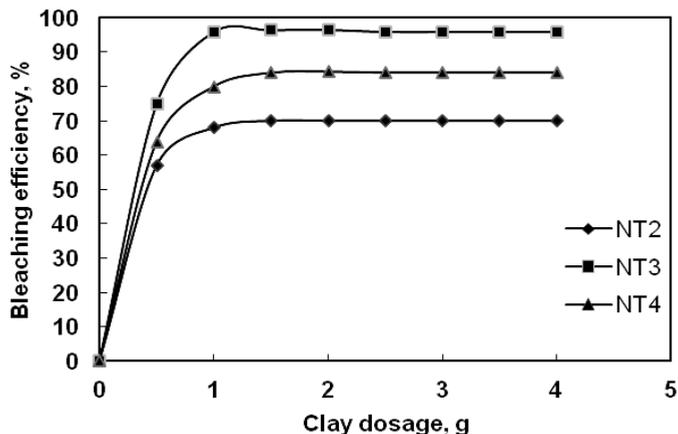


Fig. 3. Variation of bleaching efficiency with clay dosage

Effect of particle size of the adsorbent

To study the effect of particle size on the bleaching efficiency of the adsorbent, the experiment was performed at different particle sizes of 0.408, 0.212, 0.106, 0.075, and 0.045 mm. The results are shown in Fig. 4. The figure shows that the bleaching efficiency of the activated clay was increased as the particle size decreased; this is as a result of increased surface area, pore volume, and pore size of the particles. Reduced particle size creates more adsorption sites/cation exchange sites that are exposed to the sorbate. But, this positive effect of particle size reduction resulted to difficulty filtration because the oil retention of the adsorbent increased.

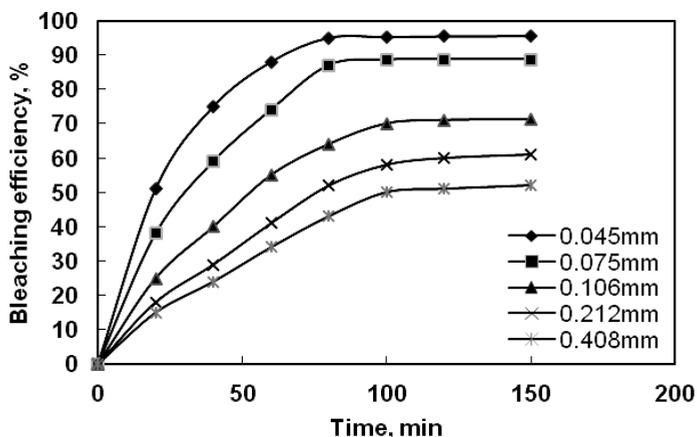


Fig. 4. Variation of bleaching efficiency with time at different particle sizes

Kinetics of bleaching

The effect of temperature on the bleaching efficiency of Nteje clay activated with 3 mol/dm³ hydrochloric acid as reflected in Fig. 2, were tested with several 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, and Elovich kinetic equations. The respective linear forms of the equations are as given below:

$$\log (q_e - q_t) = \log q_e - k_1 t \quad (\text{pseudo-first order model}) \quad (2)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{pseudo-second order model}) \quad (3)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (\text{Elovich model}). \quad (4)$$

Table 2. The kinetic parameters evaluated for colour pigment adsorption onto activated Nteje clay

Kinetic models	Parameters	Temperature (°C)				
		30	70	80	100	120
Pseudo first order	K_1	$1.16 \cdot 10^{-2}$	$1.38 \cdot 10^{-2}$	$1.61 \cdot 10^{-2}$	$1.84 \cdot 10^{-2}$	$1.15 \cdot 10^{-2}$
	q_e (mg/g)	6.98	7.23	8.93	8.67	7.53
	R^2	0.984	0.985	0.960	0.983	0.988
Pseudo second order	K_2	$1.246 \cdot 10^{-3}$	$1.947 \cdot 10^{-3}$	$3.300 \cdot 10^{-3}$	$2.600 \cdot 10^{-3}$	$2.353 \cdot 10^{-3}$
	q_e (mg/g)	8.31	9.35	10.75	11.24	9.09
	R^2	0.999	0.999	0.997	0.998	0.997
Elovich	α (mg/g min)	0.3146	0.4235	0.8195	0.7278	0.4565
	β (mg/g min)	0.5842	0.5504	0.4165	0.4083	0.5339
	R^2	0.987	0.977	0.990	0.991	0.979

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 Fig. 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.

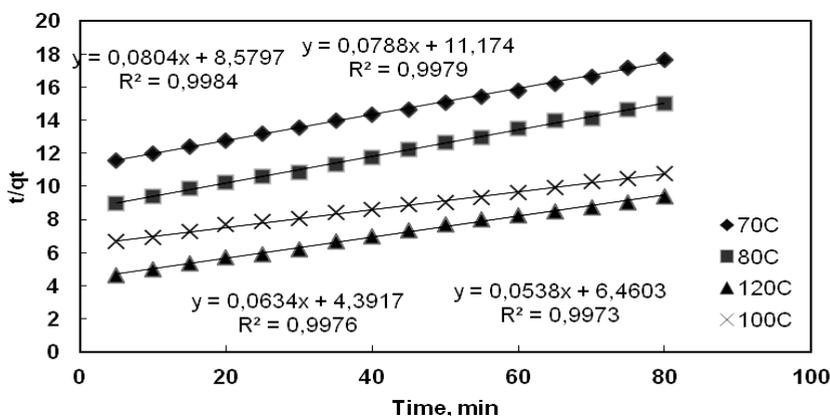


Fig. 5. Pseudo-second order kinetic fit for colour pigment removal from palm oil at different temperatures

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 chemisorption, 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:

$$\frac{P}{X/m} = \frac{1}{a} + \frac{a}{b}P \quad (5)$$

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:

$$\frac{X}{m} = KC^n \tag{6}$$

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 Eqs 5 and 6:

$$X = \frac{A_0 - A_t}{A_0} \tag{7}$$

$$X_e = \frac{A_t}{A_0} = 1 - X \tag{8}$$

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 Eqs 7 and 8, by writing X_e instead of equilibrium pressure P and the residual substance C , Eqs 5 and 6 are rearranged as follows (Topallar, 1998):

$$\frac{X_e}{X/m} = \frac{1}{a} + \frac{a}{b} X_e \tag{9}$$

$$\log \frac{X}{m} = \log K + n \log X_e . \tag{10}$$

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

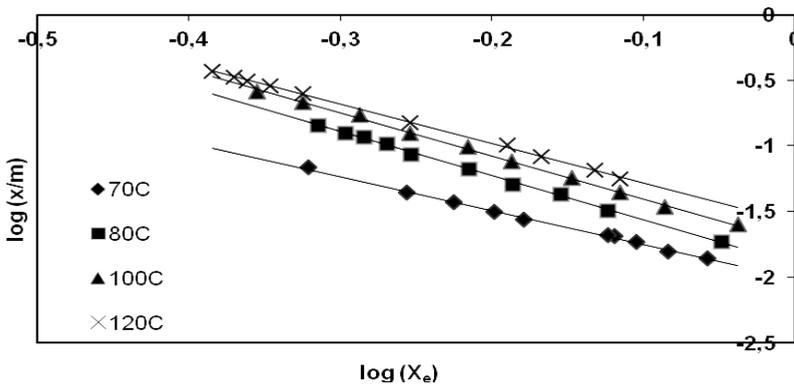


Fig. 6. Freundlich isotherm plot using NT3 for bleaching

Linear plots (Freundlich) obtained are shown in Fig. 6. The Freundlich and Langmuir model parameters and the statistical fits of the adsorption data to these models as calculated from the respective plots 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.

The values of the constant K_f increased with increasing temperature, indicating increasing access to adsorption sites.

Table 3. The isotherm parameters obtained from linear analysis of colour pigment adsorption onto Nteje clay activated with 3 mol/dm³ HCl

Isotherm models	Parameters	Temperature (°C)			
		70	80	100	120
Freundlich	K_f	$9.886 \cdot 10^{-3}$	$12.560 \cdot 10^{-3}$	$18.664 \cdot 10^{-3}$	$26.002 \cdot 10^{-3}$
	n	-0.3894	-0.2974	-0.3054	-0.3330
	R^2	0.997	0.998	0.998	0.999
Langmuir	K_a	-0.0635	-0.0318	-0.0366	-0.0437
	q_m	-5.1636	-2.8688	-2.8551	-2.8985
	R^2	0.985	0.986	0.980	0.989

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:

$$\Delta G^\circ = -RT \ln K_f \quad (11)$$

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, and

$$-RT \ln K_f = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

The above equation can then be written in the following forms

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

or

$$\ln K_f = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}. \quad (14)$$

The values of ΔH^o and ΔS^o 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^o , are all negative and show a decrease in the negative value as the temperature increases. According to Saha and Chowdhury (2009), a decrease in the negative value of ΔG^o 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 increases with increase in temperature and 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 colour pigments onto the adsorbent increased. The values of the enthalpy, ΔH^o , and entropy, ΔS^o , 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 process of colour pigments from palm oil onto locally activated clay is exothermic. 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^o gives an idea about the type of sorption. The heat evolved during physical adsorption falls in the range of 2.1–20.9 kJ/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 (Saha and Chowdhury, 2010). The value of ΔS^o as presented in Table 4 is positive and this reflects the affinity of the adsorbent towards the adsorbate species. A positive value of ΔS^o 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.

Table 4. Adsorption thermodynamic parameters

Temp. (K)	$\ln K_f$	ΔG^o (kJ/mol)	ΔH^o (J/mol)	ΔS^o (J/mol)
343	-4.61664	-56.707	-34.994	0.063
353	-4.37724	-57.339		
373	-3.98116	-57.973		
393	-3.64958	-58.606		

Conclusion

The kinetic and equilibrium studies of the adsorptive purification of palm oil using acid activated Nteje clay have been successfully investigated. The adsorption of colour pigments into the clay surfaces increased with temperature, clay dosage, contact time, and decreasing particle size. The kinetic data agree very well with the pseudo-second order equation, and the rate is film diffusion controlled. The linear isotherm analyses indicated that the equilibrium data describe the Freundlich isotherm model very well. The thermodynamic parameters evaluated reveal the spontaneous and exothermic nature of colour pigment adsorption onto acid activated Nteje clay, and the adsorption takes place with increase of entropy.

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