

Sorption Model and Kinetic Assessment of Ultramarine Blue Removal using Modified Cassava Peels Biomass

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Abstract

The efficiency of modified cassava peels biomass for the removal of ultramarine blue (UB), has been thoroughly investigated in this study. The effect of changing absorbent concentration, UB concentration, contact time and pH had been studied. Maximum absorption occurred at pH of 10. There was a general increase in UB absorption with increase in absorbent concentration, UB concentration, time and temperature, respectively. The pseudo second order equation with R^2 of 0.952, provided a better description of the adsorption process than the first order, showing that adsorption occurred mainly due to intra-particle diffusion. The Freundlich and Langmuir isotherms were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from the Langmuir isotherm was 0.952 (mg/g). The separation factor RL was obtained as 0.663 is less than unity, indicating that modified cassava peels biomass is a good absorbent for UB. The assessed thermodynamic parameters showed that the adsorption of UB on modified cassava peels biomass was endothermic.

Keywords: Adsorption kinetics; Dye removal; Adsorption isotherms and models

Introduction

Water pollution due to the discharge of dyeing industry effluent is a major concern these days. Many techniques like electrochemical coagulation, reverse osmosis, nano-filtration, adsorption using activated materials etc., are used for the removal of dye from waste water. Adsorption was proved an efficient and economical process to treat dyeing industry effluent. In recent years, many natural waste materials have been investigated to assess their suitability as an adsorbent. Exploration of a good low cost adsorbent may contribute to the sustainability of the environment and also offer promising benefits for commercial purposes in future. Recently some agricultural wastes and forestry products have been developed as adsorbents. Activated carbon prepared from different materials like agricultural wastes [1,2], and oil palmwaste [3], babool seed [4], eucalyptus bark [5], pine saw dust [6], pistachio shells [7,8], also investigated the mechanistic study of dye adsorption onto a novel non-conventional low-cost adsorbent. The Dyes production industries and many other industries which utilize dyes and pigments are increasing globally everyday as far as technology advancement is concerned. Presently, it was estimated that about 10,000 of different commercial dyes and pigments exist and over 7×10^5 tones are produced annually worldwide [9]. These industries include textile, paper, plastic, food cosmetic etc, in which textile rank first and their wastes being discharged consist majorly of these dyes and pigments. Consequently, this constitute environmental hazard due to the fact that many of these dyes and pigments are difficult to degrade. They are generally stable to light, oxidizing agents and are resistant to aerobic digestion [10]. Hence, contaminations due to dyes are not only environmentally hazardous but are also of severe public health concern because of their persistence in nature and non-biodegradability.

However, the removal of dyes from the wastes discharged by the afore-mentioned industries, especially textile industries now call for urgent attention in order to safeguard our environment and public health. In this regard, a number of conventional methods as mentioned before are available for the removal of dyes from industrial effluents, including ion exchange, adsorption, membrane technology and coagulation. But in all, adsorption, which is a process that occurs when a gas or liquid solute accumulate on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate), has

been one of the effective methods adopted so far. The adsorption has an edge over the other methods due to its sludge free clean operation and the possibility of complete dyes removal, even from the diluted solution.

Meanwhile, in adopting adsorption method in the removal of dyes, activated carbon (powdered or granular) has been one of the most widely used adsorbents. This is due to the fact that it has excellent adsorption efficiency for organic compound, through its use is limited in the industries of developing countries due to its high cost. Several studies have shown that numerous low cost material have been successfully applied in the removal of dyes from aqueous solution, some of which are coal, fly ash, wood silica, agricultural waste etc. however, only few of them could be employed effectively to remove dyes from the waste stream.

In this study, the potential of modified cassava peels in the removal of ultramarine blue dye from aqueous solution has been investigated. It is a low cost agro-industrial waste that is common in the southern part of Nigeria. Experimental parameters affecting the adsorption process such as pH, concentration, adsorbent dosage, contact time and temperature were studied. The equilibrium adsorption data were fitted into Langmuir and Freundlich isotherms, pseudo-first order and pseudo-second order kinetic equations were also considered. Thermodynamic parameters were estimated in order to study the nature of the system.

Materials and Methods

A Sample collection and preparation of the adsorbent

About 1.5 kg of cassava (*manihot esculenta cranz*) peels were

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collected from a cassava mill in Ibusa in Oshimili North Local government Area of Delta State. These were extensively washed with tap water to remove soil and dust, sprayed with distilled water and then sun-dried for five days. The dried cassava peels were burnt in the absence of free excess air in order to get the charcoal. The charcoal obtained was further ground and sieved using 450 μm sieve. The sieved adsorbent obtained was preserved in a plastic container for further studies.

Preparation of dye solution

The dye (ultramarine blue) used in this study was obtained from a commercial market without further purification. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to the required concentration for each of the experimental parameters been considered.

Experiment procedures

Effect of contact time on adsorption: The experiment on the effect of contact time on the adsorption of the dye ion by the cassava peel adsorbent was performed according to the previous works of Sumanjit et al. [11]. 2 g of the modified adsorbents was weighed into five different conical flasks. Concentration of 10mg/L of the dye was prepared using distilled water and 50 ml of the dye solution was measured into the five flasks. The flasks were then labeled for time intervals of 20, 40, 50, 60, 80 and 100 minutes. The flasks were tightly covered and agitated at the appropriate time intervals. At the end of each time intervals, the suspensions were filtered using Whatman No. 45 filter paper and then centrifuged. The dye ion concentration was determined using DR 2010 spectrophotometer.

Effect of adsorbent dosage on adsorption: The experiment on the effect of adsorbent dosage on the adsorption of dye ion by the cassava peels adsorbent was performed according to the previous works of Sumanjit et al. [11]. 2, 3, 4, 5 and 6 g of the modified adsorbent were weighed into five different conical flasks. 50ml of the dye solution was measured into the five flasks. The flasks were then labeled for dosage differences of 2, 3, 4, 5 and 6 g. The flasks were tightly covered and agitated for 20 minutes, thereafter the suspensions were filtered using Whatman No. 45 filter paper, then centrifuged. The dye ion concentration was determined using DR 2010 spectrophotometer.

Effect of dye ion concentration on adsorption: The experiment on the effect of dye ion concentration on adsorption was performed according to the previous works of Sumanjit et al. [11]. Several standard dye solutions of 10, 20, 30, 40 and 50 mg/L were prepared. 50 ml of each of the dye solution was added to accurately weighed 2 ± 0.01 g modified adsorbent in five different flasks and agitated for 20 minutes. At the end of the time, the suspension was filtered using Whatman No. 45 filter paper and centrifuge. The dyes ion concentration was determined using Dr 2010 spectrophotometer.

Effect of temperature on adsorption: The experiment on the effect of temperature on adsorption was performed according to the previous work of Mishra et al. [12]. 2 g of the modified adsorbent was weighed into five different conical flasks and 50 ml of the dye solution (10 mg/L) was measured into the five flasks. The flasks were labeled for temperature differences of 30, 40, 50, 60 and 70°C. The flasks were tightly covered and heated at the appropriate temperature using thermostatic water bath, at 20 minutes each. At the end of the time, each of the flasks were brought out and agitated for about 5 minutes. After then, the suspensions were filtered using Whatman No. 45 filter paper and centrifuged. The dye ion concentration was determined using DR 2010 spectrophotometer.

Effect of pH on adsorption: The experiment on the effect of pH on adsorption was carried out based on the previous works of Sumanjit et al. [11]. Modified adsorbent (2 ± 0.01 g) was weighed into five different flasks. 50 ml of the dye solution (10 mg/L) was measured and added into the five flasks. The solutions were adjusted to pH 2.0, 4.0, 6.0, 8.0, and 10.0 by adding a solution of HCl (0.1 M) or NaOH (0.1 M) and the pH readings were confirmed by the use of pH meters. The flasks were then tightly covered and agitated for 20 minutes. At the end, the suspensions were filtered using Whatman No. 45 filter paper and centrifuged. The dye contents were determined using DR 2010 spectrophotometer.

Data evaluation

Calculation of the degree of dye removal: The amounts of dye removal by the adsorbent during the series of the batch experiments were determined using a mass balance equation expressed as shown below.

$$q_e = \frac{V}{M}(C_o - C_e)$$

Where q_e = dye concentration on the biomass (mg/g) at equilibrium

C_e = dye concentration in solution (mg/L) at equilibrium

C_o = initial dye concentration in solution (mg/L)

V = volume of dye solution used (ml)

M = mass of adsorbent used (g)

Kinetic treatment of experimental data: In order to comprehensively investigate the mechanism of adsorption, the equations of pseudo-first order and pseudo-second order mechanisms are applied to experimental data.

The linear form of pseudo-first-order model is given as:

$$\ln(q_e - q_t) = \ln q_e - Kt$$

Where q_e = mass of dye adsorbed at equilibrium (mg/g)

q_t = mass of dye adsorbed at time t (mg/g)

K = equilibrium constant

The linear plot of $\ln(q_e - q_t)$ versus t confirms the model. The linear form of pseudo-second-order model is given as:-

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{t}{q_e}$$

Where q_t = amount of dye ions on the adsorbent surface (mg/g) at anytime t.

q_e = the amount of dye ions adsorbed at equilibrium (mg/g)

h_o = the initial adsorption rate (mg/g min).

The initial adsorption rate h_o is defined as:

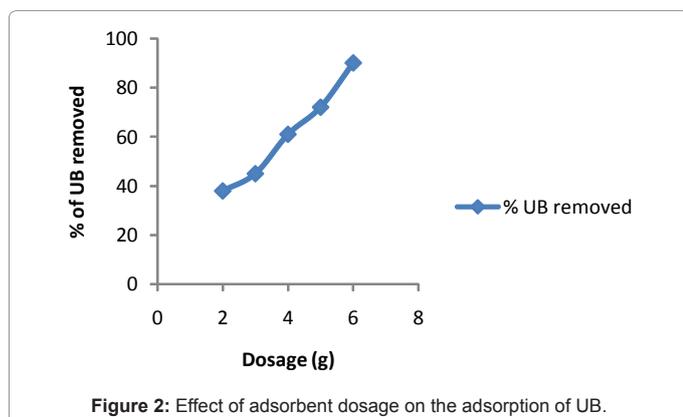
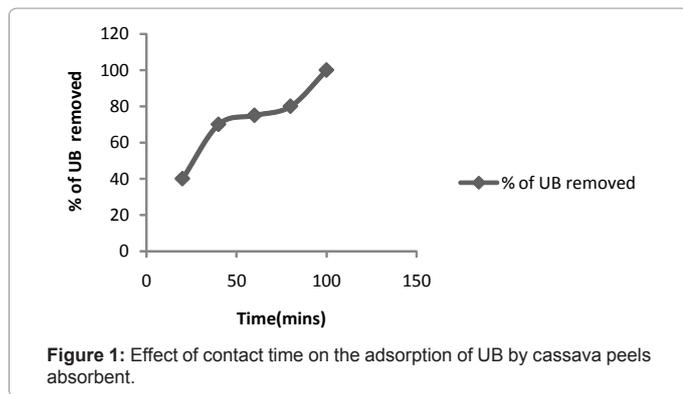
$$h_o = K_2 q_e^2$$

Where K_2 is the pseudo-second order rate constant (g/mg min).

Results and Discussions

Effect of contact time on dye removal

The effect of stay time for the adsorption of the dye was studied between the intervals of 20 minutes and was varied from 20 to 100 minutes. Figure 1 illustrates the adsorption of the dye at different time



duration. As the contact time was increased from 20 to 100 minutes, the amount of dye removed increased from 0.105 mg/g to 0.245 mg/g.

The figure also indicates that the amount of dye removed increased rapidly with increase in time, as well as the percentage of dye removed in which maximum percent (98%) was obtained at 100 minutes. This may be due to the fact that as the dye solution-adsorbent system is being agitated at longer time, more of the molecules or atoms of the dye tend to accumulate on the surface of the adsorbate until equilibrium is reached.

However, similar trends have been observed by some other researchers [11-13].

Effect of adsorbent dosage on dye removal

The effect of the amount of adsorbent (cassava peels) on the adsorption of ultramarine blue system was studied, in which the amount of adsorbent was varied from 2 to 6 g. Figure 2 shows the effect of adsorbent dosage on the removal of the dye in which the amount of dye removed increased from 0.095-0.228 mg/g as the adsorbent dosage was increased from 2-6 g.

From figure 2, it is observed that the optimized adsorbent dose is 6 g in which 0.228 mg/g of dye was adsorbed. More so, the maximum percentage (91%) of dye adsorbed at this dosage (6 g) is also shown in figure 2. However, the increase in dye uptake could be attributed to certain reasons. According to Mishra et al. [12], the increase in dye uptake is obvious with increasing adsorbent dosage as the binding sites for adsorption increases. Meanwhile similar behavior has been reported by other workers [11,14].

Effect of concentration on dye removal

The experimental results of the removal of ultramarine blue dye by

cassava peels biomass at various initial dye concentrations are as shown in figure 3. The adsorption capacity increased from 0.185 to 1.027 mg/g with an increase in the concentration of dye from 10 to 50 mg/L, having maximum adsorption of 1.027 mg/g at 50 mg/L.

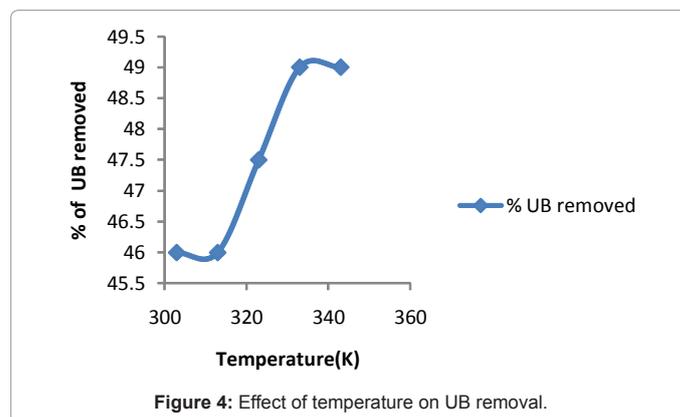
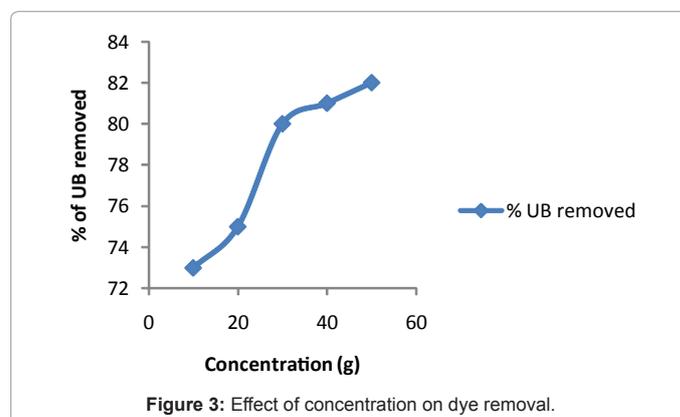
However, the actual percent removal of the dye was found to increase with increase in initial dye concentration as shown in figure 3. This may be due to the fact that as the dye concentration is increasing, more dye is available for adsorption on the adsorbent. This is due to the effect of concentration gradient which is the main driving force for the adsorption process [12]. Similarly, this trend has been observed by other workers [12,13].

Effect of temperature on dye removal

The dependence of dye adsorption on temperature was studied within the temperature range of 30-70°C at the intervals of 10°C. The effect of temperature on the adsorption of dye is shown in figure 4, in which the amount of dye adsorbed increased from 0.115 to 0.123mg/g with increases in temperature from 30 to 70°C.

Though, the increase in the amount of dye removed as the temperature increases is not much significant, according to Hiroyuki et al. the higher removal due to increasing temperature may be attributed to chemical reaction taking place between the functional groups of the adsorbate/adsorbent [15]. Moreso, at high temperature, there is increase in the mobility of the large dye ion thereby producing swelling effect within the internal structure of the adsorbent, thus enabling the large dye molecule to penetrate further [16].

Despite the afore-mentioned reasons accompanying increased adsorption with increased temperature, it has been reported, that increase in adsorption at higher temperature is difficult to explain.



However, the trend of increased adsorption with increased temperature has been reported by other workers [13,17].

Effect of pH on dye removal

The pH of an aqueous medium is an important factor that may affect the uptake of the adsorbate. The chemical characteristics of both adsorbate and adsorbent vary with pH. According to Horsfall et al. most plant materials are made up of complex organic residues such as lignin and cellulose that contain, several type of polar functional groups [18]. These groups can be involved in chemical bonding and may be responsible for the typical cation-exchange characteristics of most biomaterials.

The pH dependence data for adsorption of the dye being investigated are presented in figure 5. It is observed that as the pH of dye solution increased from 2-8, the amount of dye adsorbed decreased from 0.135 to 0.087 mg/g, though at pH10 there was a rapid increase in the amount of dye adsorbed. The initial decrease in the amount of dye adsorbed as the pH increases may be due to the fact that ultramarine blue exists in anionic form at basic pH and in cationic form at acidic pH.

However, according to Yamin et al. [14], in the study of removal of methylene blue by treated activated carbon, in which removal of methylene blue increased with the increased pH; lower adsorption of methylene blue at low pH is probably due to the presence of hydrogen ions, competing with the cation groups on the dye for adsorption sites. So on the contrary, the initial higher adsorption of ultramarine blue at low PH may be probably due to the absence of hydrogen ions which cannot complete with the cation groups on the dye for adsorption. Meanwhile similar trend has been reported in the literature for the adsorption of Congo red dye onto Mahua oil cake [12].

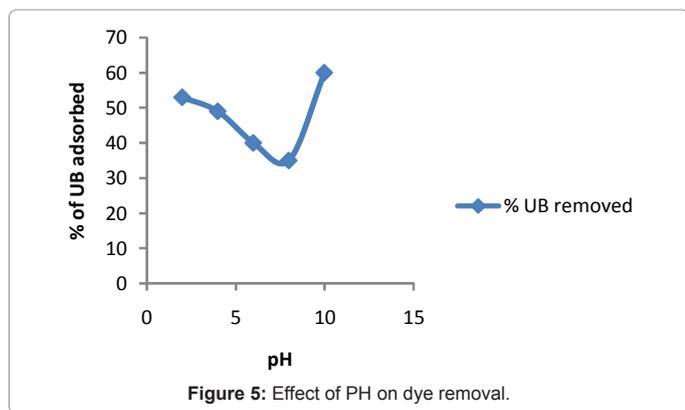


Figure 5: Effect of PH on dye removal.

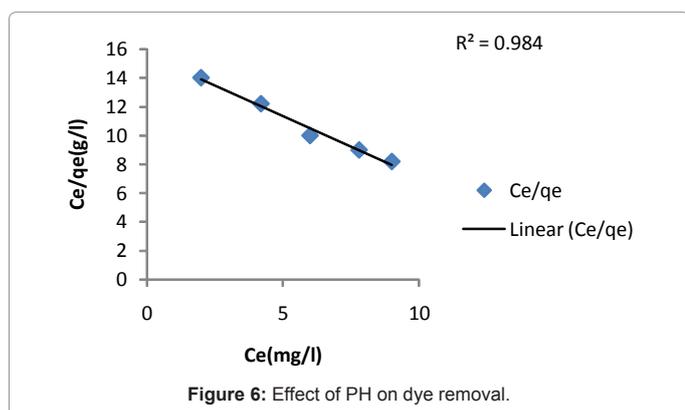


Figure 6: Effect of PH on dye removal.

Isotherm evaluation

Langmuir isotherm: The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) is shown in figure 6 and the linear isotherm parameters, q_m , K_L and the coefficient of determinations are presented in figure 6.

The R^2 value suggested that the Langmuir isotherm provides a good model of the adsorption. The favorability of adsorption of the dyes ions on the cassava peels waste biomass was tested using the essential features of the Langmuir isotherm model, expressed in terms of a dimensionless constant called separation factor, S_F proposed by Putshaka et al [19]. The separation factor S_F is defined by the following relationship.

$$S_F = \frac{1}{1 + K_L C_0}$$

Where K_L =Langmuir isotherm constant C_0 =initial dye ion concentration of 10 mg/L. The parameter indicates the shape of the isotherm as follows:

- $S_F > 1$ unfavourable isotherm
- $S_F = 1$ linear isotherm
- $S_F = 0$ irreversible isotherm
- $0 < S_F < 1$ favourable isotherm

The separation parameters for the dye is less than unity indicating that cassava peel waste biomass is an excellent adsorbent for ultramarine blue ions. The separation parameter and other Langmuir isotherm parameters are shown in table 1.

Freundlich isotherm: The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. The linear Freundlich isotherms for the adsorption of the dye ion onto cassava peel waste biomass are presented in figure 7. Examination of the plot reveals that the Freundlich isotherm is also an appropriate model for the adsorption process under consideration. Table 2 shows the linear Freundlich sorption isotherm parameters and the coefficient of determination (R^2).

Based on the value of R^2 , the linear plot form of the Freundlich isotherm appears to produce a reasonable model for the adsorption process under consideration.

Adsorption kinetics

First order plot: The kinetic of adsorption is probably the most important factor in predicting the rate at which adsorption takes place for a given system.

Dye ion	q_m (mg/g)	K_L (L_g^{-1})	R^2	S_F
UB	0.952	0.058	0.984	0.633

Table 1: Linear langmuir isotherm parameters.

Dye in	1/n	K_F	R^2
UB	1.978	0.045	0.985

Table 2: Freundlich isotherm constant.

Dye ion	H_0	K^2	q_e	R^2
	($mgg^{-1}min^{-1}$)	($mgg^{-1}min^{-1}$)	(mgg^{-1})	
U.B	0.008	0.072	0.333	0.956

Table 3: Values of pseudo-second order kinetic parameters.

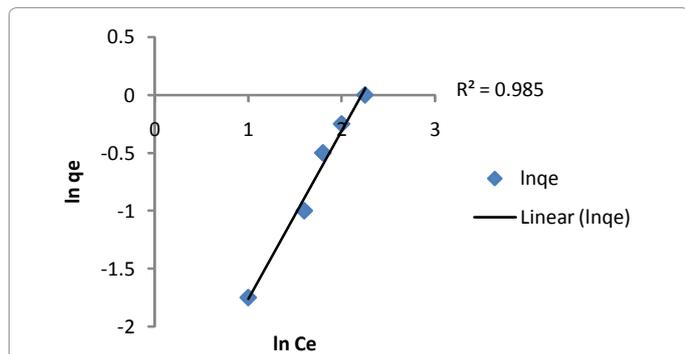


Figure 7: Freundlich equilibrium isotherm model for dye removal.

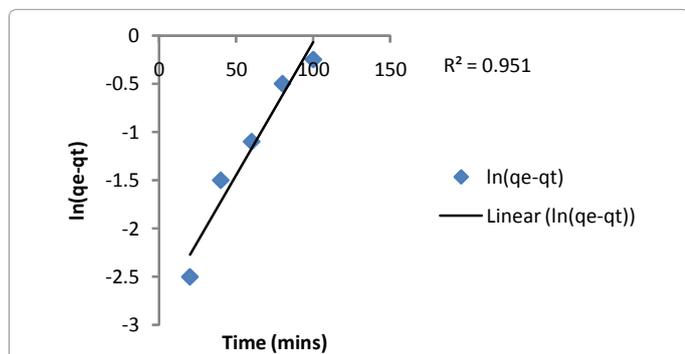


Figure 8: Pseudo - first order plot.

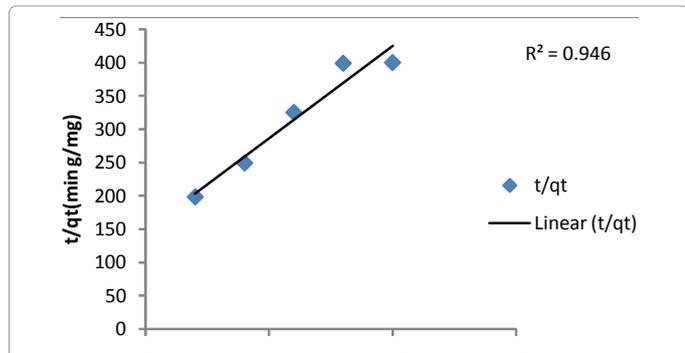


Figure 9: Pseudo - second order plot.

A plot of $\ln(q_e - q_t)$ against t as shown in figure 8 gave the pseudo-first order kinetics. From the plot, it is observed that the relationship between dye ion diffusivity, $\ln(q_e - q_t)$ and time(t) is linear which confirms the model. The value of the coefficient of determination R^2 as shown in table 2 indicates that pseudo-first order model provided a good description for the adsorption of ultramarine blue on the cassava peels biomass.

However in confirming the linearity of the pseudo-first order model, the same observation has been reported by Gunusamy for the adsorption of basic dye on strongly chelating polymer [17].

Pseudo-second order model: A plot of t/q_t against t as shown in figure 9 gave the pseudo-second order kinetics. From the plot, it is observed that the relationship between t/q_t and t is linear which confirms the model. Also, the initial sorption rate h_0 , the equilibrium adsorption capacity q_e , the pseudo-second order rate constant K_2 and the coefficient of determination R^2 are presented in table 3.

Based on the value of the coefficient of determination R^2 , the pseudo-second order model provides a better description for the adsorption process better than pseudo-first order model. This observation has been reported by Che for the adsorption of basic blue, acid blue and direct red dyes using clay-based activated carbon adsorbent [20].

Thermodynamic parameters

The values of the thermodynamic parameters like free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the adsorption process were calculated from the Langmuir constant K using the following equations.

$$\Delta G = -RT \ln K$$

$$\ln K = \Delta S / R - \Delta H / RT$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \Delta H - T\Delta S$$

The value of ΔH° and ΔS° were calculated from the slope and intercept of the linear variation of $\ln K$ with the reciprocal of temperature ($1/T$) and are given in figure 10.

The calculated values of ΔG° at different temperatures are positive, showing that the adsorption process is not spontaneous. The values of enthalpy are also positive, which reveals the endothermic nature of the process the values of entropy are negative. Meanwhile, the same observation has been reported as regards the endothermic nature of the process by Hajira et al. for the removal of basic dye methylene blue by using bioadsorbents ulva lactuca and sargassum [13].

Conclusions

Modified cassava peels biomass has been studied and found to be an excellent adsorbent for ultramarine blue (UB) removal. Increasing the dye ion (UB) concentration led to increase in percentage removal of the dye ions. Also, increase in adsorbent dosage led to a very significant increase in percentage UB removal. Adsorption of the dye ions was found to increase with increases in contact time. pH of 10 was found to be the critical pH for UB adsorption on the modified cassava peels biomass. The equilibrium data fit well into the Langmuir and Freundlich isotherm models. The separation factor obtained from the Langmuir isotherm showed that the adsorption of the dye ions onto the cassava peels biomass was favorable. Pseudo second order model was found to be a better descriptor of the UB adsorption. The investigated thermodynamic parameters showed that the adsorption process was endothermic and non-spontaneous. Given the above findings, modified cassava peels can be used as an alternative to the expensive conventional methods of dye removal from wastewater. It is therefore

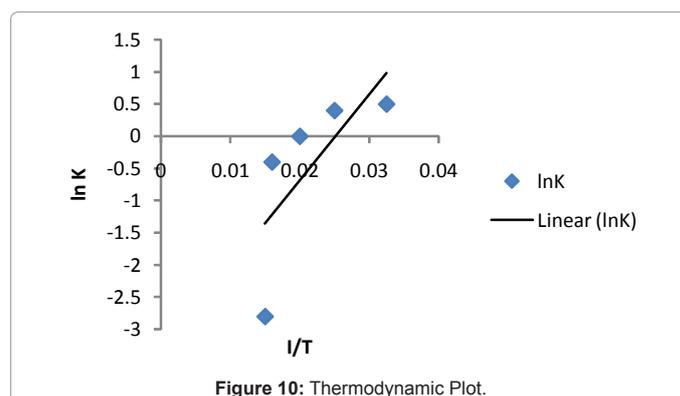


Figure 10: Thermodynamic Plot.

recommended for small and medium scale industries, whose financial status may not conveniently afford the treatment of their wastewater, using conventional methods. Again, cassava peels which are ordinarily an environmental nuisance, when used for wastewater treatment, would have served as a means for recycling it and thereby reducing its attendant public health concerns.

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