Biosorptive capacity of yam peels waste for the removal of dye from aqueous solutions

Hilary I. Owamah[1], Ilabor S. Chukwujindu [2] and Augustine K. Asiagwu[3]
1 Civil Engineering Department, Landmark University, Omu-Aran, Kwara State, P.M.B.1001, Nigeria
2 ChemistryDepartment, Federal College of Education (Technical), Asaba, Nigeria
3 Chemistry Departments, Delta State University, Abraka, Nigeria

Abstract- Removal of ultramarine blue dye from aqueous solution using yam peels waste was well investigated in this study. The effect of adsorbent concentration, dye concentration, time and pH were evaluated. Maximum adsorption occurred at pH of 10.There was a general increase in adsorption with increase in adsorbent concentration, dye concentration, time and temperature, respectively. The pseudo second order model with R^2 of 0.98, provided a better description for the adsorption process than the first order, showing that adsorption occurred mainly by intra-particle diffusion. The Freundlich and Langmuir isotherms were found suitable for describing the adsorption. Maximum adsorption capacity(q_m) was obtained as 0.940(mg/g).The separation factor S_F was obtained as 0.72 is less than unity, indicating that yam peels waste adsorption of ultramarine blue dye is quite favourable.
Keywords: Ultramarine blue, Biosorption, Adsorption kinetics, Adsorption isotherms

1. Introduction

The need for cost –effective removal of dyes from wastewater has led to a proliferation of research into the use of low cost agro-waste adsorbent for dye adsorption. Dye production industries and many other industries which utilize dyes and pigments are increasing globally by the day with advancement in technology Presently, it was estimated that about 10,000 of different commercial dyes and pigments exist and over 7x10^5 tones are produced annually world wide (Grag V.K et al., 2004). Textile, paper, plastic, food, cosmetics etc, are some of these industries. Presence of dyes and pigments in wastewater constitute environmental hazard because dyes and pigments are difficult to degrade. They are generally stable to light, oxidizing agents and are resistant to aerobic digestion (McKay and Sweeney, 1980). Many techniques like electrochemical coagulation, reverse osmosis, nano-filtration, adsorption using commercial activated carbon etc., have been used for the removal of dye from waste water (Asiagwu et al., 2012).

In the recent years, many organic waste materials have been investigated to assess their suitability as adsorbents for dye removal from wastewater. Exploration of a good low cost adsorbent may contribute to the sustainability of the environment and also offers 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(Jambulingam eta l.,2007) and (Karyhikeyan et al., 2008),oil palmwaste (Lua and Guo et al.,1998), babool seed (Sujatha et al., 2008),eucalyptus bark (Sarin et al., 2006), pine saw dust (Ozaca and Ayhan,2005), pistachio shells(Wu et al., 2005),etc. Ponnusamy and Nachimuthu(2010),also investigated the mechanistic study of dye adsorption onto a novel non-conventional low-cost adsorbent.

Meanwhile, in adopting adsorption for removal of dyes, commercial 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; however 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. Pounded yam is a delicacy highly cherished and consumed in Nigeria. This has led to the generation of large quantity of yam peels as solid wastes.

The aim of this paper is to investigate the effects of varying temperature, pH and adsorbent dosage on the adsorption of ultramarine blue on yam peels waste. The study also intends to investigate the kinetics of the adsorption ultramarine blue onto yam peels waste. Langmuir and Freundlich isotherm models were further used to interpret the equilibrium data. Adsorption of ultramarine blue dye using modified cassava peels as the biosorbent had earlier been investigated by the authors (Owamah et al., 2012).

2. Materials and Methods

2.1 Sample collection and preparation of the adsorbent

About 1.5kg of fresh yam peels was obtained from the waste bin of a restaurant in Ibusa, 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 450um sieve. The sieved adsorbent obtained was preserved in a plastic container for further studies.

2.2 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 amount of dye in distilled water to the required concentration for each of the experimental parameters been considered.

3. Experiment Procedures

3.1 *Effect of contact time on adsorption*

The experiment on the effect of contact time on the adsorption of the dye ion by the yam peels adsorbent was performed according to the previous works of Sumajit et al (2007). 2g of the adsorbents was weighed into five different conical flasks. Concentration of 10mg/L of the dye was prepared using distilled water. 50m1 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.

3.2 *Effect of adsorbent dosage on adsorption*

The experiment on the effect of adsorbent dosage on adsorption of dye ion by the yam peels waste was performed according to the previous works of Sumanjit et al (2007). 2, 3,4, 5 and 6g 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 6g. The flasks were tightly covered and agitated for 20 minutes, thereafter the suspensions were filtered using Whatman No. 45 filter paper, thereafter, it was centrifuged. The dye ion concentration was determined using DR 2010 spectrophotometer.

3.3 *Effect of dye ion concentration on adsorption*

The experiment on the effect of dye concentration on adsorption was performed according to the previous works of Sumanjit et al (2007). Several standard dye solutions of 10, 20, 30, 40 and 50mg/L were prepared. 50ml of each of the dye solution was added to accurately weighed 2±0.01g 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 dye concentration was determined using Dr 2010 spectrophotometer.

3.4 *Effect of temperature on adsorption*

The experiment on the effect of temperature on adsorption was performed according to the previous work of Mishra S. et al (2009). 2g of the yam peels adsorbent was weighed into five different conical flasks and 50m1 of the dye solution (l0mg/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.

3.5 *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 (2007). The adsorbent (2± 0.0lg) was weighed into five different flasks. 50m1 of the dye solution (l0mg/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 (0.1M) or NaOH (0.1M) 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.

4.0 Data Evaluation

4.1 *Calculation of the degree of dye removal*

The amount of dye removed 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)

4.2 Kinetic treatment of experimental data

In order to comprehensively investigate the mechanism of adsorption, the equations of pseudo-first order and pseudo-second order models were applied to the 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 $\ln(q_e\text{-}q_t)$ 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 capacity (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)

5.0 Results and Discussion

5.1 *Effect of contact time on dye removal*

The adsorption of dye onto yam peels waste was found to increase rapidly with time as shown in Figure 1.Time intervals of 20-100minutes were used for the study. As the contact time was increased from 20 to 100 minutes, the amount of dye removed increased from 0.102mg/g to 0.248 mg/g.

Figure 1 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 (95%) 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 adsorbent until equilibrium is reached. Similar trends have been observed by some other researchers (Hajira et al., 2008; Mishra et al., 2009; Sumanjit et al., 2007; Owamah et al., 2012).

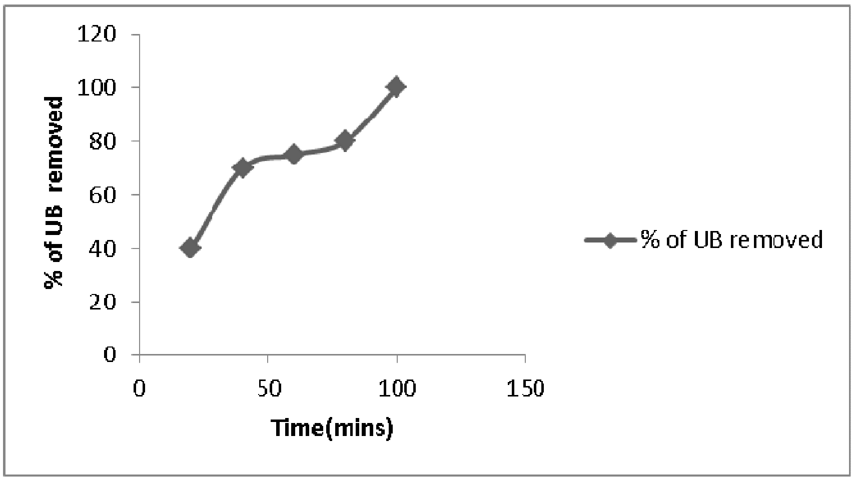

Fig. 1. Effect of contact time on the adsorption of ultramarine blue dye by yam peels absorbent

5.2 *Effect of adsorbent dosage on dye removal*

Figure 2 shows that adsorption of ultramarine blue onto yam peels waste was positive. Adsorbent doses of 2, 4 and 6g were used for the investigation. Figure 2 also shows that as adsorbent dosage increased from 2g to 6g, the amount of dye removed increased from 0.095-0.228mg/g. Maximum percentage (90%) of dye removal was obtained at (6g) as shown in Figure 2.

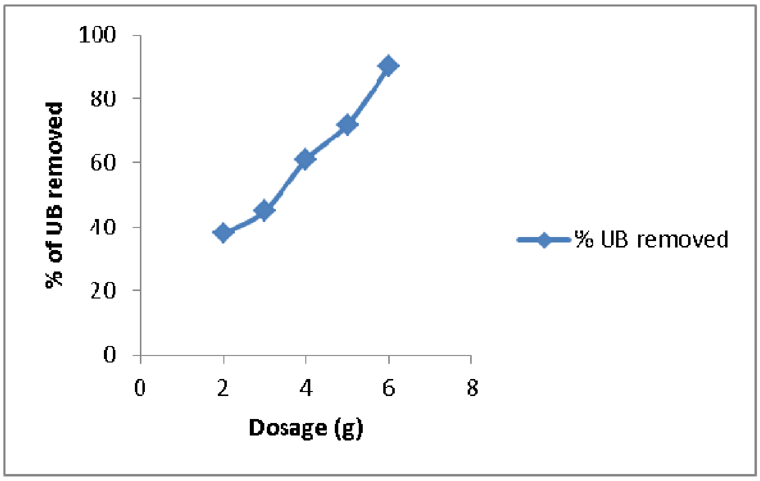

Fig. 2. Effect of adsorbent dosage on the adsorption of UB.

However, the increase in dye uptake could be attributed to certain reasons. According to Mishra et al. (2009), the increase in dye uptake is obvious with increasing adsorbent dosage as the binding sites for adsorption increase. Meanwhile similar behavior has been reported by other workers (Alok., 2006; Sumanjit et al., 2007; Yamin et al., 2007; Owamah et al., 2012).

5.3 *Effect of concentration on dye removal*

As shown in Figure 3, adsorption increased from 0.181 to 1.030mg/g as dye concentration increased from 10 to 50mg/L having maximum adsorption of 1.030 mg/g at 50mg/L. This signifies a higher percentage of dye removal. This may be due to the fact that as the dye concentration increased, more dye became available for adsorption on the adsorbent. This could have been the result of increased concentration gradient which is the main driving force for the adsorption process (Mishra et al., 2009;Hajir et al., 2008).Similar trend was observed when the authors used modified cassava peels as adsorbent for the same purpose(Owamah et al.,2012).

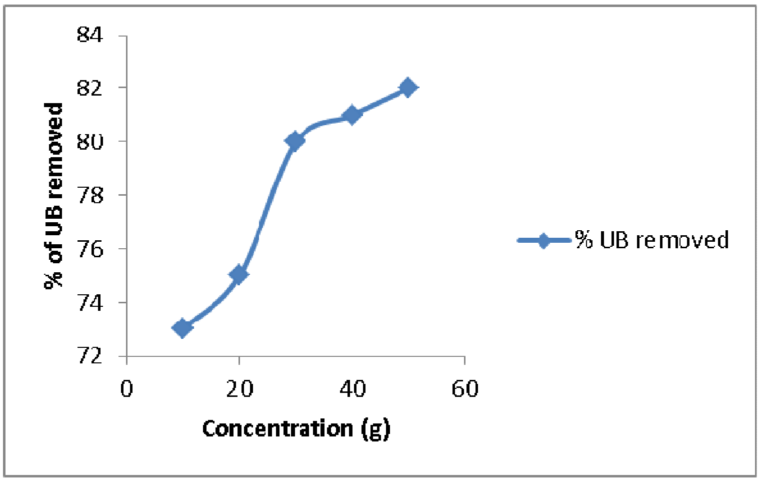

Fig.3. Effect of concentration on dye removal.

5.4 *Effect of temperature on dye removal*

Adsorption of ultramarine blue on yam peels was found to increase just a little, when temperature was increased. The temperature range of 30-70°C at intervals of 10^{0}C was carefully utilized for the study. The effect of temperature on the adsorption of dye is shown in Figure 4, in which the amount of dye adsorbed increased from 0.112 to 0.125mg/g with increase in temperature from 30 to 70°C.

Though, the increase in the amount of dye removed as the temperature increased was not very significant, according to Hiroyuki et al. (1994), the relatively high removal due to increasing temperature may be attributed to chemical reaction taking place between the functional groups of the adsorbate/adsorbent. Moreso, at high temperature, there is an 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 (Mckay, 1982).

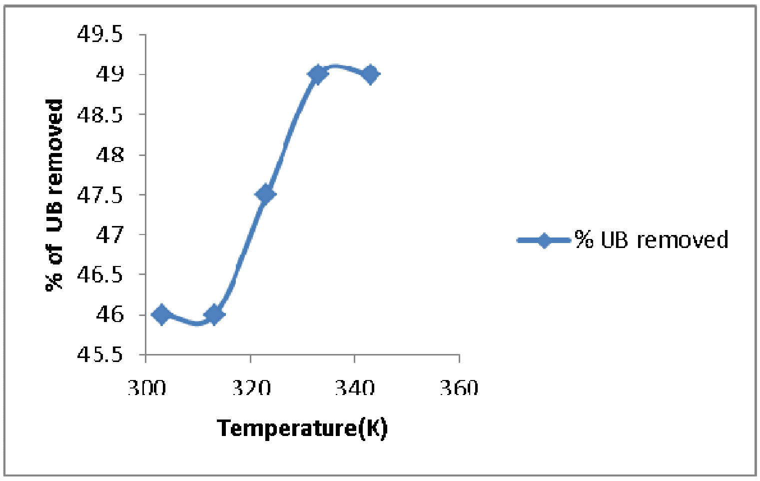

Fig. 4. Effect of temperature on ultramarine blue dye removal.

Despite the afore-mentioned reasons accompanying increased adsorption with increased temperature, it has been reported, according to Panday et al. (1968) that increase in the adsorption of dye at higher temperature is difficult to explain.

5.5 *Effect of pH on dye removal*

As shown in Figure 5, as the pH of the dye solution increased from 2-8, the amount of dye adsorbed decreased from 0.132 to 0.090 mg/g. However at pH 10 there was a rapid increase in the amount of dye adsorbed. The initial decrease in the amount of dye adsorbed as the pH increased may be due to the fact that ultramarine blue dye exists in anionic form at basic pH and in cationic form at acidic pH. 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 and Spiff (2005d), most plant materials are made up of complex organic residues such as lignin and cellulose that contain several types of polar functional groups. These groups can be involved in chemical bonding and may be responsible for the typical cation-exchange characteristics of most biomaterials.

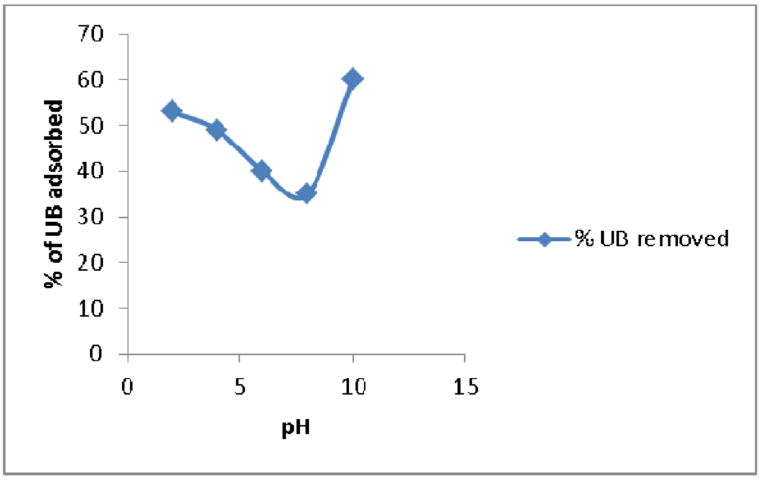

Fig. 5. Effect of P^H on dye removal

6.0 Isotherms Evaluation

6.1 *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 Fig 6.The determined linear isotherm parameters, q_m, k_L and the coefficient of determinations are presented in Table 1.

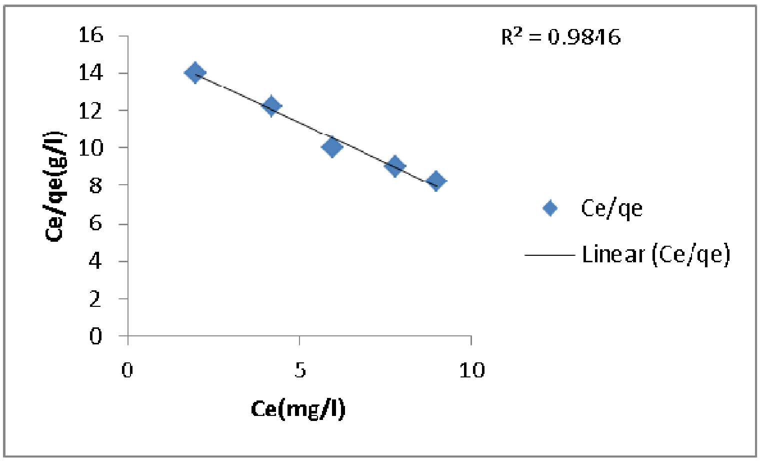

Fig. 6 Langmuir isotherm for dye removal

The R^2 value suggests that the Langmuir isotherm model can be used to describe the adsorption. The favourability of adsorption of dyes ions on the yam peels waste biomass was tested with the separation factor parameter., S_F as has been used by Putshaka et al.(2005). The separation factor S_F is defined by the following relationship.

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

Where K_L = Langmuir isotherm constant C_o = initial dye ion concentration of l0mg/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 parameter for the dye is less than unity indicating that yam peels waste biomass is an excellent adsorbent for ultramarine blue dye. The separation parameter and other Langmuir isotherm parameters' results are shown in Table 1.

TABLE 1
LINEAR LANGMUIR ISOTHERM PARAMETERS

Dye ion	q_m (mg /g)	K_L (L_g^{-1})	R^2	S_F
UB	0.940	0.06	0.984	0.72

B *Freundlich isotherm*

The plot of the Freundlich isotherm model is shown in Figure 7.The plot reveals the suitability of the Freundlich isotherm model for describing the adsorption. Table 2 shows the linear Freundlich isotherm model parameters and the coefficient of determination (R^2).

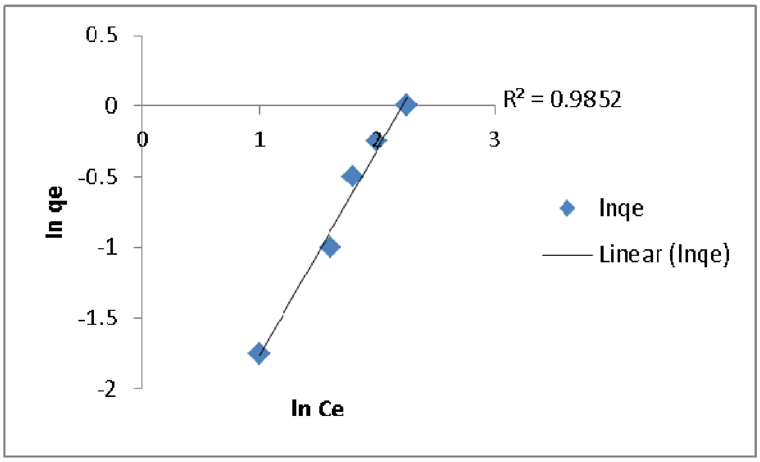

Fig. 7. Freundlich equilibrium isotherm model for ultramarine blue dye removal

TABLE 2
FREUNDLICH ISOTHERM CONSTANT

Dye in	1/n	K_F	R^2
Ultramarine blue	1.86	0.052	0.985

7.0 Adsorption Kinetics

7.1 Pseudo – first order plot

Adsorption kinetics is very useful in predicting the rate at which adsorption is occurring in a given adsorption process. A plot of In(q_e-q_t) against t as shown in Figure 8 gave the pseudo- first order kinetics. From Figure 8, it is observed that the relationship between dye ion diffusivity, In (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 Figure 3 indicates that pseudo-first order model provided a good description for the adsorption of ultramarine blue on the yam peels biomass.

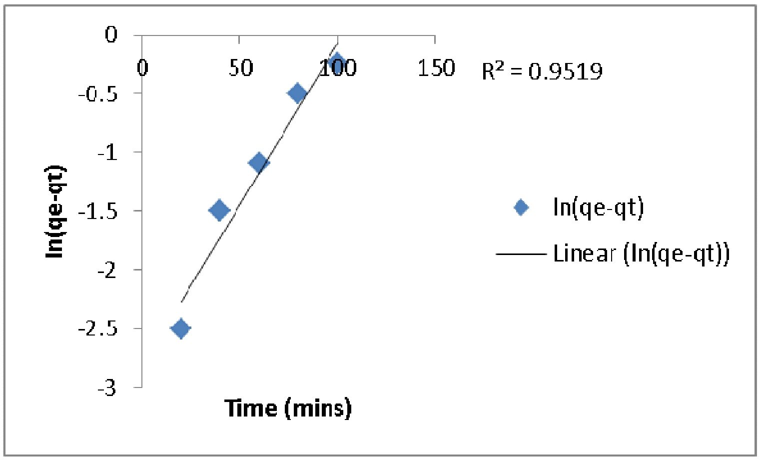

Fig. 8. Pseudo - first order plot.

7.2 Pseudo - Second Order Model

The pseudo second order kinetic plot is shown in Figure 9. The linearity of the plot indicates that the pseudo second order kinetic plot can be used for describing the adsorption mechanism of ultramarine blue dye onto yam peels waste. The initial sorption rate h_o, 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.

The higher R^2 value of the pseudo-second order model shows that it provides a better description for the adsorption process better than does pseudo-first order model. This observation has been reported for the adsorption of basic blue, acid blue and direct red dyes using clay-based activated carbon adsorbent (Che , 2004).

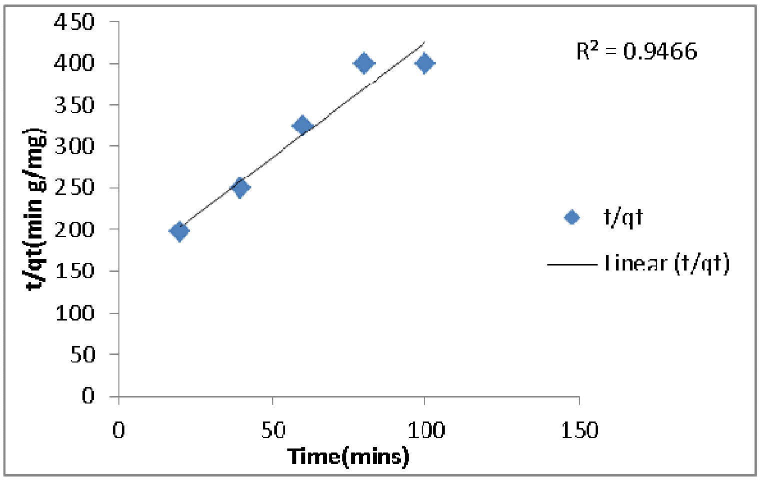

Fig. 9 Pseudo - second order plot.

TABLE 3
VALUES OF PSEUDO-SECOND ORDER KINETIC PARAMETERS

Dye ion	H_o	K_2	q_e	R^2
	(mgg^{-1} min^{-1})	(mgg^{-1} min^{-1})	(mgg^{-1})	
Ultramarine blue	0.0076	0.064	0.31	0.956

8.0 CONCLUSION

The removal of ultramarine blue dye from wastewater, using yam peels waste has been studied and found feasible. Adsorption increased with increase in temperature, adsorbent concentration and time of agitation. Although the highest adsorption occurred at pH of 10, increase in pH was found to decrease adsorption significantly. The Langmuir and Freundlich isotherm models were both found suitable for describing the equilibrium data. The separation factor obtained from the Langmuir isotherm showed that the adsorption of ultramarine blue dye onto the yam peels waste was favourable. The adsorption mechanism was better described by the pseudo second order model than did the first order model. Results from this study can be used to access the suitability of using yam peels waste for dye removal as a cheap alternative to the commercially available expensive activated carbon. This will equally provide a reuse and recycle medium of getting rid of yam peels from the environment.

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