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## SORPTION POTENTIALS OF MELON PEELS IN THE REMOVAL OF ULTRAMARINE RED (DYE) FROM AQUEOUS SOLUTION

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### ABSTRACT

This work was conducted in line with the efforts to remove coloured materials from waste water using non – conventional techniques. Therefore, this study investigated the effectiveness and efficiency of melon (*Cucumeropsis mannii*) peels in the removal of ultramarine red, from aqueous solution. The dependence of sorption parameters (contact time, dosage, temperature and pH) on dye removal were examined. Results obtained revealed that increase in the contact time between 20-100 minutes increased the dye adsorption. The maximum percentage of ultramarine red dye removed was obtained at 100 minutes. However, increase in dye concentration from 10 – 50mg/L, resulted to an increase in sorption capacity (0.437-1.062mg/g). The pH increase resulted to increase in ultramarine red adsorption. Meanwhile ultramarine red adsorption was also observed to increase from 0.054-0.079mg/g, while the temperature was varied between 30°-70°C. The data generated were further fitted to both Langmuir and Freundlich Isotherms. The separation factor ( $S_F$ ) from Langmuir was 0.48. While the coefficient of determination from Freundlich ( $R^2$ ) was 0.976, indicating that both models were favourable to the adsorption process. Pseudo-second order kinetics produced a better description of the adsorption process than the pseudo-first order kinetics. The melon peel is a good adsorbent for the sorption of ultramarine red in aqueous solution.

**Keywords:** Ultramarine red, adsorption, melon peels, and sorption isotherm.

### Introduction

Most coloured substances like dyes and pigments are of synthetic background and are made up of very complex aromatic molecular structure that make them very stable and difficult to biodegrade. Coloured materials are used in industries such as papers, plastic, food, textiles leather, cosmetics and so on. The wide use of these substances often poses pollution challenge because of coloured wastewater discharge into our water systems (Arami *et al.*, 2005). This coloured wastewater does not only affect aesthetic value but reduces

light penetration and consequently reduces several processes of photosynthesis (Arslanogwu *et al.*, 2005).

It is therefore important to remove these coloured substances from the wastewater before they are discharged by industries (Azliar *et al.*, 2005). Urgent attention is required so as to safeguard the environment and public health (Asiagwu *et al.*, 2017 and Carliel, 1996). In line with the foregoing, a number of conventional techniques have been developed for the decontamination of these

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coloured substances from industrial effluents including adsorption, ion-exchange coagulation and membrane technology (Che, 2004). Adsorption appears more effective due to its sludge-free clean operations and almost completely removes coloured materials even from the diluted solutions (Chaing *et al.*, 2004).

This present study was conducted to assess the sorption potentials of melon peels to remove ultramarine red from aqueous solution under varying kinetic variables.

## Materials and Methods

### Preparation of ultramarine red dye solution

The ultramarine red used in this work was from a commercial market without any further purification. The ultramarine red stock solution was made by dissolving 50g accurately weighed dye in 1000ml of deionised water and made to required concentration for each of the experimental variables being investigated.

### Equipment/Apparatus

The equipment/apparatus employed in this study include thermostatic bath, spectrometer, measuring cylinder, spatula, volumetric flask, whatman No. 45 filter paper, test tubes, digital balance, conical flask and pH meter.

### Sample Collection and Preparation of Adsorbent

The adsorbent (melon peels) of about 3.5g was obtained from a commercial market at Koko in Warri North Local Government Area of Delta State, and it was sun dried for several days. Then the dried melon peels were ground and sieved using 300 $\mu$ m sieve (Choy, 1999). The sieved adsorbent (melon peels) obtained was preserved in a container for further use in this study.

## Experimental Analysis

### Effect of Stay Time on Adsorption

The modified melon peels of 2g were measured into five distinct conical flasks. The amount of 10mg/l of the ultramarine red solution was prepared with deionized water. The 50ml of the ultramarine solution was measured into the five flasks. The conical flasks were further labeled for the different time intervals of 100, 80, 60, 40, 20 minutes. These flasks were tightly covered and further allowed to elute at their respective time intervals. The accompanying suspensions were further filtered with whatman No. 45 filter paper before it was centrifuged. The dye ion concentration was estimated by DR 2010 Spectrophotometer. (Gutnaz *et al.*, 2004)

### Determination of the effect of adsorbent dosage on adsorption of the ultramarine red solution

The 2, 3, 4, 5 and 6g of the melon peels modified adsorbent were weighed into the five different flasks. 50ml of the ultramarine red solution were also weighed into the five distinct flasks. The conical flasks were further labeled for 2,3,4,5 and 6g differences in dosage. The conical flasks were tightly covered then agitated for 20 minutes before the suspensions were filtered with whatman No. 45 filter paper and centrifuged. The accompanying ultramarine red ion concentration was estimated using DR 2010 spectrophotometer (Gutnaz *et al.*, 2004).

### Determination of the effect of dye ion concentration on the adsorption of ultramarine red

This work was carried out in-line with the previous works of Gutnaz *et al.* (2004). Different standard dye solution of 50, 40, 30, 20 & 10 mg/g were prepared. Only 50ml of each of the dye solution was added to weigh  $2 \pm 0.01$ g melon peels modified adsorbent in five separate flasks and then agitated for 20 minutes. Towards the end of the time, the resulting suspensions were filtered with Whatman

No. 45 filter paper before it was centrifuged. The dye ion concentrations were obtained using DR 2010 spectrophotometer.

#### Determination of the effect of temperature on the adsorption of ultramarine red in solution

This parameter investigates the effect of temperature on adsorption following the procedure as recommended by Gunmany, (2002). 2g of melon peels (the adsorbent) was measured into five several conical flasks and the 50ml of the ultramarine red dye solution (10mg/g) was weighed into the five different flasks. The flasks were further labeled for temperature readings of **30, 40, 50, 60** and **70** °C. The conical flasks were then tightly covered and heated at their respective temperatures with thermostatic bath, at 20 minutes for each. To the end of each time, each of the flasks were brought out before being agitated for another 5 minutes. The resulting suspensions were filtered using whatman No. 45 filter paper before it was centrifuged. The dye ion concentrations were obtained using DR 2010 spectrophotometer.

#### Determination of the effect of pH on adsorption of ultramarine red in solution

Modified melon peels adsorbent (2±0.01g) was weighed into (5) five different flasks. A 50ml of the ultramarine red dye solution (10mg/l) was measured and poured into the different five flasks. The solutions were then, adjusted to pH 2.0, 4.0, 6.0, 8.0 and 10.0 by the introduction of a solution of HCl (0.1m) or NaOH (0.1m). The pH values were determined by the aid of pH meter. Thereafter the conical flasks were then covered and then agitated for 20 minutes. Towards the end, the suspensions were thus filtered with the use of the whatman No. 45 filter paper and centrifuged. The dye concentrations were determined with DR 2010 spectrophotometer. (Gunmany, 2002 and Gutnaz, 2004).

#### Data Calculation

##### Estimation of the degree of sorption of ultramarine red

The quantity of the ultramarine red adsorbed by the melon peels during the series of batch determinations were evaluated using the mass balance equation as expressed below: (Gunmany, 2002 and Hajira *et al.*, 2008).

$$qe = (Co - Ce) \frac{V}{M}$$

Where

qe = dye contents on the biomass (mgg<sup>-1</sup>) at equilibrium.

Ce = dye concentration in solution (mgL<sup>-1</sup>) at equilibrium.

Co = Initial dye concentration in solution (mg/l)

V = Volume of dye solution used (ml)

M = mass of adsorbent used (g)

##### Kinetic Interpretation of experimental results

In the effort to fully understand the mechanism of adsorption process the pseudo-first-order and pseudo-second-order equations were utilized to treat the data. The linear flow of the pseudo-first order model is denoted by the equation. (Gunmany, 2002 and Hajira *et al.*, 2008).

$$\ln(qe - qt) = \ln qe - Kt$$

Where

qe = mass of dye adsorbed at equilibrium (mgg<sup>-1</sup>)

qt = mass of dye adsorbed at time t (mgg<sup>-1</sup>)

k = equilibrium rate constant.

The linear plot of  $\ln(qe - qt)$  versus t confirms this model.

However, the linear representation of pseudo-second order equation is expressed as:

$$\frac{1}{qt} = \frac{1}{ho} + \frac{t}{qe}$$

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Where

$qt$  contents of the dye ion on the adsorbent surface ( $\text{mgg}^{-1}$ ) at time  $t$ .  $q_e$  = quantity of dye adsorbed at equilibrium ( $\text{mgg}^{-1} \text{ min.}$ ) The initial adsorption rate,  $h_o$ , is further defined by the equation  $H_o = K_2 q_e^2$

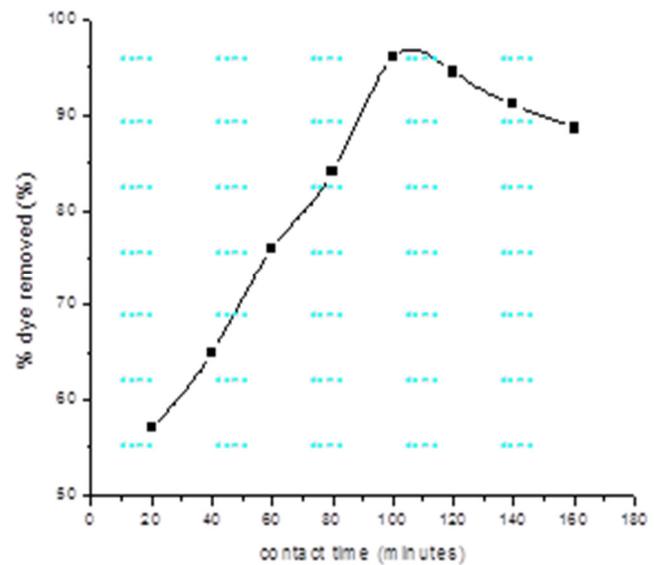
Where  $K_2$  represent the pseudo-second order rate constant ( $\text{gmg}^{-1} \text{ min.}$ ) (Gunmany, 2002 and Hajira *et al.*, 2008).

## Results

### Effect of Contact Time on Adsorption

The response of time on adsorption was in order to obtain how long the melon peel waste biomass would take to absorb the ultramarine red. This was investigated between the intervals of 20 minutes and varied from 20 to 100 minutes. The data from the time-dependent experiment for the sorption of ultramarine red by the melon peel waste is shown in the fig. 1. It is evident that as contact time was increased from 20 to 100 minutes, the fractions of dye ions removed by the biomass increased. Consequently, the results obtained also revealed that the dye adsorbed by the melon peels is very rapid with increase in time, including the percentage of dye adsorbed in which maximum percent of 96 was obtained at 100 minutes. This may be attributed to the fact that, as the dye solution sorbent system was agitated at longer time, so much of the molecules of the ultramarine red accumulate on the surface of the adsorbate until equilibrium was attained.

Related observations have been made by some researchers (Gunmany, 2002; Gutnaz *et al.*, 2004 and Hajira *et al.*, 2008).

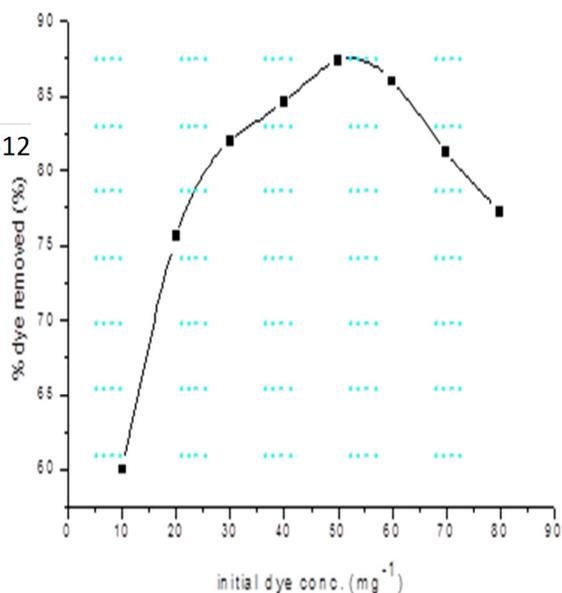


**Fig.1:** The effect of contact time on the adsorption of the dye

### Effect of dye ion concentration on adsorption

The experimental result of the adsorption of ultramarine red onto the melon peel waste biomass at various initial dye ion concentrations is shown in fig. 2. The sorption capacity increased from 0.437 to 1.062  $\text{mg/g}$  with increase in the amount of dye from 10 to 50  $\text{mgL}^{-1}$  having maximum adsorption of 1.062  $\text{mg/g}$ .

Similarly, the actual amount in percentage removed from solution was observed to increase with increase in initial dye concentration. This could be due to the fact that when the dye concentration is increasing, more dye is made available for adsorption on the adsorbent. It is also due to the effect of concentration gradient which is the principal driving force for the sorption process (Hiroyuki *et al.*, 1994).



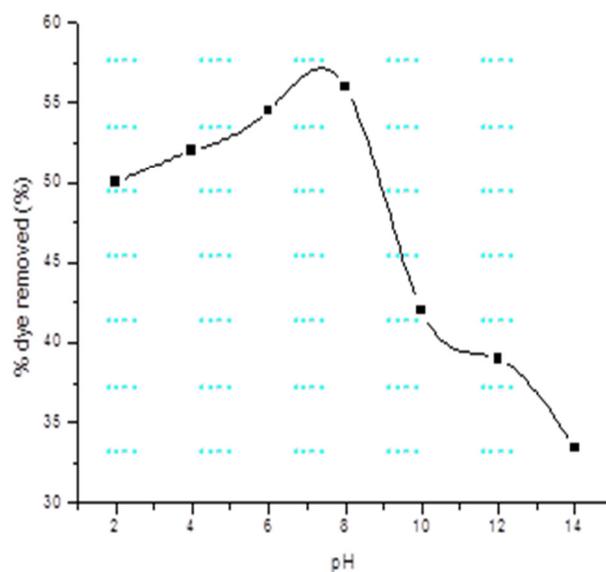
**Fig. 2:** Effect of concentration on dye removal

### Effect of pH on adsorption

The pH of an aqueous system is a crucial factor that may affect the uptake of the adsorbate. The chemical characteristics of both adsorbent vary with pH. According to Horsfall and Ho *et al.* (1996), most plant materials are made up of complex organic residues such as lignin and cellulose that contain several kinds of polar functional groups.

These groups can partake in chemical bond formation and may therefore be responsible for the cation exchange characteristics of most biomaterials. The dependence of pH on adsorption of the dye is represented in fig 3.

It was found out that when the pH of dye solution increased from 2 to 8, the percentage of the ultramarine red adsorbed increased from 50-56. However, at pH 10, there was a rapid decrease in the percentage of dye adsorbed. As reported by Horsfall *et al.* (2003), in the study of the removal of methylene blue by treated activated carbon, the

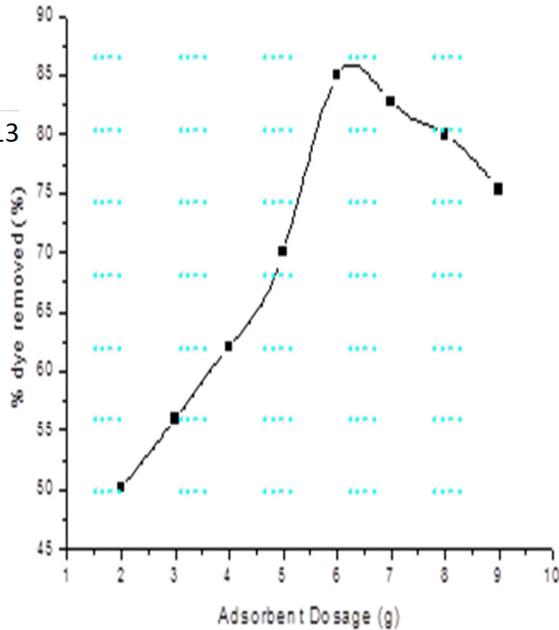


**Fig.3:** A plot of pH against dye adsorption efficiency at mass of biomass 2g, time 20 minutes, conc. 10 mg/l and volume 50ml.

removal of methylene blue increased together with increase in pH. However, the adsorption of the methylene blue at low pH may be due to the presence of hydrogen ions competing with the cation group on the ultramarine red adsorption sites. Meanwhile similar trend has been reported in literature for the adsorption of Congo red dye onto malua oil cake (Juang *et al.*, 1996).

### Effect of adsorbent dosage on the adsorption process

The effect of amount of biomass (melon peel) on the adsorption of the ultramarine red was investigated in which the quantity of biomass was varied from 2 to 9 (figure 4). From the results obtained the amount of the ultramarine red removed increased from 0.026 to 0.198 mg/g as the biomass was increased from 2 to 6 g.

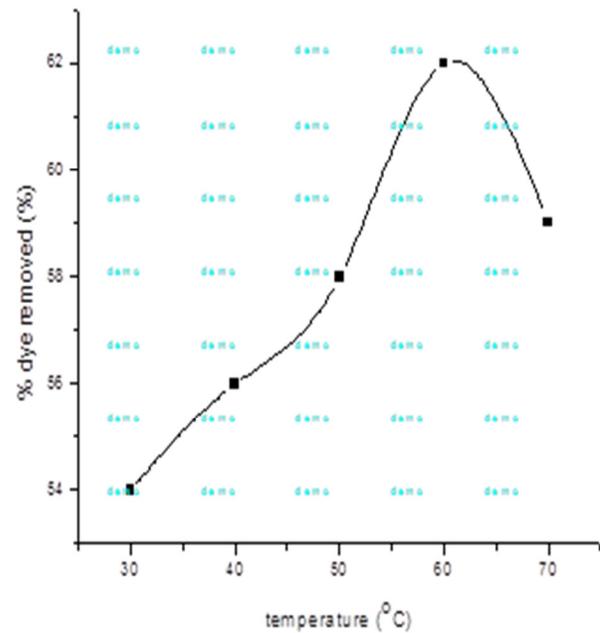


**Fig. 4:** Effect of adsorbent dosage on dye removal at Time 20 minutes, volume 50ml, conc. 10mg/l.

From the fig. 4, it was observed that the optimum adsorbent dose was 6g in which 0.198 mg/g of dye was adsorbed. Similarly, the maximum percentage 85 of dye adsorbed was obtained at the dosage 6g. Consequently, the increase the rate of dye uptake could be linked to certain reasons as reported Khan *et al.* (2002). The increase in ultramarine red uptake was due to the increasing biomass dosage as the binding sites for adsorption increased.

#### Effect of Temperature on the adsorption of ultramarine red

The dependence of ultramarine red sorption on temperature was investigated within the range of temperature 30°C to 70°C at the interval of 10°C. The effect of temperature on the sorption of dye is shown figure 5. Results obtained from figure 5 showed that the contents of ultramarine red adsorbed increased from 0.054 to 0.079 mg/g with increase in temperature from 30 to 70°C.



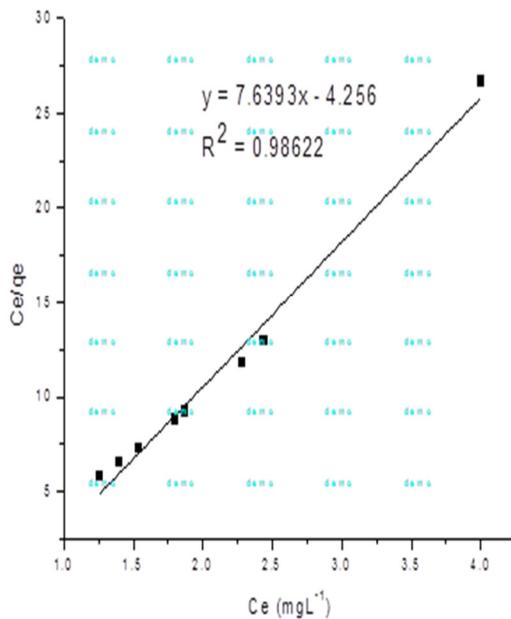
**Fig.5:** temperature dependence plot at mass of biomass 2g, volume 50ml. Conc. 10mg/l.

However, this increase in the quantity of ultramarine red removed as the temperature increased was not much significant. Similar observation was made by Laowansiri (2008). The increase in adsorption due to the increased temperature could be linked to the chemical reaction occurring between the functional groups of the melon peels biomass and ultramarine red. Similarly, at higher temperature, there is the increase in mobility potentials of the larger dye ion producing a swelling effect on the internal structure of the biomass, if thus allows the larger dye molecules to penetrate further (Mishra *et al.*, 2009). The reasons accompanying increase sorption process with increase temperature has been reported also by Carliel (1996).

**Equilibrium studies**

**a. Langmuir Isotherm**

The model, Langmuir isotherm was used for the estimation of the maximum adsorption capacity representing the complete monolayer coverage on the biomass surface. The graphs of specific adsorption  $C_e/q_e$  against the equilibrium concentration  $C_e$  is shown in fig (6) and the linear isotherm parameters.  $q_m$ ,  $K_L$  and the co-efficient of determinations also contained in table 1.



**Fig. 6:** Langmuir Equilibrium

The  $R^2$  result obtained suggests that the Langmuir isotherm is a good model of the adsorption. Langmuir isotherm defined in terms of a dimensionless constant referral to as separation factor  $S_F$  (Choy, 1999 and Horsfall *et al.*, 2003). This shown below:

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

Where

The parameter indicates the shape of the isotherm as follows

- $S_F > 1$  unfavorable isotherm
- $K_L =$  Langmuir isotherm constant
- $C_0 =$  Initial ion quantity of 10mg/L.
- $0 < S_F < 1$  favourable isotherm (Azliar *et al.*, 2005).

$S_F = 1$  linear isotherm

$S_F = 0$  irreversible isotherm

The separation factor for the ultramarine red is less than one indicating that

melon peel waste biomass is an excellent adsorption for the ultramarine red ions. The deparation parameter and other Langmuir isotherm parameters are shown below.

**Table I:** Linear Langmuir isotherm parameters

Dye ion	$Q_m$ (mg <sup>-1</sup> )	$K_L$ (Lg <sup>-1</sup> )	$R^2$	$S_F$
Ultramarine Red	0.6998	0.108	0.884	0.481

**b. Freundlich Isotherm**

The Freundlich model was employed to evaluate the adsorption intensity of the ultramarine red by melon peels on the surface. The Linear Freundlich isotherm for the sorption of ultramarine ion into melon peel waste are represented in fig (7). Critical examination of the plot revealed that the Freundlich isotherm is also an appropriate model to describe the sorption process under consideration. Table (4) shows the linear Freundlich sorption isotherm constant and the co-efficient of determination  $R^2$ .

Evident from the  $R^2$  value the linear representation of the Freundlich isotherm seem to produce a

reasonable model for the sorption process under investigation.

the value represented that the pseudo-first order mode gave or produced a good description for the study.

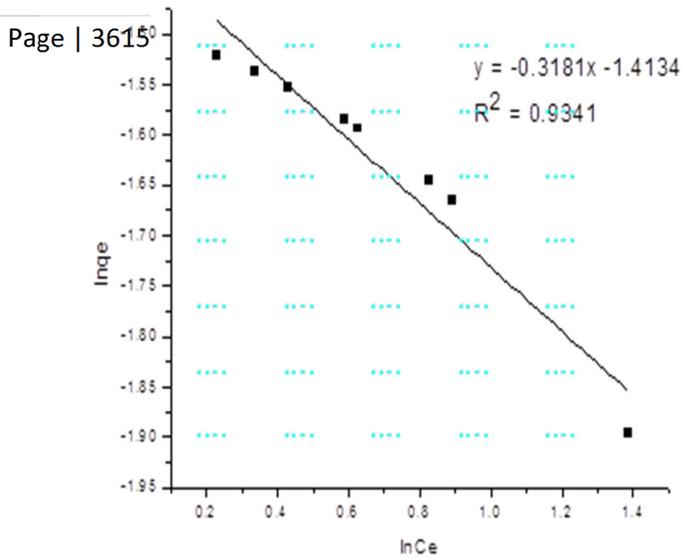


Fig. 7: Freundlich Equilibrium Isotherm Model

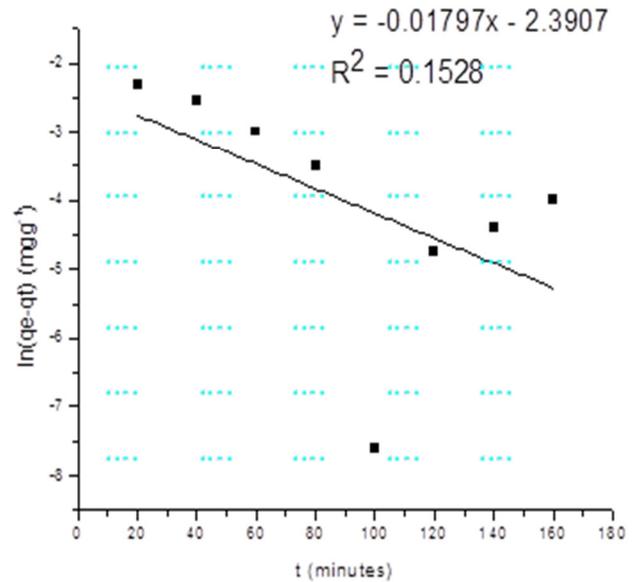


Fig. 8: Pseudo First Order Plot

Table II: Freundlich Isotherm Constant

Dye ion	1/n	Qe (mgg <sup>-1</sup> )	R <sup>2</sup>
Ultramarine red	1.747	0.038	0.9726

Table III: Values for Pseudo – First order parameters

Dye ion	K <sub>1</sub>	Qe (mgg <sup>-1</sup> )	R <sup>2</sup>
Ultramarine red	0.011	0.228	0.940

**Kinetics of Sorption**

**a. Pseudo-first-order**

The kinetic of sorption is one of the essential factors in the rate at which sorption occurs for a system and very important in understanding sorption design and analysis with sorbate residence time and reactor dimension (Choy, 1999 and Horsfall *et al.*, 2003).

The graph of ln (qe-qt) against t as shown below represents the pseudo-first order kinetics. From the flow, it is evident that the relationship between dye ion diffusivity, in (qe qt) and time is linear this confirms the model. In the figure 8 below, the value of the co-efficient of determination R<sup>2</sup> is shown and

Consequently, the sorption kinetics showed high dependence on the physical and chemical quantities of the sorbent material, which also affects the sorption process and the mechanism (Arami and Azliar, 2005).

**b. Pseudo-Second Order Model**

The plot t/qt against T shown in the figure (9) represents the pseudo-second order kinetics arising from the flow, it is evident that the relationship between t/qt and t is linear which justifies the model. However, the initial sorption rate ho, the equilibrium adsorption capacity qe, the pseudo-

second order rate parameter  $K_2$  and the co-efficient of prediction  $R^2$  are contained in table iv. Evident from the co-efficient of determination  $R^1$ , the pseudo-second order model provide a better description for the process better than pseudo-second order model. Similar report has been made by Che (2004) for the adsorption of basic acid blue and direct red types via clay based and activated carbon.

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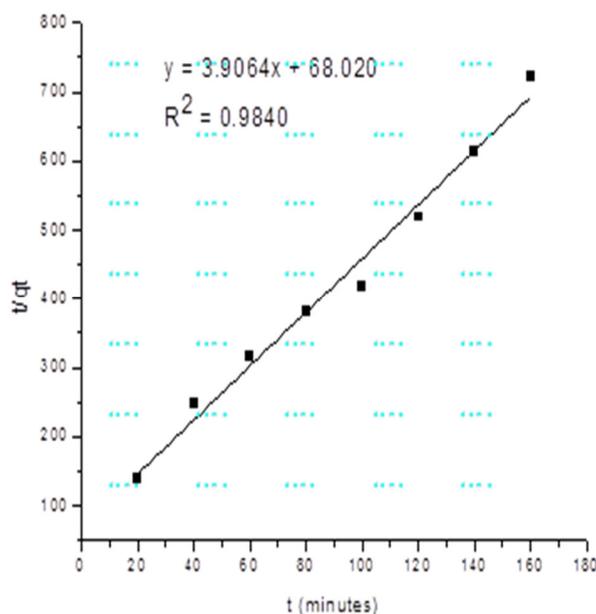


Fig. 9: Pseudo Second Order Plot

Table IV: Values of pseudo-second order parameter

Dye ion	$H_0$ ( $\text{mgg}^{-1} \text{min}^{-1}$ )	$K_2$ ( $\text{mgg}^{-1} \text{min}^{-1}$ )	$Q_e$ ( $\text{mgg}^{-1}$ )	$R^2$
Ultramarine red	0.009	0.026	0.592	.9277

### Conclusion

The effect of ultramarine red dye ion concentration on adsorption capacities showed that melon peel waste biomass adsorbed dye ions from solution,

with an increase in sorption capacity of the biomass with increase dye ion concentration solution. The actual percentage sorption of the dye ions from solution also increased with increased in initial dye ion concentration.

The effect of contact time and temperature showed the same trend in the increase on the amount of dye adsorbed and the actual percentage removal. The pH studies showed that increase in pH increased the amount of dye adsorbed. However, the data fitted the Langmuir and Freundlich Models very well. The separation quantity or equilibrium parameter obtained from Langmuir isotherm showed that adsorption of dye ion onto the melon peel waste biomass is favorable. In general, the data showed that melon peel waste biomass was successful as biosorbent for the removal of dye ion from contaminated water and may serve as an alternate to conventional means. The kinetic data clearly established that pseudo second order model provide a more appropriate description of the dye ions adsorption process ultramarine red.

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