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# EQUILIBRIUM AND KINETIC STUDIES OF ADSORPTION OF SAFRANIN-O FROM AQUEOUS SOLUTIONS USING PINEAPPLE PEELS

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#### Abstract

The aim of this work is to investigate the applicability of raw unmodified pineapple peel waste (PPW) for the removal of safranin-O in aqueous solution. The adsorption of safranin on PPW material was studied as a function of PPW dose (0.5–2.5g), initial concentration (20–100mg/L), pH, 2–10solutions, and a varying contact time. The effect of these parameters on the adsorption capacity was studied using a batch process. The experimental data were fitted to Langmuir and Freundlich adsorption models. The adsorption isotherm was found to obey the Freundlich model. The adsorption capacity was found to be 21.7mg/g. Kinetic data were fitted to the pseudo-first-order and pseudo-second-order models, and were found to follow pseudo- second-order kinetic model. The result shows that PPW adsorbent is potentially low-cost adsorbent for removal of safranin-O.

Keywords: Pineapple peel waste; Safranin-O; Adsorption; Isotherms; Kinetics; Equilibrium; Biosorption

#### **1. Introduction**

Discharge of wastewater from textile, paper, printing, and pharmaceutical industries contains colored effluent. The presence of these substances in streams or rivers beyond the permissible limits has been reported to cause potential health risks to public and aquatic environment (Rafatullah *et al.*, 2010). Untreated Industrial wastewater released into water bodies could impair normal function of both flora and fauna due to its toxicity and non-biodegradability (Han *et al.*, 2008). Safranin-O, a cationic dye discharged from textile and pharmaceutical industries (veterinary medicine) is reported to be irritating to respiratory systems, skin, and could cause digestive tract infections when ingested (Bayazit, 2013).

Industrial activities are increasing all over the world. Unfortunately, the exact amount of dyes produced is not yet known all over the world. Currently, it is estimated that more than 10,000 are commercially available with about 0.7 million tons of dyes produced per year (Suteu and Malutau 2013). Moreover, literatures on the exact quantity of dyes discharged into the environment are limited. It is assumed that a loss of 1-2% in production and 10-15% loss in use are a fair estimate (Güngördü *et al.*, 2013).

Aesthetically, dyes have adverse effect on water bodies, as they are visible pollutants. The presence of color in water bodies reduces light penetration, and impairs biological metabolic processes (Gupta *et al.*, 2011). Disposal of dye wastewater without proper treatment destroys the aquatic communities (Hu *et al.*, 2010). Environmental quality guidelines have made it mandatory to decolorize dye wastewater prior to discharge. However, complete decolorization of textile dye effluent does not occur even if the effluent is treated by municipal wastewater treatment systems. The conventional methods to remove dyes from wastewater include coagulation/flocculation (Zonoozi *et al.*, 2009), oxidation or ozonation, membrane separation precipitation, ion-exchange, reverse osmosis, complexation/sequestration and activated carbon (Reddy *et al.*, 2012). Unfortunately, the major drawback, especially for the developing countries is the high cost for recycling/regenerating ability (Mouzdahir *et al.*, 2010). Similarly, the application of the

conventional treatment of wastewater may not be economically viable. Therefore, biosorption techniques could be economically viable and efficient in such cases.

Recently, there are many researches on cheap available agricultural and/or plant-based materials such as tea (*Camellia sinensis L.*) seed shells (Gao *et al.*, 2013), pea shells (*Pisumsativum*) (Geçgel *et al.*, 2013), *Casuarin aequisetifolia* needle (Dahri *et al.*, 2013), alfa grass (Bounehdi *et al.*, 2013), neem leaf powder (Patel and Vashi 2013), corn husk (Khodaie *et al.*, 2013), papaya stems (Krishni *et al.*, 2013), and (Malekbala *et al.*, 2012) have been used as adsorbent for the removal of various dyes from industrial waste water effluents. However, there were few reports on using pineapple peel waste (PPW) by chemical and physical activation methods. The use of pineapple peel waste (PPW), an agricultural waste material as an adsorbent, will considerably replace the use of conventional treatments. Because, (PPM) as alternative raw materials is cheaper and readily available source of adsorbent, and environmentally friendly. Major advantage in the use of biomass is the renewability, abundance, reliability and availability (locally), especially, those biomass resources that are by-products of agricultural activity. Therefore, in this paper, the adsorption equilibrium and kinetics of Safranin-O on pineapple peel were studied.

## 2. Materials and Method

## 2.1 Adsorbate

Safranin-O, a cationic red dye purchased from Sigma–Aldrich, has a molecular formula  $C_{20}H_{19}CIN_4$  with IUPAC name of 3,7-Diamino-2,8-dimethyl-5-phenylphenazinium chloride. A 1000mL stock solution was prepared by dissolving 1.0g of Safranin-O in one liter of distilled water. To obtain various solutions, different concentrations were prepared by diluting the stock solution with suitable volume of distilled water. The natural pH of the stock solution was adjusted to around 5.6, and was maintained at this level even with dilution. All other chemicals used were of analytical grade. The chemical structure of Safranin-O is shown in Figure 1.



Safranin O

Figure 1: Chemical structure of Safranin-O dye

## 2.2 Adsorbent

The Pineapple peel (*Ananas comoscus*) waste was used as adsorbent in this study. The PPW wastes were collected from Pasa Raya Borong market at Sri Serdang area near Universiti Putra Malaysia (UPM), Serdang, Selangor, Malaysia. It was cut into smaller pieces and washed

thoroughly under running tapped water for several times to remove dirt and sand particles. The sample was further rinsed repeatedly with distilled water to remove dirt particles and dried in an oven at 60°Cfor 48 h. The sample was ground using mortar and pestle. Ground samples were sieved to (1.18mm) particle size and stored in a sealed plastic bag with silica gel to minimize dampness. This prepared sample (adsorbent) was used raw throughout in this work.

## 2.3 Characterization Pineapple peels Using SEM and FT-IR

After the adsorption experiment, the PPW surface morphology was determined using SEM from Chemical Engineering Laboratory, Universiti Putra Malaysia (UPM). Fourier-transform infrared (FT-IR) spectroscopy was used to characterize the PPW samples according to Feng *et al.*, (2009) and is briefly described here. The infrared spectra of the PPW were recorded with Nicolet 380 (FT-IR) spectrophotometer with potassium bromide disks. The thermal characteristics of the adsorbents were examined using TG peaks (SDT Q600) instrument. Surface morphology of the adsorbents was identified by JSM-5600LV scanning electron microscope (SEM).

## 2.4 Batch Equilibrium Studies

In this study, all experiments were carried out at room temperature. A 250 mL stopper cork conical flasks filled with 100 mL of adsorbate were prepared at different initial concentrations (20-100 ppm), the adsorbate were in contact with adsorbent for about 90min, and a pH (pH meter model Jenway 3305, England) ranging from 2 to 12 were observed, while adsorbent dose of 0.5 to 2.5g was used, and the mixture was agitated at a constant speed of 150 rpm on an orbital shaker (Model Heidolph, incubator 1000, Germany). The final concentrations of dye (adsorbate) were determined by a double beam UV-Vis spectrophotometer (Model GENESYS-10-UV) at a wavelength of 516 nm.(Liu *et al.*, 2012). The biosorption capacity of the dye was determined at equilibrium concentration,  $q_e$  (mg/g), and was computed using the following equation 1:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where:  $C_i$  is the initial dye concentration (mgL<sup>-1</sup>),  $C_e$  is the equilibrium dye concentration in solution (mgL<sup>-1</sup>), V is the volume of the solution (L), and *m* is the mass of the biosorbent used (g). The percentage removal of dye was calculated by equation 2

$$\% Removal = \frac{c_0 - c_f}{c_0} \times 100 \tag{2}$$

where  $C_o$ , is adsorbate initial concentration (mg\L), and  $C_f$  is the final concentration (mg/L)

In order to ensure accuracy of the data, the experiment was performed in triplicate and the average results were taken.

## **3** Results and Discussion

# 3.1 Characterization of the prepared adsorbent

## 3.1.1 Fourier-transform infrared (FT-IR) Analysis

The biosorption of Safranin-O on pineapple peel was attributed to active groups and bonds present on the surface. The FT-IR spectra of the biomass were taken before and after Safranin-O biosorption (Figure 2a and Figure 2b) respectively. A broad and intense absorption peak at 3349.49 cm<sup>-1</sup> corresponding to O-H stretching vibrations of cellulose, pectin, absorbed water, and lignin (Feng *et al.*, 2011) was observed for pristine biomass. The sharp peaks at 2920.72 and

2853.15 cm<sup>-1</sup> were assigned to C-H stretching and symmetric stretching vibrations of CH<sub>2</sub>, respectively. Peak at 2330.72 cm<sup>-1</sup> is attributed to the N-H or the C=O stretching vibrations. The band at 1730.28 cm<sup>-1</sup> was assigned to the carbonyl (C=O) stretching vibration. Furthermore, peak at 1626.53 cm<sup>-1</sup> was due to stretching band of carboxyl (-COO) groups. The bands at 1541.10 cm<sup>-1</sup> and 1463.38 cm<sup>-1</sup> were assigned to a strong asymmetric and a weak symmetric stretching bands of carboxylate groups (COO-) respectively. Moreover, a band at 1374.17 cm<sup>-1</sup> was probably due to amides functional groups (Dyke *et al.* 2011). A broad peak at 1044.59 cm<sup>-1</sup> is an indication of C-N stretching in -CO-NH- (Nagpal *et al.*, 2011).

The spectrum after safranin biosorption on pineapple peel showed disappearance, shifting or decrease in peaks intensities at 3395 cm<sup>-1</sup>, 2920 cm<sup>-1</sup>, 2853 cm<sup>-1</sup>, 2330 cm<sup>-1</sup>, 1730 cm<sup>-1</sup>, 1626 cm<sup>-1</sup>, 1541 cm<sup>-1</sup>, 1463 cm<sup>-1</sup>, 1374cm<sup>-1</sup>, 1044cm<sup>-1</sup>(Figure 2b). Similar results were achieved by (Guptal *et al.*, 2011). In addition, a peak at 3349 cm<sup>-1</sup> disappeared after safranin biosorption showing active involvement of O-H group in the biosorption. The results were summarized in the Table 1 below:



Figure 2a: FT-IR spectra PPW Before Adsorption



Figure 2b: FT-IR spectra PPW after Adsorption

Table 1. FT-IR spectral characteristics of Pineapple peel before and after Safranin-O biosorption

IR	Wave number $(cm^{-1})$		Assignation
Peak	Before biosorption	After biosorption	
1	3349	300.5	Bonded O-H groups
2	2920	-	Aliphatic C-H groups
3	2853	1825	CH <sub>2</sub> stretching
4	2330	1680	N-H or C=O stretching
5	1730	1304	Carbonyl group (C=O)
6	1626	1192	Carboxyl stretching (-COO)
7	1541	937	Strong Asymmetric (COO-)
8	1463	-	Weak symmetric (COO-)
9	1374	-	Amides functional groups
10	1044	937.60	C-N stretching in –CO-NH -

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## 3.1.2 Scanning Electron Microscopy (SEM) Analysis

The SEM image of pineapple peels prior to use as adsorbent, shows an irregular surface with a low and non-porous surface area (Figure 3a). Biosorption of safranin leads to multiple attachment on the rough surface and occupation of pores (Figure 3b). Pores in solids medium like adsorbents may have properties such as shape, location, connectivity, and surface chemistry. Perhaps one of the properties of a pore was easily visualized, its size, and its extent in one spatial dimension. This is probably one of the reasons why the pore size is often of the main property to be characterized.



(a) (b)
 Figure 3: SEM images of *pineapple peel waste (PPW)* (Magnification: 5.00kv 9.9x300 SE, 100μm) (a) before, and (b) after safranin-O biosorption

# **3.2 Batch Adsorption Studies**

# 3.2.1 Effect of Initial Concentration and Contact Time

The adsorption data for the removal of Safranin-O versus contact time at different concentrations are presented in (Figure 4), ranging from 20 to 100ppm.It can be observed from the contact time curve that, the removal shows rapid adsorption of safranin in the first 3 min, thereafter, the adsorption rate decreased gradually and the adsorption reached equilibrium in 90min. The sorption capacity of the sorbent increased from 3.9mg/g to 21.7 mg/g as the initial dye concentration increased from 20 to 100 mg/L. The increment in sorption capacity of the biosorbent may be due to the increase in dye quantity, which resulted in higher concentration gradient of the dye, thus leading to higher sorption capacity (Han *et al.*, 2008; Yeddou-Mezenner 2010a; Feng, *et al.*, 2009).



Figure 4. Effect of Initial Concentration and Contact Time on amount of safranin-O adsorbed (Adsorbent dose: 1g, agitation speed: 150rpm)

### 3.2.2 Percentage Uptake of Safranin-O with Time at Different Initial Concentration

The percentage uptake of safranin-O increases with increase in initial dye concentration, and the sorption capacity of the adsorbent are directly proportional to the initial dye concentration. Figure 5 shows the plot of percentage uptake of safranin-O at different initial concentration against contact time, it can be seen that the trend of increments starts from 58.3 to 72.5% as the initial dye concentration increased from 20 to 100 mg/L. This increment may be attributed to increase in the quantity of dye and, as result the removal concentration also becomes high(Yeddou-Mezenner 2010b).



Figure 5: Percentage Uptake of Safranin-O at Different Initial Concentration (Adsorbent dose: 1g, agitation speed: 150rpm)

## 3.2.3 Effect of Adsorbent Dose on Adsorbate Removal

The amount of pineapple peels used to remove safranin-O was varied from 0.5 g to 2.5 g for investigation of the relationship between adsorbent dosage and dye removal performance in which the results are shown in Figure 6.The effect of adsorbent dose on the amount of adsorbate removed increases with increase in adsorbent dose. The higher the quantity of adsorbent use, the higher the uptake of safranin-O that is from 6.7 mg/g at 0.5 g to 17.6 mg/g at 2.5g. The reason for such behavior may be attributed to greater surface area and large number of vacant biosorption sites thus favoring more dye biosorption (Gandhi *et al.*, 2012; Vinod *et al.*, 2012; Saidutta *et al.*, 2013).



Figure 6: The Effect of Adsorbent Dose to the Uptake of Safranin-O (Initial concentration 50ppm, adsorbate 100mL, agitation speed: 150rpm, contact time: 90 minutes)

### 3.2.4 Effect of pH on Adsorbate Removal

Treatment of (safranin –O) wastewater is pH dependent. Therefore, the pH of the solution is known to affect its structural stability. Figure 7 shows the dye removal trend from aqueous solution. At pH above 6, the colour of safranin-O change irreversibly indicating an alteration in the structure of safranin-O molecules. Moreover, optimum removal due to pH was achieved at pH 6. Therefore, since the solution that changed colour was no longer safranin-O. pH above 6 cannot be used for this experiment because it is a neutral stage. The adsorption behavior of such adsorbent at various pH may be due to parameters such as surface charges and active sites, also to the chemistry of the dye solution (Gupta *et al.*, 2011).



Figure 7: The Effect of pH on uptake of safranin-O (Initial concentration: 60 ppm, adsorbent dose: 1g, contact time: 90minutes, agitation speed: 150rpm)

#### 3.3. Adsorption Isotherm

Fundamentally, equilibrium adsorption isotherm is very significant in the design of adsorption systems. This study provides the adsorption capacity of the adsorbent. Moreover adsorption isotherm describes the equilibrium relationships between adsorbent and adsorbate, which is usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature. In this study, 20 to 100ppm concentration of adsorbate and 1g of adsorbent dose was used. The equilibrium data obtained experimentally were fitted to two most common models, the Langmuir and Freundlich isotherm model.

#### 3.3.1Langmuir isotherm

The Langmuir model is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecule on the adsorbent surface. Once the molecules are concentrated on the adsorbent, there will be no transmigration of the solute (adsorbate) in the plane of the surface (Langmuir 1916). The adsorption energy will be uniform throughout the surface area otherwise the pollutant will have uniform adsorption or attractive forces.

$$q_e = \frac{Q_{max}K_L C_e}{1 + \alpha_L C_e} \tag{3}$$

where:  $q_e$  is the equilibrium concentration of adsorbate (mg/g),  $Q_{max}$  is adsorption capacity,  $K_L$  is the Constant related to efficiency of solute adsorption (L/mg), Ce is Equilibrium concentration of adsorbate in solution (mg/L) and  $\alpha_L$  is Constant related to energy of adsorption (L/mg).

The above equation is termed as non- linear form of Langmuir, and can be linearized to form equation as

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{\alpha_L C_E}{K_L} \tag{4}$$

The essential characteristic of Langmuir isotherm can be expressed by separation or equilibrium parameter ( $R_L$ ), a dimensionless constant, and can be define as:

$$R_L = \frac{1}{1 + bC_o} \tag{5}$$

The value of  $R_L$  indicates the nature of adsorption and it is shown in Table 2. If the separation factor is greater than one ( $R_L$ >1), it means the adsorption of safranin is unfavorable. While if the range is between 0 and 1 i.e. (0<R<1), this shows that, biosorption of safranin is favorable. But if the value of  $R_L$  equals to unity, the adsorption process is linear. If it is equal to zero ( $R_L$  = 0), then it is an indication of an irreversible process. Below is the summary of the process above.

Table 2: Values of  $R_L$  and corresponding isotherm type (Hameed *et al.*, 2009)

Values of $R_L$	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L > 1$	Favorable
$R_L = 0$	Irreversible

A Langmuir isotherm plot of 1/qe against 1/Ce is shown in Figure 8 below. From this plot, it can be seen that,  $R^2 = 0.9593$  which is relatively closed to unity indicates a good absorption.



Figure 8: Langmuir Isotherm for Adsorption of Safranin-O on Pineapple peel Adsorbent

This suggested that the Langmuir isotherm might be a suitable isotherm model. Thus, the biosorption process of pineapple peels exhibit monolayer biosorption. Table 3 shows the value of Langmuir constants, aL and kL as 12.77695 mg/L and 18.58736 mg/L respectively.

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Isotherm	$K_L (mg/L)$	a <sub>L</sub> (mg/l)	$R^2$
Langmuir	18.58736	12.77695	0.9593

## 3.3.2 Freundlich Isotherm

Freundlich, (1906) proposed a model based on the assumption that biosorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of adsorbate at equilibrium. Mathematically, it is characterised by the heterogeneity factor 1/n

$$q_e = K_f C_e^{\frac{1}{n}} \tag{6}$$

where:  $K_f$  = constant that indicates sorption capacity of adsorbate (mg/g). The unit is given as (L/g)<sup>(1/n)</sup>, and *n* are constants indicating the intensity of adsorption. This constant can be one or any integer or decimal number. If *n* =1 (linear), *n*<1 (Chemisorption process), and *n*>1 is physic-sorption process (Hameed *et al.*, 2009). The linear expression of this model can take the logarithm of the equation on both sides, and is given as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

Figure 9 shows a plot of log*q*e versus log*C*e, gives a straight line with  $K_F$  and 1/n determined from the intercept and the slope, respectively. Table 4 shows the values of  $K_F$  with about R<sup>2</sup> =0.985, which indicates a good sorption capacity of the adsorbate.



Figure 9: Freundlich Isotherm for Adsorption of Safranin-O on *Pineapple peel* Adsorbent

Table 4: Freundlich Isotherm Parameter for Safranin-O	) Adsoi	rption on	pineapple	<i>e peel</i> Adsorben <sup>•</sup>
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Isotherm	n	1/n	$\mathbf{k}_{\mathbf{f}}$	$\mathbf{R}^2$	
Freundlich	1.5222	0.656	0.6973	0.985	

### **3.4 Kinetics Studies**

The kinetic adsorption data provides the understanding of dynamics of adsorption process in terms of the order of rate constant (Ahmad *et al* 2007). The adsorption experiment was carried out at concentration of 20 to 100ppm, pH 5.7, adsorbent dose of 1gand contact time varied was from 3 to 90 minutes. Two kinetic models were used to find which model fits the experiment: Lagergren's Pseudo-First Order and Second- Order Kinetic models.

### 3.4.1 Pseudo-First Order Model

The pseudo-first-order rate model equation was first developed by Lagergren (Ho *et al.*, 2000). The relationship can be represented as

$$\frac{d_{q_t}}{dt} = k_1(q_e - q_t) \tag{8}$$

where:  $k_1$  is the pseudo-first-order rate constant (1/min),  $q_e$ = amount of adsorbate at equilibrium (mg/g) and  $q_t$  = are biosorption capacities at equilibrium with respect to time t (mg/g). Integrating equation 8 for the boundary conditions are t = 0 to t = t and  $q_t$ = 0 and  $q_t$  yields,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
(9)

The constant value  $k_1$  were obtained by plotting a straight-line graph of  $log (q_e \_q_t)$  against *t*. Correlation coefficients  $R^2$  for different safranin concentrations are shown in Table 5. The coefficient 0.9148 is for concentration at 20mg/L while 0.8407 for 100 mgL<sup>-1</sup>. The calculated values of adsorption capacity ( $q_{cal}$ ) were obtained as 3.543 mg/g at 20 mgL<sup>-1</sup> and 6.929 mg/g at 100 mgL<sup>-1</sup>. Based on the observed, calculated, and experimental values it can be seen in Figure 10 that, adsorption of safranin-O did not follow pseudo-first-order kinetic model.



Figure 10: Pseudo -first Order Model for Adsorption of Safranin-O on pineapple peel Adsorbent

### 3.4.2 Pseudo-Second-Order Kinetic Model

The pseudo-second-order equation based on equilibrium adsorption (Ho et al., 2000) and is expressed in Equation 10

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{10}$$

where:  $k_2$  (g/mg-min) is the pseudo-second-order rate constant. Integrating Eq. (10) for the boundary conditions are t = 0 to t and  $q_t$ = 0 to qt

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{11}$$

The linear form of this model is represented as

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t\tag{12}$$

where:  $h = k_1 q_e^2$  (13)

The plot of  $t/q_t$  against t gives a straight line. Figure 11 shows the linear form of pseudo-secondorder kinetic at different safranin concentration on pineapple peel. Table 5 presented the coefficient  $R^2$  for the pseudo-second-order kinetic at different concentration was 0.998 (for 20 mgL<sup>-1</sup>) to 0.974 (for 100 mgL<sup>-1</sup>). In addition, the  $R^2$  at (20 mgL<sup>-1</sup>) is higher than all the other concentrations both in the first and second order models respectively; suggesting adsorption is higher at this level. On the other hand, the calculated values of adsorption capacity ( $q_{cal}$ ) tend to be higher than that of the pseudo-first-order kinetic, its value ranges from 11.9 (for 50 mgL<sup>-1</sup>) to 161.3 (for 1000 mgL<sup>-1</sup>) at different concentrations. In addition, the  $R^2$  at (20 mgL<sup>-1</sup>) is higher than all the other concentrations, suggesting adsorption is higher at this level. These facts suggest that the pseudo-second-order adsorption mechanism is predominant, and that the overall rate of the dye adsorption process appears to be controlled by the chemisorption process (Liu *et al.*, 2012).



Figure 11: Pseudo-Second Order Model for Adsorption of Safranin-O on pineapple peel Adsorbent

Table 5. Adsorption Kinetic Parameters of Safranin-O on pineapple peel Adsorbent

First-order Model				Second-order Model					
C <sub>o</sub> (mg/L)	$R^2$	q <sub>e</sub> call (mg/g)	q <sub>e</sub> exp (mg/g)	K <sub>1</sub> (min-1)	$R^2$	q <sub>e</sub> call (mg/g)	q <sub>e</sub> exp (mg/g)	K <sub>2</sub>	
20	0.9148	3.543235	3.8829	2.298394	0.998	3.895598	3.8829	0.155806	
40	0.8289	3.990249	8.3891	2.300006	0.9987	8.488964	8.3891	0.066491	
60	0.8288	5.367845	12.7518	2.301618	0.9994	12.85347	12.7518	0.067064	
80	0.8075	6.419482	17.1992	2.301158	0.9992	17.30104	17.1992	0.053916	
100	0.8407	6.92947	21.6253	2.301618	0.9994	21.73913	21.6253	0.030767	

## 4. Conclusion

The experimental result from this study suggests that pineapple peels is a potential adsorbents for removal of safranin-O from aqueous solutions. Conclusion can be drawn from the effect of parameters, such as initial dye concentration, adsorbent dosage, and pH of solutions. Furthermore, from the result obtained, the adsorbent is found to effectively remove safranin-O by 86.9% percent at initial dye concentration of 100ppm in 90 min contact time. The removal was due to adsorbent dosage increase, while percentage uptake due to pH was 84.5%, which occurs at pH 6 showing acidic condition that is favourable for sorption process. Adsorption isotherms behavior suggests that, the present adsorption exhibit both Freundlich isotherm model characteristics were very good, reflecting the presence of more than one kind of adsorbent–adsorbate surface interaction. Thus heterogeneous surfaces and adsorption capacity is related to the concentration of adsorbate at equilibrium. The adsorption kinetics data followed pseudo-second-order kinetic model with high correlation coefficient almost reaching a unit value (0.99). This indicates that, chemisorption's or an effective electrostatic interaction is dominant.

## Nomenclature

b <sub>F</sub>	Freundlich constants	
Co	Influent concentration	mg/L
Ct	Effluent concentration at time t	mg/L
Ce	Solution phase concentration at equilibrium	mg/L
$\mathbf{k}_1$	Rate constant of first order adsorption	1/min
k <sub>2</sub>	Pseudo-second-order rate constant of adsorption	g/mg.min
$K_{\mathrm{F}}$	Constant related to the overall adsorption capacity	mg/g
K <sub>L</sub>	Langmuir isotherm constant	L/g
М	Mass of the adsorbent	g
q <sub>e</sub>	Amount of Safranin adsorbed at equilibrium	mg/g
$q_{m}$	Langmuir monolayer saturation capacity	mg/g
q <sub>t</sub>	Amount of Safranin adsorbed on adsorbent at equilibrium	mg/L
►L	Langmuir isotherm constant	L/mg
1/n	Constant indicates the heterogeneous surface of the adsorbent	
SEM	Scanning Electron Microscopy	
FTIR	Fourier transform infrared spectra	
R <sub>L</sub>	Dimensionless separation factor	
R <sup>2</sup> PP	Correlation coefficient Pineapple peel	

## References

Ahmad, AA., Hameed, BH. and Aziz, N. 2007. Adsorption of direct dye on palm ash: kinetic and equilibrium modeling. Journal of Hazardous Materials, 141(1):70-76.

Bayazit, SS. 2013. Investigation of Safranin O adsorption on superparamagnetic iron oxide nanoparticles (SPION) and multi-wall carbon nanotube/SPION composites. Desalalination and Water Treatment, 52(37-39):6966-6975.

Boumehdi Toumi, L., Hamdi, L., Salem, Z. and Allia, K. 2015. Batch adsorption of methylene blue from aqueous solutions by untreated Alfa grass. Desalalination and Water Treatment, 53(3):806-817.

Dahri, MK., Kooh, MRR. and Lim, LBL. 2013. Removal of Methyl Violet 2B from Aqueous Solution Using Casuarina equisetifolia Needle.ISRN Environmental Chemistry.

Dyke, SF., Floyd, AJ., Sainsmbury, M. and Theobald, RS. 1981. Organics spectroscopy, An introduction. Longman, 107.

Feng, N., Guo, X., Liang, S. 2009. Adsorption study of copper (II) by chemically modified orange peel. Journal of Hazardous Materials, 164(2): 1286-1292.

Feng, N., Guo, X., Liang, S., Zhu, Y. and Liu, J. 2011. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. Journal of Hazardous Materials, 185(1):49-54.

Freundlich, H. 1907. Über die adsorption in lösungen. Zeitschrift für physikalische Chemie, 57(1): 385-470.

Gandhi, N., Sirisha, D., Smita, A., Manjusha, A., Change, C., Padmavathi, S. and Viswa, M. 2012. Adsorption Studies of Fluoride on Multani Matti and Red Soil. Research Journal of Chemical Science, 2:32-37.

Gao, JJ., Qin, YB., Zhou, T., Cao, DD., Xu, P., Hochstetter, D., Wang, YF. 2013. Adsorption of methylene blue onto activated carbon produced from tea (Camellia sinensis L.) seed shells: kinetics, equilibrium, and thermodynamics studies. Journal of Zhejiang University. Science. B, 14:650-680.

Geçgel, U., G. Özcan, G. C. Gürpınar, 2013. Removal of Methylene Blue from Aqueous Solution by Activated Carbon Prepared from Pea Shells (Pisum sativum). Journal of Chemistry

Güngördü, A., Birhanli, A, and Ozmen, M. 2013. Biochemical response to exposure to six textile dyes in early developmental stages of Xenopus laevis. Environmental Science and Pollution Research International, 20(1):452-460.

Gupta, VK., Jain, R., Saleh, T., Nayak, A., Malathi, S. and Agarwal, S. 2011. Equilibrium and Thermodynamic Studies on the Removal and Recovery of Safranine-T Dye from Industrial Effluents. Separation Science and Technology, 46(5):839-846.

Hameed, BH., Krishni, RR. and Sata, SA. 2009. A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions. Journal of Hazardous Materials, 162(1):305-311.

Han, R., Ding, D., Xu, Y., Zou, W., Wang, Y., Li, Y. and Zou, L. 2008. Use of rice husk for the adsorption of congo red from aqueous solution in column mode. Bioresource Technology, 99(8): 2938-2946.

Ho, YJ., Ng, GM., and Ng, 2000. Kinetics of pollutant sorption by biosorbents. Separation of Purification Methods 29(2):189-232.

Hu, Z., Chen, H., Ji, F., Yuan, S. 2010. Removal of Congo Red from aqueous solution by cattail root. Journal of Hazardous Materials, 173(1-3): 292–297.

Khodaie, M., N. Ghasemi, B. Moradi, and M. Rahimi, 2013. Removal of Methylene Blue from Wastewater by Adsorption onto ZnCl 2 Activated Corn Husk Carbon Equilibrium Studies. Journal of Chemistry,

Krishni, R.R., Foo, KY., and Hameed, BH. 2014. Adsorption of cationic dye using a low-cost biowaste adsorbent: equilibrium, kinetic, and thermodynamic study. Desalalination and Water Treatment, 52(31-33):6088-6095.

Langmuir, I. 1916. The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids. J ACS, 38 2221.

Liu, T., Li, Y., Du, Q., Sun, J., Jiao, Y., Yang, G., ... & Zhu, H. 2012. Adsorption of methylene blue from aqueous solution by graphene. Colloids and Surfaces B: Biointerfaces, 90: 197-203.

Malekbala, M.R., S. M. Soltani, S. K. Yazdi, S. Hosseini, S. 2012. Equilibrium and Kinetic Studies of Safranine Adsorption on Alkali-Treated Mango Seed Integuments. International Journal of Chemical Engineering Applications, 3(3):160

Mouzdahir, YE., Elmchaouri, A., Mahboub, R., Gil, A., and Korili, SA. 2010. Equilibrium modeling for the adsorption of methylene blue from aqueous solutions on activated clay minerals. Desalination, 250(1): 335-338.

Nagpal, UMK., Bankar, AV., Pawar, NJ., Kapadnis, BP., and Zinjarde, SS. 2011. Equilibrium and kinetics studies on biosorption of heavy metals by leaf powder of paper mulberry (Broussonetiapapyrifera). Water, Air & Soil Pollution, 215(1-4): 177-188.

Patel, H., and Vashi, RT. 2013. A comparison study of removal of methylene blue dye by adsorption on Neem leaf powder (NLP) and activated NLP. Journal Environmental Engineering Landscape Management, 21(1):36-41.

Rafatullah, M., Sulaiman, O., Hashim, R., and Ahmad, A. 2010. Adsorption of methylene blue on low-cost adsorbents: a review. Journal of Hazardous Materials, 177(1-3): 70-80.

Reddy, MCS., Sivaramakrishna, L. and Reddy, RV. 2012. The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. Journal of Hazardous Materials, 203: 118-127.

Saidutta, MKS. and Murty, MB. 2013. Adsorption of basic Dye from Aqueous Solution using HCl Treated Saw Dust (Lagerstroemia microcarpa): Kinetic, Modeling of Equilibrium, International Research Journal of Environment Sciences, 2(8): 6–16.

Suteu, D., and Malutan, T. 2013. Industrial Cellolignin Wastes as Adsorbent for Removal of Methylene Blue Dye from Aqueous Solutions. BioResources, 8(1):427-446.

Vinod, V., Kailash, D., Suresh, C. and Madan, L. 2012. Adsorption Studies of Zn (II) ions from Wastewater using Calotropis procera as an Adsorbent. Research Journal of Recent Science, 1: 160-165.

Yeddou-Mezenner, N., 2010a. Kinetics and mechanism of dye biosorption onto an untreated antibiotic waste. Desalination, 262(1-3): 251-259.

Zonoozi, MH., Moghaddam, MRA. and Arami, M. 2009. Coagulation/flocculation of dyecontaining solutions using polyaluminium chloride and alum. Water Science and Technology 59(7):1343-1351.