Parkia speciosa (Petai) pod as a potential low-cost adsorbent for the removal of toxic crystal violet dye

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Abstract

This study focused on the use of *Parkia speciosa* (Petai) pod as a potential adsorbent for the removal of crystal violet (CV) dye. Batch adsorption isotherm experiments carried out under optimized conditions were fitted to six isotherm models, namely Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Redlich-Peterson and Sips. Of these, the Sips model best described the adsorption isotherm of Petai pod for the removal of CV dye, giving a desirable maximum adsorption capacity (q_{max}) of 163.2 mg g^{-1}. Adsorption kinetics was found to follow the pseudo-second order, and further, intra-particle diffusion played a significant role. This study also revealed that the adsorption of CV by Petai pod is influenced by the ionic strength of the medium. However, Petai pod showed resilience towards changes in medium pH.

Index Terms: Parkia speciosa, adsorbent, adsorption isotherm, crystal violet dye

1. Introduction

The past few decades have seen a rise in industries to cater to the rapidly increasing world population. As a result, the amounts of industrial wastes being discharged into water systems have resulted in detrimental problems to both the ecosystem and human health. Hence, there is an urgent need to remove these pollutants and to provide clean water. Various methods have been devised over the years, of which adsorption has gained popularity as it utilizes low-cost materials and unused wastes, which would otherwise be disposed of, to remove toxic environmental pollutants.[1-4]

Of the pollutants being discharged into water systems, dyes cause not only health problems, but also destroy aesthetic nature of water. A common dye widely used in textile, paint and printing industries is crystal violet (CV), or methyl violet 10B, which belongs to the triarylmethane class of dyes. Being non-biodegradable and poorly metabolized by microbes, CV would be persistent in a variety of environments. If present in the human cells, this dye is highly cytotoxic and carcinogenic. CV has been reported to cause skin and digestive tract irritation, and may also cause respiratory and kidney failure.[5]

This study focuses on the use of the pod of a popular local vegetable, *Parkia speciosa*, locally known as Petai, for the removal of CV dye. In South East Asia, this vegetable is usually cooked with spicy prawn paste or "sambal" as a vegetable dish. The pods, being inedible, are discarded as waste. To date, there have been limited reports on the use of Petai as adsorbents for the removal of pollutants. Seeds of Petai were successfully used for the removal of methylene blue dye,[6] while Petai pods have been used to remove Coomassie Brilliant Blue R-250 dye.[7]

2. Experimental approach

Sample preparation

Petai pods were separated from the edible seeds and dried in an oven at 80 ^oC until a constant mass was obtained. The dried sample was then blended and sieved using stainless steel brass laboratory test sieves to obtain the desired particle size of 355-850 μm which was used throughout this study.

Instrumentation

Thermo Scientific, MaxQ 3000 orbital shaker, set at 250 rpm, was used to agitate the mixture of solution, unless otherwise stated. pH was measured using EDT Instruments, GP 353 pH meter. Concentration of CV dye solutions was determined using Shimadzu, UV-1601PC spectrophotomer set at the wavelength of 590 nm. Shimadzu, IRPrestige-21 spectrophotometer was used for functional group characterization. Surface morphology of adsorbent's surface was analysed using Tescan Vega XMU scanning electron microscope (SEM) and the adsorbent was sputter coated with gold using SPIMODULETM Sputter Coater for 60s.

Optimization of parameters

The effects of contact time, medium pH and ionic strength were investigated following the methods as described by Cheing *et al.*[8] with slight modifications. Briefly, 100 mg L^{-1} CV was used and the adsorbent:adsorbate ratio was kept at 1:500 (wt:vol). For medium pH, the range used was from pH 3 to 10. Ionic strength effect was studied using KNO_3 with concentration ranging from 0.01 M to 1.0 M.

Adsorption studies

Adsorption isotherm and kinetics studies were carried out using similar methods as reported by Dahri *et al.*[9] with slight modifications. Briefly, batch adsorption isotherms were performed with dye concentration in the range of 0 – 1000 mg L^{-1} under optimized contact time. Kinetics of the adsorption of CV dye onto Petai pod was investigated using 500 mg L^{-1} CV dye.

Regeneration studies of spent adsorbent

Regeneration studies were carried out based on the method reported by Lim *et al.*[10] with some modifications. The Petai pod was first treated with 100 mg L^{-1} CV dye. Four desorption methods were used on the spent Petai pods *i.e.*, treatment with 1 M HCl, 1 M NaOH, distilled water and heat (200 ^{o}C).

3. Results and Discussion

Effect of contact time

Establishing the contact time required for the adsorbate-adsorbent system to reach equilibrium is an important parameter in adsorption studies. As shown in ***Figure 1***, rapid uptake of CV dye was observed within the first 30 minutes, which then became unchanged during the period of investigation up to 4.0 h. Such observation can be attributed to the immediate occupation of the limited number of available adsorption sites of the adsorbent. In this study, a contact time of 2.5 h was used for all subsequent experiments.

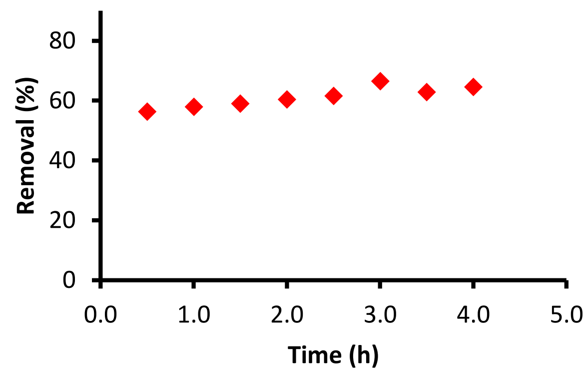

Figure 1. Effect of shaking time for the removal of crystal violet dye using Petai pod

Effect of pH

Another important parameter in adsorption studies is the medium pH. Any change in pH would cause surface characteristics of the adsorbent to alter, thereby affecting its ability to adsorb adsorbates. From ***Figure 2***, it is observed that the ability of Petai pod to attract CV is very resilient to the change in pH, maintaining its constant ability to adsorb CV over a pH range from 3 to 10. This demonstrates the superior adsorption ability of the adsorbent under investigation in contrast to many adsorbents which show pH-dependent dye removal abilities. For example, breadfruit skin[11] reported 60% reduction in removal of CV at pH 2 while adsorbents such as water lettuce,[12] breadnut core[10] and dragon fruit skin[13] displayed drastic reduction with cationic dyes at low pH. In this study, no adjustment of pH was necessary since the untreated (ambient) pH of dye solution (pH = 5.2) gave a reasonably high extent of removal of CV.

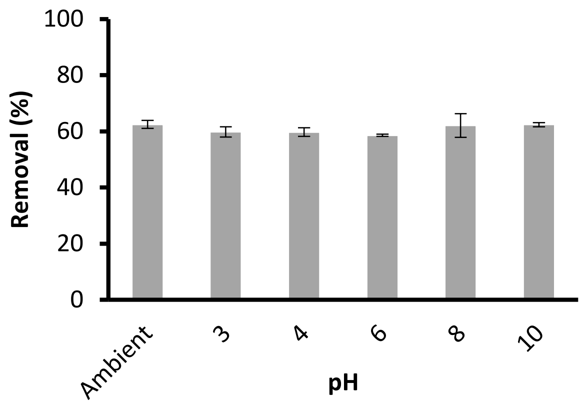

Figure 2. Effect of medium pH on the removal of crystal violet dye by Petai pod

Effect of ionic strength on adsorption of CV

The maximum reduction of approximately 50% in the removal of CV was observed in 0.4 M KNO_3 (***Figure 3***). Clearly, Petai pod's ability to adsorb CV is influenced by the concentration of salt solution. The reduction in dye removal could be due to competition between K^+ with the cationic CV dye for the limited active sites on the adsorbent's surface. Beyond 0.4 M, no further reduction of dye removal was observed which suggests that the inner Helmholtz plane of adsorbent particles gets saturated with 0.4 M KNO_3.

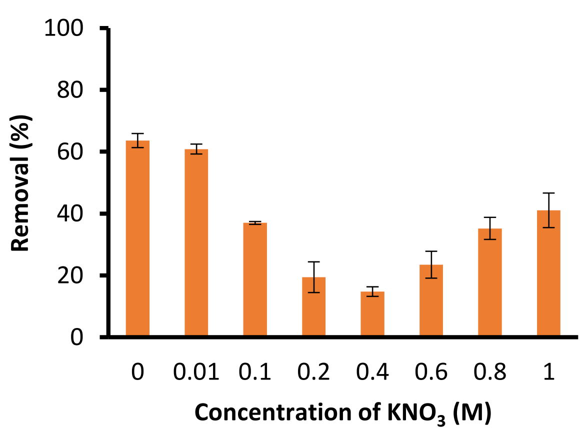

Figure 3. Effect of ionic strength on the removal of crystal violet dye by Petai pod

Adsorption isotherm for the removal of CV by Petai Pod

Adsorption isotherm studies (***Figure 4***) on the removal of CV by Petai pod, carried out over 0 to 1000 mg L^{-1} dye concentration range, indicate the gradual buildup of the adsorbate layer until the initial dye concentration of 400 mg L^{-1} at which the monolayer coverage is complete. Based on the solution analysis, the number of adsorbate dye molecules, more than what is required for monolayer coverage, has been transferred to the adsorbent phase after the initial concentration of 800 mg L^{-1}. This is attributed to the transfer of CV molecules that had been initially present in the monolayer to the interior of the adsorbent phase, probably through inter-particle and intra-particle diffusion with the concomitant transfer from the solution phase to the adsorbent surface. This process would lose adsorbate molecules from the solution phase demonstrating the behavior observed in ***Figure 4***.

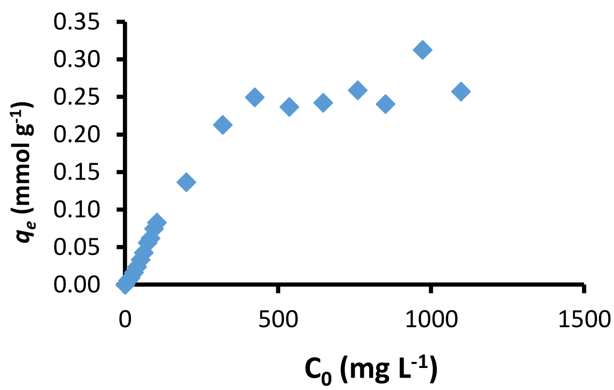

Figure 4. Adsorption isotherm for the removal of crystal violet dye using Petai pod

In an attempt to further understand the adsorption behavior, the data on the extent of adsorption of CV and equilibrium concentrations were fitted to six different isotherm models, namely, Langmuir,[14] Freundlich,[15] Temkin,[16] Dubinin-Radushkevich (D-R),[17] Redlich-Peterson (R-P)[18] and Sips,[19] and analyzed using four different error functions. The isotherm equations and error functions are presented in ***Table 1*** and ***Table 2***, respectively.

Table 1. Linearized equations of the six isotherm models used

Isotherm model	Linear
Langmuir	$\frac{C_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{C_e}{q_{max}}$
Freundlich	$ln q_e = \frac{1}{n} ln\, C_e + ln\, k_F$
Temkin	$q_e = B\, ln k_T + B\, ln C_e$
D-R	$ln q_e = ln q_s - \beta\varepsilon^2$
R-P	$ln\left(k_R \frac{C_e}{q_e} - 1\right) = g\, ln C_e + ln\, a_R$ *where* $0 \leq g \leq 1$
Sips	$ln\left(\frac{q_e}{q_{max} - q_e}\right) = {}^{1}/_{n}\, ln\, C_e + ln\, k_s$

where k_L, k_F, k_T, k_R and k_S are the adsorption isotherm constants for the Langmuir, Freundlich, Temkin, Redlich-Peterson and Sips models, respectively. C_e is the equilibrium dye concentration, q_e is the amount of dye adsorbed and q_{max} is the maximum adsorption capacity. n in the Freundlich equation represents the empirical parameter which is related to the strength of the adsorption process and if it falls within 1 to 10, this indicates the adsorption process is favourable. Constant B is related to the heat of adsorption, R is the gas constant (8.314 J K^{-1} mol^{-1}), T is absolute temperature in Kelvin, β gives the mean free energy of sorption per molecule of sorbate. a_R is the Redlich-Peterson constant and g is the exponent which lies between 0 and 1. The 1/n is the Sips model exponent.

Table 2. Four error functions used

Type of errors	Equations
Average relative error (ARE)	$\frac{100}{n}\sum_{i=1}^{n}\left\|\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}}\right\|_i$
Sum square error (SSE)	$\sum_{i=1}^{n}(q_{e,calc} - q_{e,meas})_i^2$
Hybrid fractional error function (HYBRID)	$\frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}}\right]_i$
Marquardt's percent standard deviation (MPSD)	$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}}\right)_i^2}$

Based on R^2 values, error analyses (***Table 3***) and simulation of data with the above six isotherm models (Figure not shown for brevity), it was concluded that even though the Temkin model gave the highest R^2 value, its large errors clearly indicate that this model does not fit with the experimental data. The D-R and R-P models were also ruled out due to similar arguments. The Langmuir and Freundlich models gave lower R^2 values and slightly higher errors. The Sips isotherm model, a three-parameter isotherm model that combines both the Langmuir and Freundlich models, which gave a high R^2 value with the lowest errors, is thus selected as the most suited model to explain the adsorption of CV on Petai pod.

Table 3. R^2 and their error values of Adsorption isotherm models

Model	R^2	ARE	SSE	HYBRID	MPSD
Langmuir	0.901	26.74	0.02	0.60	37.80
Freundlich	0.865	40.76	0.09	2.36	53.49
Temkin	0.951	66.72	0.01	2.63	202.30
D-R	0.850	400.04	0.24	64.68	790.05
R-P	0.506	40.76	0.09	2.51	55.13
Sips	0.928	26.82	0.02	0.69	37.64

Table 4 shows all the parameters obtained for the six isotherm models used in this study. The maximum adsorption capacity (q_{max}) of CV determined from the Sips adsorption isotherm is 163.2 mg g^{-1}, which is superior to many natural adsorbents, as shown in ***Table 5***. As this is relatively higher, surface modification methods were not attempted.

Table 4. Adsorption isotherm parameters

Model	Parameters	Values
Langmuir	q_{max} (mg g^{-1})	141.3
	K_L (L $mmol^{-1}$)	0.01
Freundlich	K_F (mg g^{-1})	1.42
	n	1.39
Temkin	K_T (L $mmol^{-1}$)	0.10
	b_T (kJ mol^{-1})	38249
D-R	q_{max} (mg g^{-1})	79.17
	B (J mol^{-1})	2.27E-06
	E (kJ mol^{-1})	469.7
R-P	K_R (L g^{-1})	3.00
	α	0.28
	a_R (L $mmol^{-1}$)	864.3
Sips	q_{max} (mg g^{-1})	163.2
	K_S (L $mmol^{-1}$)	0.00
	n	1.01

Table 5. Comparison of maximum adsorption capacity of various adsorbents for the removal of crystal violet dye

Adsorbent	q_{max} (mg g^{-1})	Reference
Parkia speciosa	163	This work
Breadfruit skin	150	[11]
Peat from Brunei	108	[5]
Yeast-treated peat	18	[20]
Tarap skin (TS)	118	[21]
NaOH-treated TS	195	[21]
Pumice stone	7	[22]
Biomass combustion residue	19	[23]

Adsorption Kinetics of Petai Pod on the removal of CV dye

Adsorption mechanism for the removal of 500 mg L^{-1} CV by Petai pod was investigated, and the data obtained were fitted to the Lagergren pseudo-first order (***Equation 1***) and pseudo-second order (***Equation 2***) models.[24,25]

Linearized equation of Lagergren pseudo-first order:

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303}t \qquad (1)$$

Linearized equation of Pseudo-second model:

$$\frac{t}{q_t} = \frac{q}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (2)$$

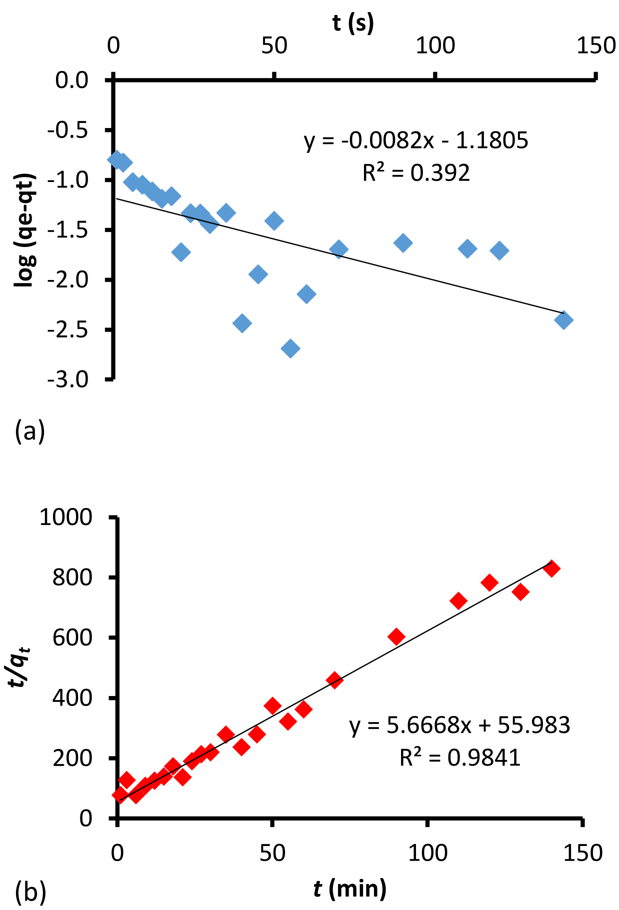

Figure 5. Adsorption kinetics of Petai pod for the removal of crystal violet dye showing pseudo-first order (a) and pseudo-second order (b).

From ***Figure 5***, it is clearly observed that the kinetics follows the pseudo-second order mechanism with high R^2 close to unity. Further, the adsorption capacity determined from experiment (0.24 mmol g^{-1}) and that determined by the pseudo-second order model (0.18 mmol g^{-1}) are comparable. On the other hand, the pseudo-first order model led to the R^2 value of 0.392 with the adsorption capacity of 0.07 mmol g^{-1}, which is much deviated from the value obtained from the isotherm studies. The validity of the pseudo-second order model provides the condition that the possibility of having two reactive moeties for adsorption of CV molecules.

To investigate diffusion mechanisms in the adsorption of CV by Petai Pod, the Weber-Morris intra-particle diffusion (***Equation 3***) and Boyd (***Equation 4***) models were applied.[26,27]

Weber Morris intraparticle diffusion:

$$q_t = k_{id}t^{1/2} + C \qquad (3)$$

Boyd model:

$$F = 1 - \frac{6}{\pi^2}exp(-B_t) \qquad (4)$$

where F = q_t / q_e, F is the fraction of solute adsorbed at any time, t and B_t is mathematical function of F.

The Weber-Morris plot shown in ***Figure 6*** indicates two regions. The initial region involves gradual surface adsorption of CV due to intra-particle diffusion, followed by a slow equilibrium region reaching a plateau. According to the Weber Morris model, intra-particle diffusion is the rate-determining step, if the linear segment passes through the origin. The very small intercept of 0.007 in the plot given in ***Figure 6*** is in support that the intra-particle diffusion providing a significant contribution to mass transfer. The rate constant determined from this model, k_{id} is 0.027 mmol g^{-1} min^{-1}.

In order to determine whether film or particle diffusion also contributes to the adsorption process, the Boyd model was applied. According to the model, if the linear plot passes through the origin, the diffusion is governed by particle diffusion, or otherwise, film diffusion takes control. From ***Figure 6***, the linear plot shows a very small intercept of 0.082, suggesting that particle diffusion is the rate-determining step.

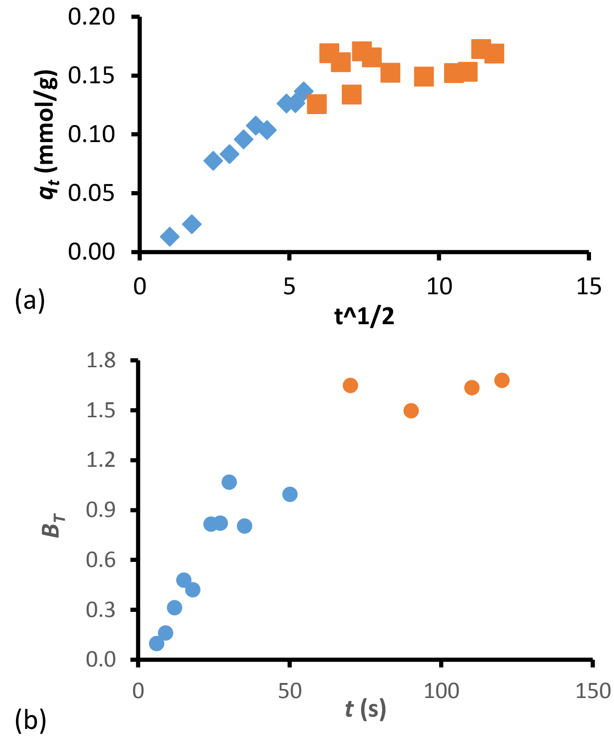

Figure 6. Weber Morris Intraparticle diffusion (top) and Boyd model (bottom) of Petai pod for the removal of crystal violet dye.

Regeneration of spent Petai Pod

Spent adsorbents which are of no use need to be disposed of as wastes. These can pose problems as they can be toxic, inflammable, hazardous and even explosive if incinerated. Therefore, to minimize problem, one way is to regenerate and reuse spent adsorbents. In this study, spent Petai pod was regenerated using various methods. Of these, it was found that NaOH treatment was not only able to retain its adsorption capacity but enhanced the adsorption of CV by 35% even after the 4th cycle (***Figure 7***). On the other hand, treatment with HCl and washing with water reduced the adsorption by 20% and 40%, respectively by the 4th cycle. Heating proved to be the most unfavorable method as 60% reduction was observed as early as the first cycle. It can thus be concluded that spent Petai pod can be regenerated and reused through NaOH treatment, maintaining high adsorption capacity.

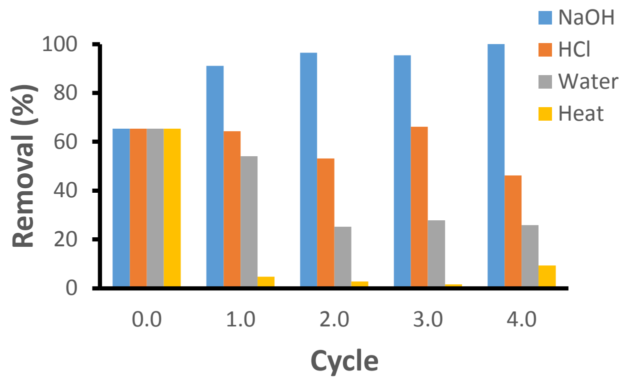

Figure 7. Regeneration studies of Petai pod.

Characterization of Petai pod

Surface morphology from ***Figure 8*** of SEM imaging clearly shows a distinct change upon adsorption with CV dye. The point of zero charge (pH_{pzc}) of Petai pod was determined to be at pH 4.6 indicating, that at this pH, the surface charge is zero. Below this pH, the surface of Petai pod would be predominantly positively charged, while the converse is true for pH > pH_{pzc}.

4. Conclusion

It is concluded that Petai pod has the potential to be used as a low-cost adsorbent for the removal of CV dye. Its high adsorption capacity compared to most reported adsorbents coupled with its resilience to medium pH support it being used in real life wastewater treatment. Another attractive feature is its ability to be regenerated and reused through base treatment while being able to maintain very high percentage removal of CV dye even after four consecutive cycles.

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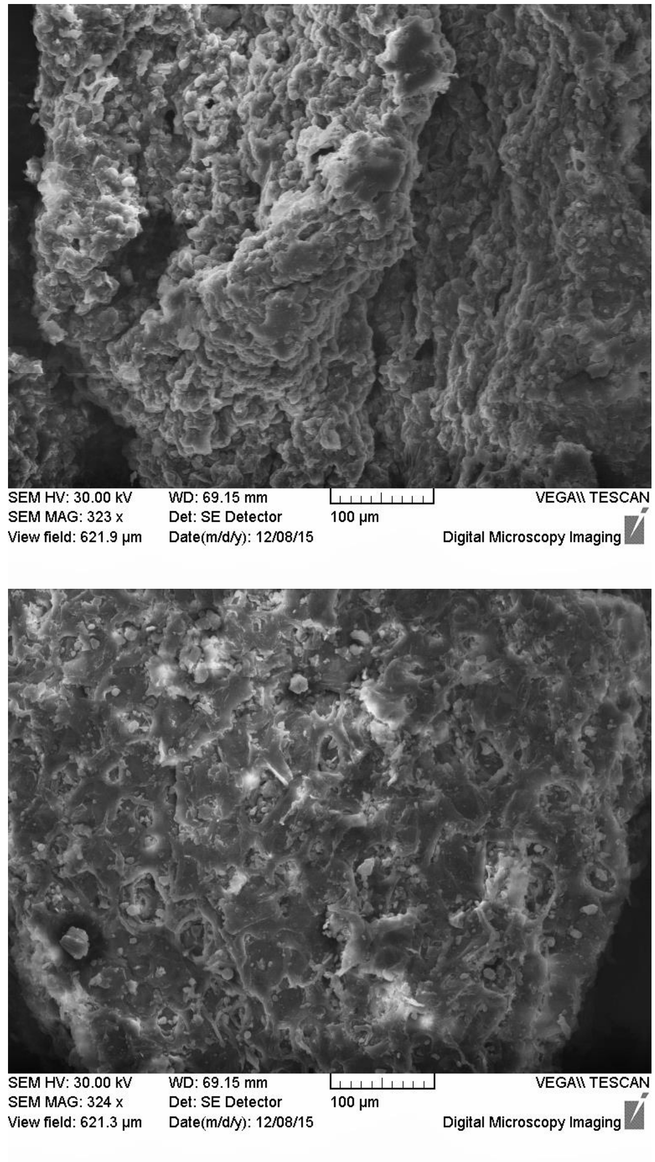

Figure 8. Surface morphology of Petai pod before (top) and after (bottom) adsorption with CV

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