

Adsorption characteristics of *Artocarpus odoratissimus* leaf toward removal of toxic Crystal violet dye: Isotherm, thermodynamics and regeneration studies

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ABSTRACT

Artocarpus odoratissimus leaf (AOL) was investigated in this study as a potential low-cost adsorbent for the removal of toxic crystal violet (CV) dye. Experimental data obtained from batch adsorption isotherm studies were analyzed using six isotherm models namely the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Redlich-Peterson and Sips. Based on R^2 and error values, as well as comparison of experimental data with simulation plots of these various isotherm models, it was concluded that the Langmuir was the best fit isotherm model with maximum adsorption capacity (q_{max}) of 50.5 mg/g. AOL displayed resilience when tested against various medium pH. However, ionic strength influenced the ability of AOL to adsorb CV, in particular KCl showed a greater influence than KNO_3 . The adsorbent also showed potential to be regenerated and reused under both acid and basic treatment, maintaining high adsorption of CV even after four consecutive cycles.

KEYWORDS

adsorbent; adsorption isotherm; *Artocarpus* spp; crystal violet; regeneration; thermodynamics

1. INTRODUCTION

Adsorption technique to remove waste effluents has gained popularity as it is a simple, low-cost and yet an effective method (Vijayaraghavan, 2016). The last decade has seen the emergence of various adsorbents from a broad spectrum ranging from industrial wastes (Nagy et al., 2016), agricultural wastes (Priyantha et al., 2015; Kooch et al., 2016), aquatic plants (Lim et al., 2014; Vijayaraghavan, 2015), sludge (Kang et al., 2014), peat (Chieng et al., 2015a; Zehra et al., 2015), yeast (Anagnostopoulos et al., 2015), synthetic adsorbents (Ying et al., 2016), fungi (Idowu et al., 2016) and many others (Pathak et al., 2015; Kavitha, 2016; Politi and Sidiras, 2016).

In recent years, the use of wastes from *Artocarpus* spp. as adsorbents has gained popularity where the fruits such as jackfruit, cempedak and breadfruit are very popular and its inedible skin and core, which are often discarded, can attribute to as much as 50% of the whole fruit (Tang et al., 2013; Lim et al., 2011). This has led to various studies on the use of *Artocarpus* wastes, including the leaves, for the adsorption of heavy metals (Inbaraj and Sulochana, 2004; Okolo et al., 2012; Priyantha et al., 2013; Lim et al., 2015a) and dyes (Hameed, 2009; Lim et al., 2016a and b; Dahri et al., 2015).

This study focuses on the use of *Artocarpus odoratissimus* leaf (AOL) as a low-cost adsorbent for the removal of crystal violet (CV) dye, otherwise known

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as methyl violet 10B. Various parameters such as the effects of contact time, medium pH and ionic strength were investigated. Batch adsorption experiments were carried out to provide insight into the adsorption characteristics of CV onto AOL. Surface and functional group characterizations of AOL were analyzed using scanning electron microscopy (SEM) and Fourier Transform Infrared spectroscopy (FTIR), respectively.

There have been few reports on the use of *A. odoratissimus* wastes as low-cost adsorbents. Its core has been used for the removal of heavy metals (Lim et al., 2012) while the skin showed ability to adsorb cationic dyes such as crystal violet (Lim et al., 2016c), methylene blue and methyl violet (Lim et al., 2015c). However, to date, the use of AOL as an adsorbent has not been reported. Thus the focus of this work is to study the characteristics of AOL in order to find out its feasibility to be used as a potential adsorbent for the removal of CV dye. This dye is often used in paint, textile and printing industries. Being a non-biodegradable dye, it is not easily metabolized by microbes. Hence, when discharged into the water system, this dye would remain in the environment. Since CV is highly cytotoxic and carcinogenic, its presence in the water system may result in adverse health effects to both aquatic and human lives.

2. MATERIALS AND METHODS

2.1. Sample preparation and chemical reagents

Artocarpus odoratissimus (Tarap) leaves were randomly collected and dried at 80 °C in an oven until a constant mass was obtained. The dried samples were then blended and sieved to obtain the desired particle size of 355-850 µm which was used throughout this study. Crystal violet (CV) [molecular formula of $C_{25}N_3H_{30}Cl$, molecular weight of 407.98 g/mol] was purchased from Sigma-Aldrich and used without further purification.

2.2. Instrumentation

The absorbance of CV was measured using Shimadzu, UV-1601PC spectrophotometer at wavelength of 590 nm. The Stuart Scientific Flask Shaker SF1 was used to agitate mixture of adsorbate-CV solution set at a speed of 250 rpm. The Shimadzu IRPrestige-21 spectrophotometer (FTIR) was used for functional group characterization of AOL. The Tescan Vega XMU Scanning Electron Microscope (SEM) was used for

surface morphological analysis of TL.

2.3. Adsorption studies

Optimization of parameters (contact time, pH and ionic strength) and batch experiments for both adsorption isotherm and thermodynamics were carried out following the methods as described by Lim et al. (2016c) with slight modification. Briefly, for contact time optimization, the adsorbent (0.05 g) was mixed with 100 mg/L dye (25 mL) and agitated using an orbital shaker set at 250 rpm for 4 h. The filtrates were collected at every 30 min interval, diluted accordingly and analyzed using UV-Vis spectrophotometer. The effect of pH was studied by adjusting the dye solution (100 mg/L) to pH ranging from 3 to 10. The effect of ionic strength on the removal of 100 mg/L of CV dye was studied using different concentrations of salt (KNO_3 and KCl) ranging from 0.01 to 1.0 M. Isotherm studies were carried out at different concentrations of CV ranging from 0 to 1000 mg/L and shaken at the optimized shaking time while thermodynamic experiments were carried out by using a fixed CV concentration of 500 mg/L and shaken at different temperatures. All experiments were carried out in duplicate, unless otherwise stated.

2.4. Regeneration studies

Regeneration studies were investigated following the methods as described by Chieng et al. (2015b) with slight modification. Briefly, four different treatments were used: 1 M HCl, 1 M NaOH, distilled water and heat (200 °C). Initially, the adsorbent (3.0 g) was mixed with 100 mg/L CV dye and shaken at the optimum shaking time. The filtrate was measured for its absorbance and the spent adsorbent was washed with distilled water to remove excess CV and kept in oven until dry. Once dried, it was then divided into five portions and treated by using the stated treatments. After the desorption treatment, the washed adsorbents were placed in an oven. Then, another cycle of adsorption was continued and the regeneration studies were carried for four consecutive cycles.

3. RESULTS AND DISCUSSION

3.1. Surface morphological analysis of AOL using SEM

Surface morphology of AOL, analyzed using SEM at

481x magnification, clearly revealed the presence of stomata on the leaf surface. Apart from that, it can be observed from Figure 1 that the surface of AOL is a combination of both smooth and rough texture. It can also be seen that many irregular folds were present within the rough surface which could be potential active adsorption sites for the adsorption of CV dye.

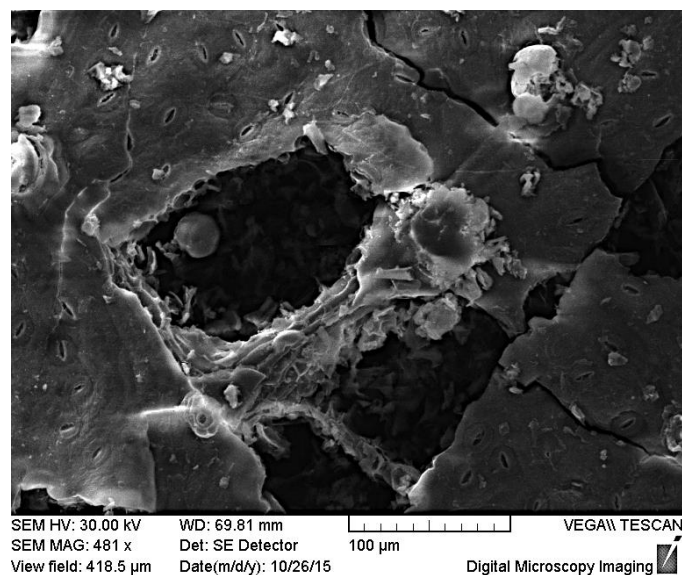


Figure 1. SEM surface morphology of AOL at 481x magnification.

3.2. Effect of contact time

The contact time generally plays a vital role in adsorption studies as it provides information on the time required for the adsorbate-adsorbent system to reach full equilibrium. In this study, under the studied condition, AOL required 3.5 h to attain equilibrium (Figure 2). Fast adsorption was observed within the first 30 min to 1 h which can be explained by the initial availability of vacant active sites for the adsorption of CV dye molecules. Over time, as these sites are being filled, the rate of adsorption decreases until a plateau was observed, indicating full equilibrium has been reached. Hence, a contact time of 3.5 h was used throughout the adsorption experiments in this study, unless otherwise stated.

3.3. Effect of medium pH on the removal of CV

Generally, pH plays a significant role in adsorption studies as both adsorbent and adsorbate are usually sensitive to change in medium pH. The medium pH alters the ability of adsorbent to adsorb the adsorbate

and/or the affinity of adsorbate toward the active sites on the adsorbent surface. For example, under acidic condition, competition between H^+ ions and cationic dyes for the active sites may arise thereby affecting the percentage removal of the dye molecules from aqueous solution. Investigation on the effect of medium pH on the adsorption ability of AOL (Figure 3) showed that within the range of pH studied (pH 3 to 10), the removal of CV by AOL remain unaltered and the AOL was able to maintain good adsorption capacity with an observed 64% removal at pH 3. This suggests that electrostatic interactions might not be the major influence in the adsorption of CV onto AOL.

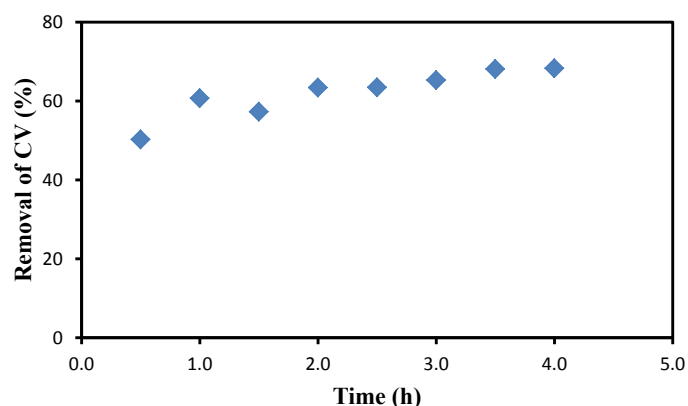


Figure 2. Effect of contact time on the removal of 100 mg/L CV by AOL.

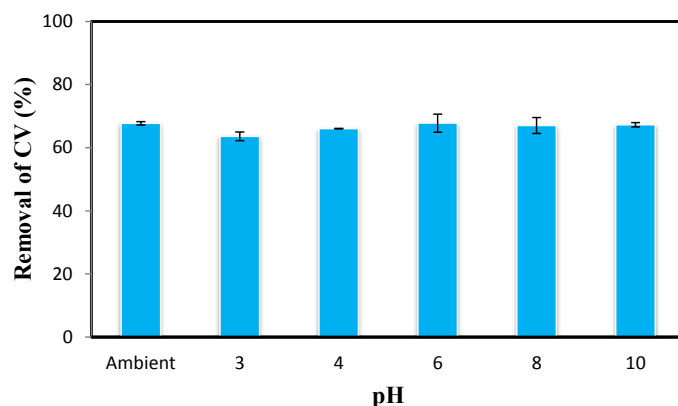


Figure 3. Effect of medium pH on the removal of 100 mg/L CV by AOL.

3.4. Effect of ionic strength on the removal of CV

Wastewater usually contains various salts which could affect the performance of adsorbent toward adsorbate. In this study, two different salts (KNO_3 and KCl) were used to investigate if adsorption of CV onto AOL will be affected by the presence of these

salts in solution. Among the two salts examined, KNO_3 showed a greater influence to affect the adsorption potential of AOL toward CV. A steady decrease in the removal of CV was observed as the salt concentration increased. In contrast, KCl showed very little effect on the overall adsorption; and there was a reduction of approximately 12% at 0.1 M KCl after which the removal of CV was enhanced as the salt concentration increased, specifically an increase of 10% dye removal was observed at 1 M KCl.

3.5. Adsorption isotherm for the removal of CV by AOL

Batch adsorption studies were performed under optimized contact time of 3.5 h with CV concentration ranging from 0 – 1000 mg/L in order to provide insight into the adsorption characteristics of AOL. The experimental data obtained were then fitted to six adsorption isotherm models (Table 1) and the parameter values for each of these models are as shown in Table 2.

Selection of the best fit isotherm model to describe the adsorption process was based on linear regression coefficient (R^2), error analyses using six error functions whose equations are shown in Table

3, and simulation of the experimental data with the various models used.

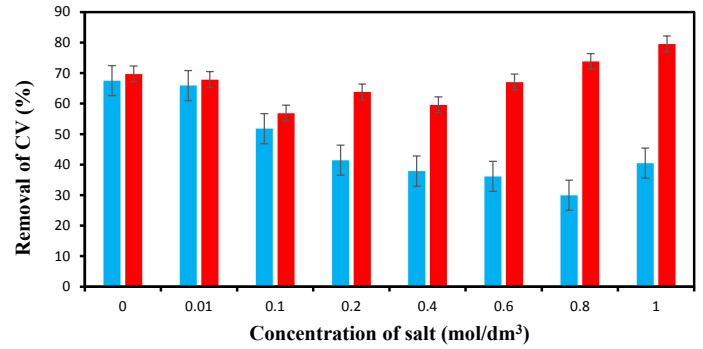


Figure 4. Effects of ionic strength on the removal of CV by AOL using KNO_3 (blue bar) and KCl (red bar).

Of the six models used, in decreasing order of R^2 values are as follows: Langmuir > Redlich-Peterson (R-P) > Temkin > Sips > Dubinin-Radushkevich (D-R) > Freundlich. Hence, the Freundlich model, which is based on multi-layer adsorption onto heterogeneous surface, is the least fitting of all the models used in this study. Based on error analyses (Table 4), even though R-P, a three parameter isotherm model which is a combination of the Langmuir and Freundlich models, has the second highest R^2 (> 0.93), its overall

Table 1. The linearized equations of the six isotherm models used for the adsorption of CV onto AOL.

Isotherm model	Linear Equation	Plot	Reference
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$	C_e/q_e vs. C_e	Langmuir, 1916
Freundlich	$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$	$\ln q_e$ vs. $\ln C_e$	Freundlich, 1906
Temkin	$q_e = B \ln K_T + B \ln C_e$	q_e vs. $\ln C_e$	Temkin and Pyzhev, 1940
Dubinin-Radushkevich (D-R)	$\ln q_e = \ln q_s - \beta \varepsilon^2$ where $\varepsilon = RT \ln(1 + 1/C_e)$ and $E = 1/(2\beta)^{1/2}$	$\ln q_e$ vs. ε^2	Dubinin and Radushkevich, 1947
Redlich-Peterson (R-P)	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right) = g \ln C_e + \ln a_R$ where $0 \leq g \leq 1$	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right)$ vs. $\ln C_e$	Redlich and Peterson, 1959
Sips	$\ln \left(\frac{q_e}{q_{max} - q_e} \right) = 1/n \ln C_e + \ln K_S$	$\ln \left(\frac{q_e}{q_{max} - q_e} \right)$ vs. $\ln C_e$	Sips, 1948

where q_{max} is the maximum adsorption capacity; K_L , K_F , K_T , K_R and K_S are the isotherm constants with respect to the Langmuir, Freundlich, Temkin, Redlich-Peterson and Sips isotherm models, respectively; n is the empirical parameter which is related to the adsorption intensity; q_e is the amount of dye adsorbed; C_e is the equilibrium dye concentration in solution; B is related to the heat of adsorption; T is absolute temperature; β gives the mean free energy; E is sorption per molecule of sorbate; $1/n$ is the Sips model exponent; a_R is the R-P constant; and g is the exponent which lies between 0 and 1.

errors were in fact the second largest with D-R being the largest errors of all. Thus both R-P and D-R were deemed unsuitable models for the adsorption of CV by AOL. Simulation plots as shown in Figure 5 further confirmed that the Freundlich, Temkin and D-R models provided unsatisfactory fit to the present data. Of the other three models, the Temkin has the highest error values while both the Langmuir and Sips models have very similar overall errors, with the Langmuir being slightly lower. Hence, based on the analysis, the Langmuir model exhibited highest R² (0.99) and smallest errors. It can be concluded that the Langmuir, which predicts a monolayer adsorption process, is the better model to describe the adsorption of CV onto AOL.

Table 2. Parameter values of the six isotherm models used for the adsorption of CV onto AOL.

Model	Parameters	Values
Langmuir	q_{max} (mg/g)	50.50
	K_L (L/mg)	0.001
Freundlich	K_F (mg ^{1-1/n} L ^{1/n} /g)	6.10
	n	2.76
Temkin	K_T (L/mg)	0.003
	B (kJ/mg)	0.001
D-R	q_{max} (mg/g)	43.35
	β (J/mg)	1.68E-12
	E (kJ/mg)	0.002
R-P	K_R (L/mg)	0.001
	g	0.71
	a_R (L/mg)	0.098
Sips	q_{max} (mg/g)	57.12
	K_S (L/mg)	0.001
	$1/n$	1.14

From Table 5, it can be seen that when compared to the skin of *A. odoratissimus* and *A. altilis*, the leaf in this study showed a lower adsorption capacity toward CV dye. This could be due to the difference in surface morphology of the adsorbents, where skin tends to have more irregular and uneven surface with pores and cavities (Priyantha et al., 2013; Lim et al., 2015d), thus being able to provide more adsorption active sites for the dye. Compared with leaf of another *Artocarpus* spp. i.e. *A. heterophyllus*, the leaf in this study showed a slightly better adsorption capacity. Adsorbents such as peat and *Gracilaria corticata*, on the other hand, were able to adsorb CV better. Nevertheless

AOL gave a much higher value when compared to adsorbents such as pumice stone, bottom ash, biomass combustion residue and even NaOH-modified rice husk. The observed q_{max} is similar to the synthesized nano-titanium tannate complex. Hence, overall it can be said that AOL is a reasonably good adsorbent for the removal of CV dye.

Table 3. The six 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)	$\frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right]_i$
Sum of absolute error (EABS)	$\sum_{i=1}^n q_{e,meas} - q_{e,calc} $
Marquardt's percent standard deviation (MPSD)	$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right)_i^2}$
Non-linear chi-square test (χ^2)	$\sum_{i=1}^n \frac{(q_{e,calc} - q_{e,meas})^2}{q_{e,meas}}$

where $q_{e,meas}$ is the amount of dye adsorbed experimentally while $q_{e,calc}$ is the calculated q_e value, n is the number of parameters, and p is the number of data points.

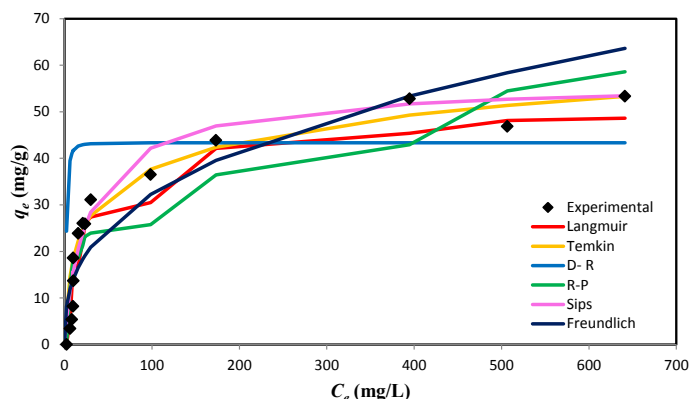


Figure 5. Comparison of experimental isotherm data with the six isotherm models.

Table 4. Linear regression coefficients (R^2) and error analyses of the six isotherm models used.

Model	R^2	ARE	SSE	HYBRID	EABS	MPSD	χ^2
Langmuir	0.9912	23.84	0.002	0.35	0.15	42.89	0.05
Freundlich	0.7071	42.02	0.013	0.77	0.40	55.54	0.17
Temkin	0.8743	32.05	0.004	0.59	0.21	57.21	0.10
D-R	0.8339	135.85	0.032	9.88	0.61	258.77	1.49
R-P	0.9333	51.00	0.009	1.19	0.35	93.06	0.21
Sips	0.8723	24.98	0.003	0.36	0.18	41.02	0.06

Table 5. Comparison of q_{max} of some reported adsorbents for the removal of CV dye.

Adsorbent	q_{max} (mg/g)	Reference
<i>Artocarpus odoratissimus</i> leaf	51	This work
<i>Artocarpus odoratissimus</i> skin	118	Lim et al., 2015c
<i>Artocarpus altilis</i> (Breadfruit) skin	150	Lim et al., 2015d
<i>Artocarpus heterophyllus</i> leaf	43	Saha et al., 2012
Peat from Brunei	108	Chieng et al., 2013
Yeast-treated peat	18	Zehra et al., 2016
Coco-peat	119	Vijayaraghavan et al., 2016
Pumice stone	7	Shayesteh et al., 2016
Biomass combustion residue	19	Roy et al., 2015
Cocoa shells	44	Chinniagounder et al., 2011
Coniferous <i>Pinus</i> bark powder	33	Ahmad, 2009
Bottom ash	5	Nidheesh et al., 2012
NaOH modified rice husk	45	Chakraborty et al., 2011
<i>Gracilaria corticata</i>	193	Vijayaraghavan et al., 2015
Chitosan-graphite oxide modified polyurethane	65	Qin et al., 2015
Nano-titanium tannate complex	59	Elmorsi et al., 2015

3.6. Thermodynamics studies

Thermodynamics study plays an important role as the data obtained can provide practical application in real world and help in equilibrium-based design of operation unit for that system. In this study, we exploited the thermodynamics behind the adsorption

of CV onto AOL. The Gibbs free energy (ΔG°) is expressed as:

$$\Delta G^\circ = -RT \ln K_c \quad (1)$$

where R is the universal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin (K) and K_c is the equilibrium constant (C_s/C_e), where C_s is the concentration of CV dye on the adsorbent (mg/L) and C_e is the equilibrium concentration of CV (mg/L).

The Van't Hoff equation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, when combined with the Gibbs expression gives the following equation:

$$\ln K_c = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2)$$

From the above equation, the values of enthalpy (ΔH°) and entropy (ΔS°) can be obtained from the slope and the y-intercept of the plot of $\ln K_c$ versus $1/T$ as shown in Figure 6.

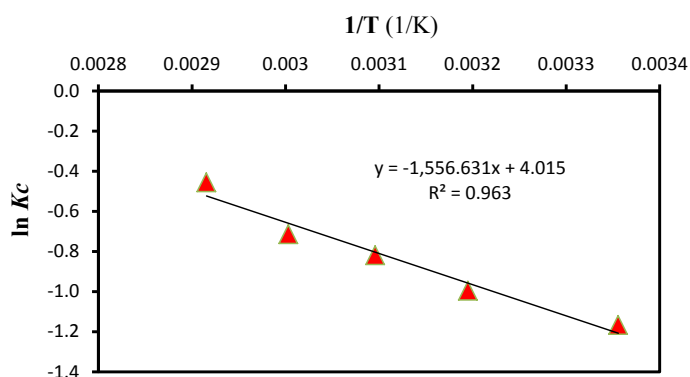


Figure 6. Thermodynamics plot for adsorption of CV onto AOL.

Decrease in ΔG° values with increasing temperature is indicative of the adsorption process being in favor of higher temperature. The adsorption of CV onto AOL is an endothermic process as shown by the positive ΔH° value in Table 6. This means that heat is being absorbed from the surroundings during the adsorption process. Positive ΔS° value suggests that there may be an increase in the randomness at the solid-liquid interface with possibility of significant internal structural change of AOL (Alkan et al., 2007; Kooh et al., 2015).

Table 6. Thermodynamics parameters for the adsorption of CV onto AOL.

Temp (K)	$\ln K_c$	$1/T$	ΔG° (kJ/mol)	ΔS° (kJ/mol K)	ΔH° (kJ/mol)
298	-1.167	0.0034	2.89	33.38	12.94
313	-0.997	0.0032	2.59		
323	-0.819	0.0031	2.20		
333	-0.714	0.0030	1.98		
343	-0.456	0.0029	1.30		

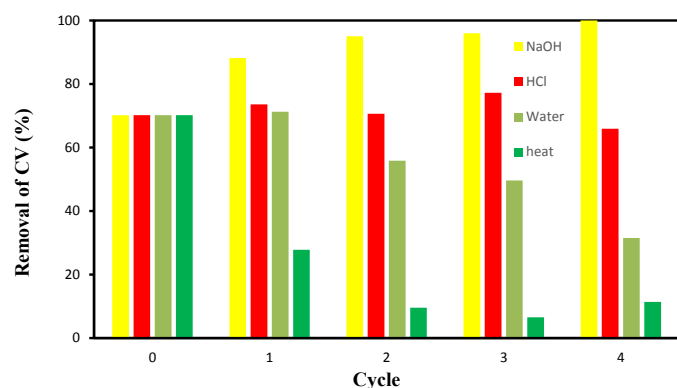


Figure 7. Regeneration of AOL.

3.7. Regeneration of AOL

Four different methods were used to regenerate the spent AOL: treatment with NaOH, HCl, heating at 200 °C, and washing with distilled water. Of these, as shown in Figure 7, heating turned out to be the least favorable of all the methods used with a reduction of 42% as early as the first cycle and eventually reaching almost 60% in reduction of its adsorption capacity in cycle 4. This could be due to structural damage under high heat thereby causing the adsorbent to lose its adsorption ability. Washing with distilled water was able to maintain adsorption capacity in the first cycle but a reduction of approximately 38% was observed by

the 4th cycle. Treatment with HCl, on the other hand, was found to be a good method to regenerate the spent AOL, with only 4% reduction at the end of the 4th cycle. The best method to regenerate AOL was found to be with NaOH. Not only was it able to maintain its adsorption toward CV dye, in fact its adsorption ability was enhanced by 30% at the end of the 4th cycle. Studies have shown that base treatment has the ability to not only remove the surface fats and waxes but also deprotonate the functional groups making them more attracted toward cationic CV dye.

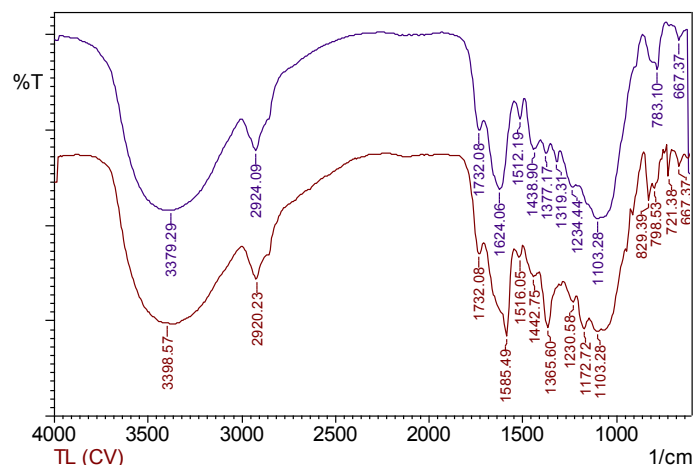


Figure 8. FTIR spectra of AOL before (top) and after (bottom) adsorption of CV.

3.8. Functional group characterization using FTIR

Functional group characterization using FTIR is shown in Figure 8. There was an obvious shift in wavelength of the broad band at around 3379 to 3399 cm^{-1} , which indicates that hydroxyl group (-OH) and amino acids (N-H) were involved in the bond formation with CV dye molecules. A band at 1624 cm^{-1} was shifted to 1586 cm^{-1} and this could be due to alkene (C=C) or asymmetric C=O of COOH stretching. Symmetric C=O stretch at 1439 cm^{-1} was shifted to 1442 cm^{-1} while C-O of COOH was shifted from 1234 to 1231 cm^{-1} . A band at 1732 cm^{-1} in both spectra indicates the presence of carbonyl group (C=O) of COOH group.

4. CONCLUSIONS

Based on the above study, it can be concluded that:

- *Artocarpus odoratissimus* leaf has potential to be utilized as a low-cost adsorbent for the removal of CV dye.

- Adsorption isotherm fitted the Langmuir model with maximum adsorption capacity of 50.5 mg/g.
- Adsorbent showed resilience toward medium pH.
- Adsorption of CV onto *Artocarpus odoratissimus* leaf was endothermic in nature.
- Adsorbent was successfully regenerated and was able to retain its good adsorption capacity especially with NaOH and HCl treatment.

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