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Removal of crystal violet dye from aqueous solutions using rubber (*hevea brasillensis*) seed shell-based biosorbent

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ABSTRACT

The need of safe and economical methods for the elimination of hazardous dyes from contaminated waters has necessitated research interest towards the production of low-cost adsorbent. The present study aims to investigate the feasibility of rubber seed shell-based biosorbent for removal of crystal violet dye from aqueous solutions. The biosorbent was prepared using sulfuric acid treatment. Fourier transform infrared analysis showed that the main functional groups present on the surface of the biosorbent were aliphatic compounds. Batch adsorption studies were conducted to determine the effects of contact time, initial dye concentration and biosorbent dosage on the uptake of dye at 30 °C. The equilibrium data were analyzed by using Langmuir and Freundlich isotherm models. Equilibrium data fitted well with the Langmuir model, yielding maximum monolayer adsorption capacity of 23.81 mg/g. The kinetic data were found to conform to pseudo-second-order kinetic model with good correlation. Rubber seed shell-based biosorbent was shown to be a promising low-cost material for adsorption of crystal violet dye from aqueous solutions.

Keywords: Rubber seed shell; Crystal violet; Biosorption; Equilibrium; Isotherm; Kinetics

1. Introduction

Crystal violet is a triphenylmethane dye used as a biological stain or as dermatological agent. For many years it was used as oral medication for treatment of pinworms and other tropical diseases because of its great effect in controlling fungal growth under varying conditions [1]. Crystal violet dye is carcinogenic and has been classified as a recalcitrant molecule since it is poorly metabolized by microbes, is non-biodegradable, and can persist in a variety of environments. The dye is responsible for causing moderate eye irritation, causing painful sensitization to light. It is highly toxic to mammalian cells and if absorbed in harmful amounts through the skin, it can cause skin irritation and digestive tract irritation. In extreme cases it may also lead to respiratory and kidney failures [2]. Techniques such as coagulation, chemical precipitation, membrane filtration, solvent extraction, reverse osmosis, photocatalytic degradation, sonochemical degradation, micellar enhanced ultrafiltration, cation exchange membranes, electrochemical degradation, integrated chemical–biological degradation, integrated

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iron(III) photoassisted-biological treatment, solar photo-Fenton and biological processes, and adsorption have been tested and evaluated for the treatment of dye bearing effluents [3]. However, these methods either entail high cost, incomplete ion removal and high reagent cost [4]. Therefore, there are needs of safe and economical methods for the elimination of dyes from contaminated waters. Agricultural waste materials are economical and eco-friendly due to their unique chemical composition, availability in abundance, renewability, low cost and high efficiency. Oladojo et al. [5] reported that the ability of rubber seed shell to remove methylene blue dye from aqueous solution was high. Rubber seed shell was shown to be an attractive source of raw material for preparing high quality activated carbon by physical activation with steam [6]. Rubber seed shell-based activated carbon was found to be an effective remover of metal ions and organic compounds from aqueous solution [7]. Hence, the feasibility of applying adsorbent from rubber seed shell towards the removal of dyes from aqueous solution was approached. The focus of this research was to evaluate the adsorption potential of rubber seed shell-based adsorbent for crystal violet dye. The kinetic and equilibrium data of the adsorption studies were analyzed using various models to determine the adsorption mechanism of crystal violet dye on the prepared adsorbent.

Crystal violet, also called methyl violet 10B, is a dark purple staining dye used in biology and microbiology, which likes many staining dyes, is acidic. The acidic nature of crystal violet dye has many implications in chemistry, determining how it will interact with other substances, which microorganisms will absorb or repel it, and how it will affect structures such as cell walls. Since many acidic staining dyes are caustic or carcinogenic, they can pose logistical, legal, and ethical problems during disposal [2]. Numerous studies have been launched in order to find cost-effective ways to degrade, absorb, neutralize or deactivate these chemicals. Knowledge of the acidic nature of such substances is among several important considerations in devising such approaches.

Adsorption process using commercial activated carbons is very effective for removal of dyes from wastewater, but its high cost has motivated the search for alternative materials. Most of the adsorption studies have been focused on untreated plants and agricultural wastes such as wheat bran, rice husk, oil palm trunk fiber, dead leaves, wheat straw, durian peel, guava leaf powder, almond shells, coconut husk, pomelo peel, de-oiled soya, coniferous pinus bark powder, babassu coconut mesocarp and granular kohlrabi peel [8–19]. An extensive list of adsorbent literature for dye removal has been compiled by Allen and Koumanova [20].

Although the application of untreated agricultural waste attracted much research recently, two problems are associated with it: low adsorption capacity and release of soluble organic compounds contained in the plant materials. Therefore, raw materials should be modified or treated before being applied for the removal of dyes from aqueous solutions. In general, chemically treated plant wastes exhibit higher adsorption capacities than the untreated materials [21].

Hevea brasiliensis or commonly known as rubber tree is the main source of natural rubber. *Hevea brasiliensis* belongs to the family *Spurge* or *Euphorbiaceae*. The tree is cultivated in large commercial scale in several countries in the tropics. Apart from its latex, rubber tree has also been harnessed for its wood for making furniture and the seeds for para rubber seed oil used for manufacturing soap, paint, varnishes, fertilizer and animal feeds. Therefore, a huge amount of rubber seed waste is expected to be generated. Conversion of such waste to a value-added product such as adsorbent for dye removal will be rather useful. Therefore, the focus of this research was to evaluate the adsorption potential of the rubber seed shell-based adsorbent for removal of crystal violet dye from aqueous solutions. The equilibrium and kinetic data of the adsorption process were then evaluated to study the adsorption mechanism of crystal violet molecules onto the prepared adsorbent.

2. Materials and methods

2.1. Preparation and characterization of activated carbon

The rubber seed shell obtained from the Department of Agriculture Sarikei Division, Sarawak, Malaysia was used as the precursor for the preparation of adsorbent in this work. The rubber seed shell was washed with deionized water to remove any attached dirt and soluble impurities, dried in open air and then pulverized. It was then ground to particle size of −6 to +40 mesh. The precursor was soaked in sulfuric acid (H_2SO_4) for 2 h. Then, the acid-treated rubber seed shell was dried in oven at 100 °C for 24 h to chemically activate the rubber seed shell in order to enhance the porosity and surface chemistry. Then, the adsorbent was washed with deionized water for several times to remove the H_2SO_4, until the pH of the washing solution reached 6–7. Then, the sample was dried again in the oven at 100 °C for 24 h. The dried adsorbent was stored in air-tight container for further characterization and adsorption studies. The Fourier transform infrared (FTIR) spectroscopy analysis was conducted using a FTIR spectrophotometer (Model Perkin Elmer 1600) with the wavelength range of 4000–400 cm^1. The rubber seed shell sample of 0.0001 g was mixed with 0.001 g of KBr, spectroscopy grade

(Merck, Darmstadt, Germany), in a mortar. Part of this mixture was introduced in a cell connected to a piston of a hydraulic pump giving a compression pressure of 15 kPa/cm^2. The mixture was converted to a solid disc. Then, it was transferred to the FTIR spectrophotometer and a corresponding spectrum was obtained.

2.2. Batch equilibrium studies

A stock solution of 1000 mg/l of crystal violet was prepared by dissolving 1 g of the dye in 1000 ml of deionized water. All experiments were carried out in duplicate and the mean values were reported, where the maximum deviation was within 2%. Crystal violet has a chemical formula of $C_{25}H_{30}ClN_3$, with molecular mass of 407.979 g/mol. The stock solution of crystal violet was diluted to the required concentration in the range of 40–140 mg/l. Batch mode adsorption studies were carried out with a specific dosage of adsorbent and 100 ml of dye solution of desired concentration in 250 ml Erlenmeyer flasks, which were agitated at 120 rpm for predetermined time intervals at room temperature (30 ± 2°C) in an isothermal water bath shaker. Following agitation, the adsorbent and adsorbate were separated through centrifugation and the dye concentration in the supernatant solution was determined using UV–visible spectrophotometer at wavelength of 580 nm.

To study the effect of initial dye concentrations from 40 to 140 mg/l, fixed amount of the adsorbent dosage at 30 mg/100 ml dye solution was applied. The effect of adsorbent dosage on the dye uptake was studied using adsorbent dosage varying from 50 to 100 mg/100 ml dye solution while maintaining the dye concentration at 80 mg/l. The pH of the solutions was original without any pH adjustment. In order to correct any adsorption of dye on containers, control experiments were carried out in duplicate. Aqueous samples were taken from each of the dye solutions at preset time intervals using disposable syringes and the concentrations were then analyzed. All samples were filtered prior to analysis in order to minimize interference of the adsorbent particle fines with the analysis. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e (mg/l) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (l) and W is the mass of dry adsorbent used (g).

The equilibrium data were then fitted using the Langmuir and Freundlich isotherm models.

2.2.1. Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [22]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{2}$$

where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 (mg/g) and b (l/mg) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

2.2.2. Freundlich isotherm

Freundlich isotherm on the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [23]. The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_F and n are Freundlich constants with n giving an indication of how favorable the adsorption process. K_F (mg/g (l/mg)$^{1/n}$) is the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon for a unit equilibrium concentration. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [24]. A value for $1/n$ below 1 indicates a normal Langmuir isotherm while $1/n$ above 1 is indicative of cooperative adsorption [25].

2.3. Batch kinetic studies

The procedure of kinetic tests was identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of crystal violet dye were similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{4}$$

where C_t (mg/l) is the liquid-phase concentrations of dye at time, t.

The kinetic data were then fitted using the pseudo-first-order and pseudo-second-order kinetic models.

2.3.1. Pseudo-first-order kinetic model

The rate constant of adsorption is determined from the pseudo-first-order equation given by Lagergren and Svenska [26] as:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{5}$$

where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and at time t (h), respectively and k_1 is the rate constant adsorption (1/h).

2.3.2. Pseudo-second-order kinetic model

The pseudo-second-order equation [27] based on equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

where k_2 (g/mg h) is the rate constant of second-order adsorption.

3. Results and discussion

3.1. FTIR characterization of rubber seed shell-based biosorbent

From the FTIR spectrums as shown in Fig. 1(a), the untreated rubber seed shell showed three major peaks at absorption bands of 3416 cm^{c1}, 1641 cm^{-1} and 1035 cm^{-1} as well as a minor peak at 2370 cm^{-1}. A wide band with two maximum peaks could be noticed at 3416 cm^{-1} and 1035 cm^{-1}. The peak at 3416 cm^{-1} was due to the absorption of water molecules as a result of NH stretching mode of strong OH alcohols or phenols groups [28] and absorbed water, while the peak at 1035 cm^{-1} was attributed to strong P–O–C interaction with the surface of the untreated rubber seed shell. It indicated that the peaks were the strongest and had the highest frequencies for aliphatic compounds. However, it was in the range that attributed to the C–O bonding which might be associated with ether C–O symmetric and asymmetric stretching vibration (–C–O–C– ring) [29]. In medium region of 1641 cm^{-1}, tertiary amides could be distinguished on the surface of the untreated rubber seed shell. It was attributed to the C=O stretching vibrations of alkenes and aromatics group. The peak at 2370 cm^{-1} might be attributed to the NH stretching vibration or in the P–H groups.

Referring to the FTIR spectrums as shown in Fig. 1(b), the acid-treated rubber seed shell showed six major peaks at absorption bands of 3437 cm^{-1}, 1634 cm^{-1}, 1193 cm^{-1}, 1065 cm^{-1}, 850–890 cm^{-1} and 380–580 cm^{-1}. The peaks at 3437 cm^{-1}, 1634 cm^{-1} and 1065 cm^{-1} were the same functional groups as the untreated rubber seed shell which remained even after the acid treatment. However, new peak at 1193 cm^{-1} was obtained for the acid-treated biosorbent. This peak was assigned to C–O carboxylic acid, which was due to the H_2SO_4 remaining on the surface of the adsorbent. The peak at 2370 cm^{-1} for the untreated rubber seed shell disappeared after the acid treatment. A narrow band with two peaks could be noticed at 883 cm^{-1} and 850 cm^{-1}, which were in the aromatic carbon functional group as a result of CH stretching mode out of plane deformation and happened to be a substitution. The peaks at 382 cm^{-1} and 580 cm^{-1} were assigned to the out-of-plane C–H bending mode. These spectra were also suggested to be due to alkaline groups of cyclic ketons and their derivatives added during the treatment [30].

3.2. Effect of contact time and initial dye concentration on adsorption equilibrium

Fig. 2 shows the adsorption uptake versus the adsorption time at various initial crystal violet dye concentrations at 30 °C. It indicated that the contact time needed for crystal violet dye solutions with initial concentrations of 40–140 mg/l to reach equilibrium ranged between 80 min to 100 min. In the range of crystal violet concentrations studied, the uptake of the crystal violet dye was rapid in the first 20 min. The rapid uptake then gave way to a much slower adsorption, which became constant after 80 min. This initial rapid uptake could be attributed to the concentration gradient created at the start of the adsorption process between solute concentration in solution and that at the adsorbent surface. As the dye loading increased, this gradient reduced and gave way to a slower uptake. The adsorption capacity at equilibrium, q_e increased from 18.8 mg/g to 56.6 mg/g with an increase in the initial dye concentrations from 40 mg/l to 140 mg/l.

Three consecutive mass transport steps were associated with the adsorption of solute from solution by porous adsorbent [31]. First, the adsorbate migrated through the solution, i.e., film diffusion, followed by solute movement from particle surface into interior site by pore diffusion and finally the adsorbate was adsorbed into the active sites at the interior of the adsorbent particle. The kinetic studies of the sorption process were paramount because the data obtained from such studies were necessary to understand the variables that influenced the sorption of solutes. The results were used to determine the equilibrium time and the rate of adsorption were used to develop predictive models for column experiments. Owing to these facts, Lagergren pseudo-first order and the chemisorption pseudo-second order [27] models were employed to study the concentration–

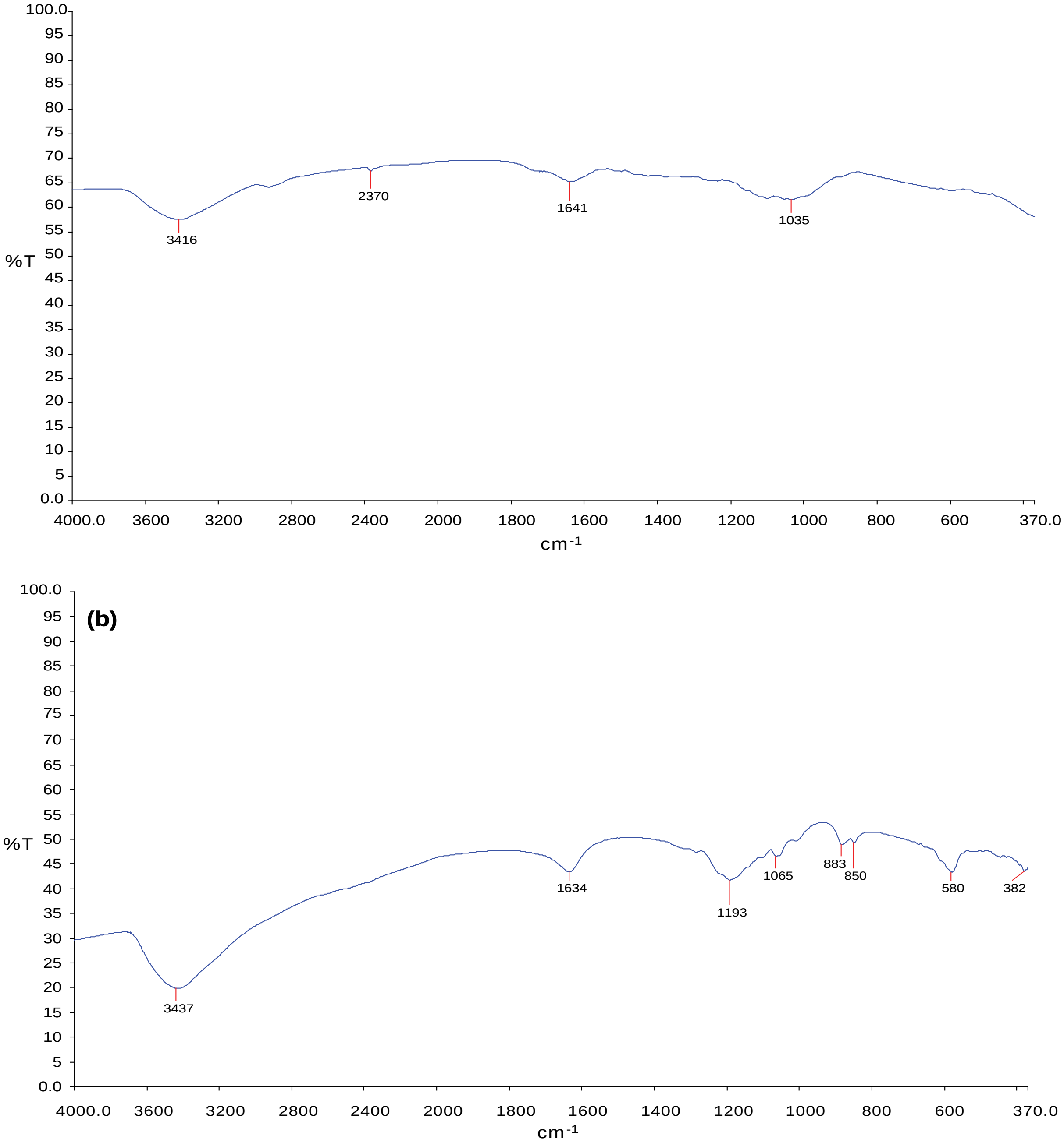

Fig. 1. FTIR spectrums of (a) untreated rubber seed shell and (b) acid-treated rubber seed shell-based biosorbent.

time profile features of the sorption processes. It was noted that variation in the initial concentration of crystal violet dye did not affect much on the time in which equilibrium was attained.

3.3. Effect of adsorbent dosage on dye uptake

The effect of adsorbent dosage on the crystal violet dye uptake is presented in Fig. 3. The extent of adsorption, calculated as a percentage of crystal violet dye adsorbed by the adsorbent, increased as the dosage of the adsorbent was increased. This was expected because an increase in adsorbent dosage led to an increase in the quantity of adsorption sites available for adsorbent–adsorbate interaction [32]. Therefore, the higher the adsorbent dosage, the larger the amount of dye that the fixed dosage could be adsorbed [33]. The increase in the percent removal of crystal violet dye with the

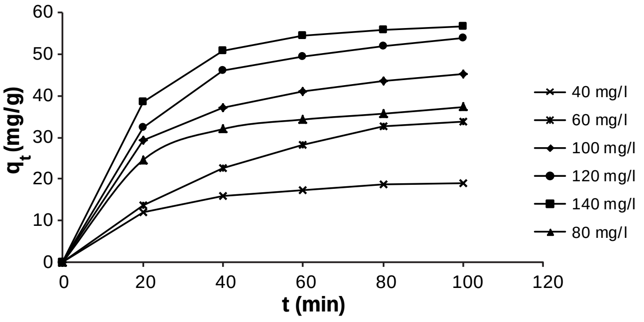

Fig. 2. Time variation of crystal violet adsorption on rubber seed shell-based biosorbent at different initial dye concentrations.

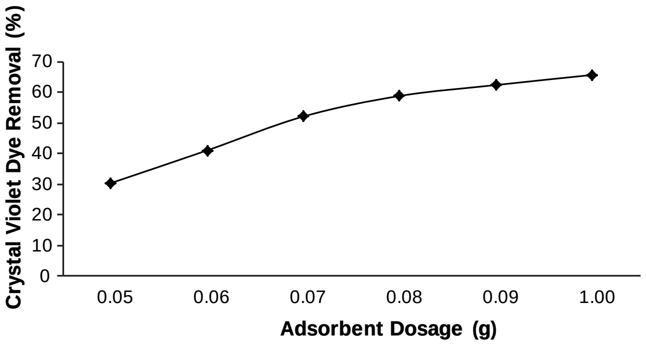

Fig. 3. Crystal violet dye removal at different adsorbent dosages.

increasing adsorbent dosage was due to the increase in the surface area consequent to the number of adsorbent particles with more number of active surface sites for the adsorption and the saturation occurred as a result of non-availability of dye molecules for adsorption.

3.4. Adsorption isotherms

The equilibrium relationship between the concentration of the crystal violet in the fluid phase and the crystal violet in the biosorbent at a given temperature was studied through adsorption isotherms. The results obtained were analyzed using two common isotherm models which were Langmuir and Freundlich isotherm equations. In order to understand the mechanism of crystal violet adsorption on the biosorbent, the experimental data were fitted to the aforementioned equilibrium isotherm equations.

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [22]. When C_e/q_e was plotted against C_e, a straight line with slope of $1/Q_0$ was obtained. As shown in Table 1, the R^2 value of 0.973 indicated that the adsorption data of crystal violet dye onto the biosorbent fitted well to the Langmuir isotherm model. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [22]. The value of R_L indicated the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The value of R_L was found to be 0.024 at 30 °C, and this again confirmed that the Langmuir isotherm model was favorable for adsorption of crystal violet dye onto the rubber seed shell-based biosorbent under the conditions used in this study. The equilibrium data were further analyzed using the linearized Freundlich isotherm, by plotting log q_e versus log C_e. The calculated Freundlich isotherm constants and the corresponding R^2 value are shown in Table 1. The R^2 value was lower than that obtained from Langmuir model. The result showed that the value of n was greater than unity (n = 1.14), indicating that crystal violet dye was favorably adsorbed on the rubber seed shell-based biosorbent.

The isotherm parameters obtained are presented in Table 1. An error function was required to evaluate the fitness of each isotherm equation to the experimental data obtained. The description of the sorption of crystal violet on rubber seed shell-based biosorbent by the Langmuir isotherm model was a pointer to monolayer

Table 1
Equilibrium isotherm parameters of sorption of crystal violet on rubber seed shell-based biosorbent

Langmuir isotherm parameter			Freundlich isotherm parameter		
Q_0 (mg/g)	b (l/mg)	R^2	K_F (mg/g (l/mg)$^{1/n}$)	n	R^2
23.81	0.29	0.973	0.51	1.14	0.960

Table 2
Comparison of crystal violet dye adsorption capacity of different bisorbents

Biosorbents	Q_0 (mg/g)	References
Rubber seed shell-based	23.81	Present study
Rice husk-based	44.87	[3]
Sagaun sawdust-based	2.10–3.50	[34]
Coir pith-based	2.56	[35]
Sugarcane fiber-based	10.44	[36]

Table 3
Comparison of the pseudo-first-order and pseudo-second-order kinetic models at varying adsorbent dosages

Adsorbent dosage (g)	Dye removal (%)	Pseudo-first-order parameter		Pseudo-second-order parameter	
		k_1 (min^{-1})	R^2	k_2 (g/mg min)	R^2
40	30.42	2.38	0.92	0.56	0.99
60	41.10	1.45	0.97	0.45	1.00
80	52.17	1.85	0.96	1.26	1.00
100	58.88	1.49	1.00	0.84	0.99
120	60.44	1.62	0.94	0.63	0.99
140	65.74	1.64	0.85	0.42	0.95

adsorption onto a surface containing a finite number of identical sites. The maximum adsorption capacity, Q_0 (mg/g), obtained in the present study was compared with adsorption capacity of other biosorbents, as shown in Table 2. The results of this comparison showed that rubber seed shell-based biosorbent has a great potential as an alternative low cost biosorbent for crystal violet adsorption from wastewater and is able to compete favorably with other biosorbents which had been studied by other researchers.

3.5. Adsorption kinetics

The kinetic data obtained from this study were tested with pseudo-first-order and pseudo-second-order kinetic models. As shown in Table 3, a comparative analysis of the linearity of the plots obtained from the test of the two kinetic models with the adsorption data showed that the pseudo-second-order kinetic model had better linearity (R^2 = 0.95–1.00) and would be said to describe the mechanism of adsorption of crystal violet dye by the rubber seed shell-based adsorbent at varying adsorbent dosages. This suggested that the overall rate of the adsorption process was controlled by chemisorption which involved valency forces through sharing or exchange of electrons between the adsorbent and adsorbate [37].

4. Conclusions

The present investigation showed that rubber seed shell could be a potential precursor to be used in the preparation of low cost adsorbent for the removal of crystal violet dye from aqueous solutions over a wide range of concentrations. FTIR study showed that the main functional groups present on the surface of the adsorbent were aliphatic compounds. Langmuir isotherm equation had a better correlation for the adsorption process as compared to Freundlich isotherm, giving maximum monolayer adsorption capacity of 23.81 mg/g at 30 °C. Both the initial dye concentration and adsorbent dosage were found to affect the adsorption process and the adsorption kinetics was found to follow the pseudo-second-order mechanism more than the pseudo-first-order model.

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