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Rubber seeds (*Hevea brasiliensis*): an adsorbent for adsorption of Congo red from aqueous solution

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ABSTRACT

This study aims to investigate the use of rubber (*Hevea brasiliensis*) seeds, a solid agricultural waste, as a novel adsorbent for the adsorption of Congo red (CR) from aqueous solution in batch mode. Experiments were carried out as a function of contact time, dye concentration, adsorbent dosage, pH, and temperature. Langmuir, Freundlich, and Sips adsorption isotherm models were applied to describe isotherm parameters. The results showed that equilibrium contact time was 90 min. The experimental results indicate that, the percentage of dye adsorption increases with an increase in the adsorbent dosages and temperature. The CR adsorption percentage decreased with increasing dye concentration and pH solution from 3 to 12. Thermodynamic parameters data indicated that the CR adsorption process was non-spontaneous and endothermic under the experimental conditions, with the Gibbs free energy (ΔG°) in the range of 9.13–8.12 kJ/mol, enthalpy (ΔH°) and entropy (ΔS°) of 14.15 kJ/mol and 16.85 J/mol, respectively. The Langmuir isotherm model fit the equilibrium data better than both the Freundlich and Sips isotherm models, with adsorption capacity 9.82 mg/g. The kinetic data for adsorption processes were described by pseudo-second-order model with a rate constant in the range of 0.043–0.156 g mg/g min^{-1}. The rubber seeds investigated in this study showed a high potential use for the adsorption of CR from aqueous solution.

Keywords: Adsorption; Congo red; Langmuir isotherm; Kinetic; Rubber seed

1. Introduction

The dyeing effluent discharged from textile industries is one of the largest components of textile effluent. Discharging even a small amount dyeing effluent poses serious environmental harms not only because it would damage the aesthetic nature of the receiving streams, but also it can affect aquatic life and food webs. This is due to the carcinogenic and mutagenic effects of the synthetic dyes [1–3]. Treatment of dyeing effluent is very difficult since the effluent contains salts, dyes, enzymes, yeasts, surfactants, scouring agents, oil, grease, oxidizing, as well as reducing agents [4]. Congo red (CR) is an anionic dye widely used in the textile, paper, rubber, and plastic industries. CR is difficult to biodegrade due to their complex aromatic structures, which provide them physicochemical, thermal, and optical stability [2,5].

Several treatment methods such as ion exchange, coagulation, flotation, oxidation, biosorption, biodegradation, UV photodecomposition, and reverse osmosis

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have been applied to remove CR molecules from aqueous solution. Due to its simplicity and high efficiency, adsorption treatments have been extensively applied to remove organic pollutants in the aqueous environment [2,5]. Activated carbons (ACs) are the most widely used adsorbents for removing contaminants from wastewater because of its extended surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity [6,7]. However, the application of AC is not always technically advantageous due to the high regeneration cost involved and the need to further dispose of the waste AC. Thus, there is a need to continue the search and development of alternative adsorbents with high adsorptive capacity and low cost for CR removal.

In recent years, some papers had reported several kinds of adsorption behavior of CR on numerous low-cost materials such as chitosan carboxymethyl [3], phyrophyllite [4], jujuba seeds [5], AC prepared from sawdust [6], bentonite [7–9], montmorillonite [10], egg shells [11,12], pine cone powder [13], alkaline treated Eucalyptus sawdust [14], bagasse [15], bottom ash [16], kaolin [17,18], fruit shell [19], jute stick powder [20], chitosan hydrogel [21], and other adsorbents [2,22].

The rubber tree, also referred to as rubber wood, is a tree belonging to the family of Euphorbiaceae. It is the most economically important member of the genus *Hevea*. It is a major economic importance because the milky latex extracted from the tree is the primary source of natural rubber. Rubber (*Hevea brasiliensis*) trees start to bear fruits at four years of age. Each fruit contains three or four seeds, which fall to the ground when the fruit ripens and splits. Each tree yields about 800 seeds (1.3 kg) twice a year. A rubber plantation is estimated to produce about 800–1,200 kg of rubber seeds per ha per year [23], all of which is normally regarded as waste. Rubber seeds contain polar functional groups such as ketone, carboxylic, hydroxylic, and phenolic acid groups in their molecular structure [24], which can be involved in adsorption, and it appears to have a good potential for adsorption of polar organic molecules.

Different investigations have been conducted to explore useful applications for rubber seeds and its different parts. Such research has shown that rubber seeds and their different parts may be used as an adsorbent, which appears to effectively adsorb certain heavy metals and organic compounds. Removal of copper ion from dilute aqueous solution by rubber leaves powder-treated sodium hydroxide as an adsorbent has been reported by [25]. Hanafiah et al. [26] have also used the rubber leaf powder-treated potassium permanganate for the removal of lead ion from aqueous solution. AC prepared from the coat of rubber seeds has been reported and it is being used as an adsorbent in the removal of basic dye [27] and phenol [28]. Oladoja et al. [29] also found that the shell of rubber seeds was able to effectively remove the cationic dye, methylene blue, from its aqueous solution. However, no work has been reported on the use of raw rubber seed biomass as an effective adsorbent for the removal of the anionic dye CR from aqueous solution. Therefore, the present study aims to study a convenient and economical method for CR removal from aqueous solution by adsorption using a low cost and an abundantly available adsorbent such as raw rubber seeds biomass (*H. brasiliensis*). The removal of CR on rubber seeds as a function of contact time, dye concentration, biosorbent dosage, pH, and temperature was investigated.

2. Materials and methods

2.1. Materials

The rubber seeds were obtained from a rubber estate in the Siak district in Riau Province, Indonesia. CR, a diazo dye, was obtained from Merck and used as adsorbate. The properties and characteristics of the CR are given in Table 1. Hydrochloric acid and sodium hydroxide were purchased from Merck (USA). The dye solution was prepared to the desired concentrations using Milli-Q water. All chemicals used were of analytical grade and without further purification.

2.2. Adsorbent preparation

The adsorbent (rubber seed) was crushed and the hard outer layer was separated from the soft inner seed. The outer seed was used as the adsorbent in this

Table 1
The properties and characteristics of the CR [4]

Parameter	Results
CI Number	22120
CAS Number	573-58-0
Chemical formula	$C_{32}H_{22}N_6Na_2O_6S_2$
Molecular weight (g/mol)	696.7
Width (nm)	2.62
Depth (nm)	0.74
Thickness (nm)	0.43
pKa	5.5
λ max (nm)	498
Azo groups	2
Sulphonic groups	2

study. The adsorbent was washed with distilled water to remove any contaminants. After cleaning, the adsorbent was dried for 24 h at 110˚C. The adsorbent was then grinded using a FRITSCH pulverisette-25 grinder machine to powder form. The machine automatically sieved the grinded sample at a particle size of 100 μm.

2.3. Adsorbent characterization

A Fourier infrared spectrophotometer (FTIR, Perkin Elmer 3100) was used for the investigation of functional groups of rubber seeds. The samples were examined within the range of 400–4,000 cm^{-1}. The zeta potential of rubber seed, as a function of pH in 0.01 mol/L sodium chloride, was measured using a ZetaPlus 4 Instrument (Brookhaven Instruments Corp.).

2.4. Batch adsorption studies

Batch adsorption experiments were conducted in 100 mL Erlenmeyer flask containing 50 mL of CR solutions with different initial concentrations (20–100 mg/L) and 0.1 g of rubber seeds adsorbents. The mixtures were stirred in a thermostatic shaker bath (Innova 3000) at 100 rpm for 1, 5, 10, 20, 30, 40, 60, 90, 120, and 150 min at a temperature of 25˚C. After that, the suspension was taken out and the supernatant was centrifuged at 2,500 rpm for 15 min. The supernatant was analyzed by spectrophotometric method using an ultraviolet–visible spectrophotometer model UV–Vis 1601 (Shimadzu, Japan) at 495.7 nm. The percent removal of CR was calculated using the following equation:

$$\%\,\mathrm{Removal} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

where C_i and C_e are initial and final concentrations of CR in the solution (mg/L), respectively. The adsorption capacity of an adsorbent obtained from the mass balance on the sorbate in a system with solution volume V is expressed as:

$$q_e\,(\mathrm{mg/g}) = \frac{C_i - C_e}{m} \times V \tag{2}$$

where C_i and C_e are the initial and final concentrations of CR in solution (mg/L), respectively. V is the volume of solution (L) and m is mass of rubber seeds (g) used. The influence of pH on the CR removal was studied by adjusting CR solutions (60 mg/L) to different pH values (3–12) using 0.1 M HCl or NaOH solution, and shaking 50 mL dye solution with 0.1 g adsorbent at 25˚C for 90 min. The effect of dosage on CR removal was determined by shaking several bottles containing different dosages (0.1, 0.2, 0.3, 0.5, 0.7, 1, 1.5, and 2 g) of rubber seeds and 50 mL CR solution (60 mg/L) for 90 min at pH 6. The effect of temperature on CR removal was determined by shaking 50 mL CR solution (60 mg/L) at four different temperatures 25, 45, 65, and 85˚C with 0.1 g of rubber seeds at pH 6.

2.5. Adsorption isotherm

CR adsorption isotherm experiments using rubber seeds were conducted under a variety of CR concentrations (20–100 mg/L) with 50 mL solution, with other conditions held constant at a contact time of 90 min, dosage of 0.1 g, temperature of 25˚C, and pH 6. The experimental data were calculated to determine the adsorption isotherm by using the Langmuir, Freundlich, and Sips models.

2.6. Adsorption kinetics

In each kinetic experiment, a definite volume (50 mL) of 20–100 mg/L CR concentration was added to 100 mL conical glass bottles together with 0.5 g of rubber seeds with a thermostated jacket (the experiments were carried out at 25˚C and pH 6) for 1, 5, 10, 20, 30, 40, 60, 90, 120, and 240 min.

3. Results and discussion

3.1. Adsorbent characterization

The FTIR spectra of dried rubber seeds are shown in Fig. 1. As shown in the figure, it can be observed that the dried rubber seeds have broad absorption peaks at around 3,300–3,500 cm^{-1}, indicating the presence of carboxylic acid and amino groups. The absorption band at 2,926 cm^{-1} could be assigned to asymmetric vibration of –CH. Simultaneously, the stretching vibration of methoxy group (CH_3–O) in the 2,854 cm^{-1} region was also found. The stretching vibration band 1,747 cm^{-1} is due to asymmetric stretching of the carboxylic C=O double bond. A 1,458 cm^{-1} is of phenolic –OH and –C=O stretching of carboxylates. A 1,377 cm^{-1} band could be stretching vibration of –COO. The band at 1,083 cm^{-1} could be due to the vibration of –C–O–C and –OH of polysaccharides.

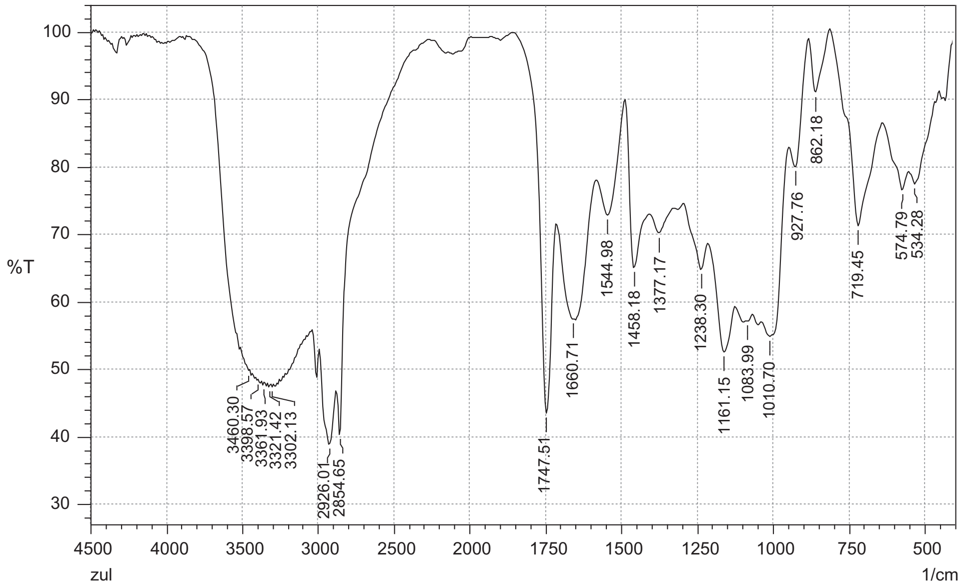

Fig. 1. FTIR spectrum of rubber seed.

The zeta potential is an electrical potential in the double layer at the interface between a particle, which moves in an electrical field and the surrounding liquid [30]. From the experiment, the zero zeta potential of rubber seeds was found about at pH 5.2 (figure not shown). At pH below 5.2, the charge of rubber seeds will be positive; this can be attributed to the protonation of polar functional groups in the rubber seeds. Above this pH, rubber seeds will be negatively charged, which may be due to the deprotonation of polar functional groups in the rubber seeds.

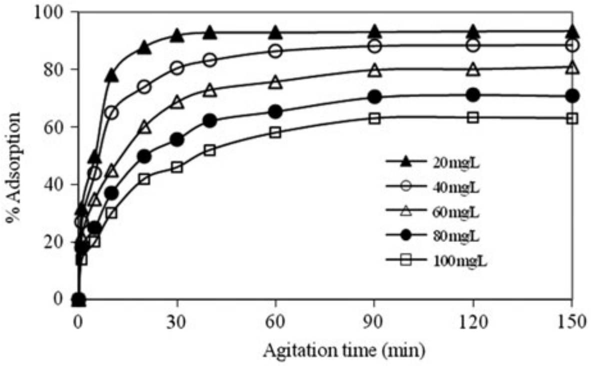

Fig. 2. Effect of contact time and dye concentration on CR adsorption onto rubber seed (dosage 100 g/L, pH 6, particle size 100 μm and temp 25˚C).

3.2. *Effect of contact time and dye concentration*

The effects of the contact time on the percentage of CR adsorption at various dye concentrations are shown in Fig. 2. As shown in the figure, it is remarkable that fast percentage of CR adsorption had occurred initially at all initial concentrations. The initial fast adsorption may be explained due to the availability of more adsorption sites [9,25,31]. After 90 min, it can be observed that for all CR concentration the adsorption remained constant, indicating that equilibrium has been established.

As shown in Fig. 2, the initial dye concentration had a significant effect on CR adsorption. The percentage of CR adsorption at equilibrium decreased from 98.4 to 48.5 as the dye concentration increased from 20 to 100 mg/L. This is because, an increase in the initial concentration provides an important driving force to overcome all resistances of the dye between the aqueous and solid phases [7,11,13,14,27,32–36]. At lower concentrations, all sorbate ions present in the sorption medium could interact with the binding sites; hence, higher percentage of adsorption results. At higher concentrations, because of the saturation of the sorption sites, the percentage adsorption of the dye shows a decreasing trend [11,33,35,37]. Comparable results were obtained for sorption of CR on phyrophyllite [4], on jujuba seed [5], on bentonite [7], on Eucalyptus wood saw dust [14], and on sugarcane bagasse [15]. The curves are distinct, smooth, and continuous indicating monolayer coverage of rubber seed by dye [28].

3.3. *Effect of adsorbent dosage*

The percentage of CR adsorption was dependent on the sorbent dosage employed. The results of experiments indicate that with an increase in rubber seeds dosage from 1 to 10 g/L, the percentage of CR adsorption increases from 20 to 90% (figure not shown). A further increase in rubber seed dosage beyond 10 g/L exhibited no extra improvement in dye adsorption. The increase of CR adsorption with increasing rubber seed dosage is attributed to the increase of total adsorbent surface area and adsorption site [5,13–18,36]. Hence, under economical consideration, 10 g/L is optimized as the rubber seeds dosage for all experiments.

3.4. Effect of pH

The pH of an aqueous solution is an important controlling parameter in the process of adsorption. Solution pH affects both the aqueous chemistry and surface binding sites of the adsorbent. The effect of pH on CR adsorption using rubber seeds as a function of pH value is shown in Fig. 3. As shown in the figure, the CR adsorption decreased with increase in the pH of solution. With further increase in pH up to 12, there has been a steady decrease in percentage of adsorption. The maximum of CR adsorption occurred in the pH range of 5–6.

As it has been said, the rubber seeds used contain polar functional groups such as ketone, carboxylic, hydroxylic, and phenolic acid groups in their molecular structure. Those functional groups develop positive or negative charge depending on the acid or alkaline medium. It has been stated above that the point zero charge for rubber seeds is 5.2. At low pH, the concentration of H^+ ions in the system increases and these functional groups are protonated. So the surface of the rubber seeds acquires a positive charge. The effect of pH on CR removal can be explained by the fact that the pH of dye solution can significantly affect the surface charge of the adsorbent and degree of ionisation and speciation of the dye [7,17]. Some literature shows that the reduction of CR adsorption over the pH range may relate to two possible mechanisms: (a) electrostatic interaction between the adsorbent and the dye and (b) the chemical reaction between the adsorbent and the dye [3,7,17].

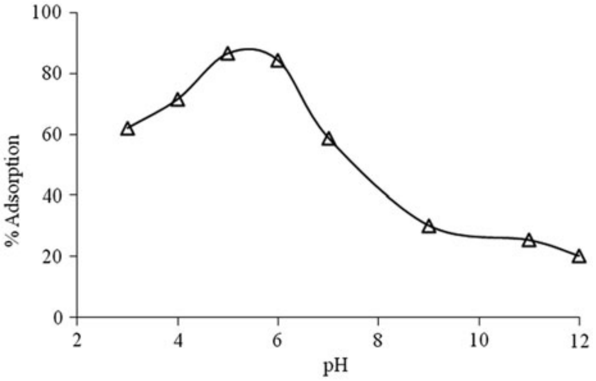

Fig. 3. Effect of pH on CR adsorption onto rubber seed (C_0: 60 mg/L, contact time 90 min, dosage 100 g/L, particle size 100 μm and temp 25˚C).

CR exists as an anionic form (negative charge) at high pH (sulfonate groups), and as a cationic form (positive charge) at low pH. According to Zhang et al. [15], the isoelectric point of CR is ~3 and so CR would be positively charged at the $pH < 3$, and negatively charged at $pH > 3$. When pH of CR dye solution is lower than 5.2 (below point zero charge rubber seeds), an increase in adsorption of CR takes place due to the attraction between the positive charges of the surface of the rubber seeds and the negative charges of the anionic CR molecules. As the pH system increases, the number of negatively charged sites on rubber seeds surface also increases. On the other hand, at high pH, the surface of the rubber seeds becomes negatively charged and unfavorable for the adsorption of negatively charged CR molecules. Therefore, the decrease in the CR removal at high pH may be attributed to the ionic repulsion between the negatively charged rubber seeds surface and the anionic CR molecules.

3.5. Effect of temperature

Our results revealed that the amount of CR adsorption using rubber seeds increases with higher temperature (Fig. 4). These results show that these adsorption processes were endothermic and appeared to have a favorable adsorption at higher temperature. This arises from the increase in the mobility of dye molecules with increasing temperature [4,12–14,38] and more molecules across the external boundary layer and the internal pores of the adsorbent particles. Furthermore, increasing the temperature may produce a swelling effect within the internal structure of adsorbent, penetrating the large dye molecule further [3,10,12,13,35,38,39]. Similar results have been reported on N, O-CMC [3], on pyrophyllite [4], on jujuba seeds [5], on surfactant-modified montmorillonite [10], on phyrophyllite [4], on Ca-bentonite [9], on pine cone powder [13], as well as on Eucalyptus wood saw dust [14].

The values of thermodynamic parameters for CR sorption on rubber seed such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated using the following equations:

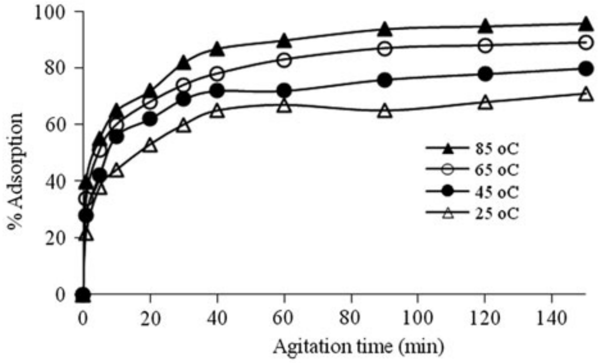

Fig. 4. Effect of temperature on CR adsorption onto rubber seed (C_0: 60 mg/L, contact time 90 min, dosage 100 g/L, particle size 100 μm and pH 6).

$$\Delta G^\circ = \Delta H^\circ - \mathrm{T} \cdot \Delta S^\circ \tag{3}$$

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R \cdot T} \tag{4}$$

where R (8.314 J/mol K) is the gas constant, T (K) is absolute temperature, and b (L/mg) is the Langmuir isotherm constant. The values of ΔH° and ΔS° can be obtained from the slope and intercept of a linear plot between ln b and $1/T$, respectively. The obtained thermodynamic parameters for the adsorption of CR on rubber seed are given in Table 2. A positive value of the ΔH° indicates that the adsorption of CR on rubber seed takes place as an endothermic process. Generally, the magnitude of the ΔH° value lies in the range of 2.1–20.9 kJ/mol, indicating physisorption. At higher value from 80 to 200 kJ/mol, chemisorption becomes predominant [7,12,17]. The value of ΔH° for the present study is 14.12 kJ/mol (Table 2), indicating that CR adsorption on rubber seed is likely a physisorption process.

The positive values of Gibbs free energy (ΔG°) indicate the non-spontaneous nature of adsorption. The value of ΔG° becomes more negative with the increase of temperature, which indicates that the reaction is more favorable at high temperatures. The positive entropy change (ΔS°) value suggests an increase in randomness at their solid-solution interface.

3.6. Adsorption isotherm

To identify the mechanism of the adsorption process, the adsorption of CR onto rubber seeds is determined as a function of equilibrium (residual). CR concentration (C_e) and the corresponding adsorption isotherms are plotted in Fig. 5. The data can then be correlated with a suitable isotherm. In this experiment, three isotherm models of Langmuir, Freundlich, and Sips isotherms have been used. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. The Langmuir equation is given in the following equation:

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e} \tag{5}$$

where C_e is the equilibrium concentration (mg/L), q_e is amount of adsorbate adsorbed per unit weight of absorbent (mg/g), and q_m and b are the maximum adsorption capacity (mg/g) and Langmuir constant (L/mg), respectively.

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$. Hence, the empirical equation can be written as:

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

where C_e is the equilibrium concentration (mg/L), q_e is amount of adsorbate adsorbed per unit weight of absorbent (mg/g), and K_f [(mg/g)/(mg/L)$^{1/n}$] and n are Freundlich constants. A value of $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity. A value for n greater than one indicates a favorable adsorption process. The

Table 2
Thermodynamic parameters of adsorption process at different temperature

Temperature (°C)	b (L/mg)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)
25	0.0242	9.129	14.15	16.85
45	0.0374	8.792		
65	0.0514	8.455		
85	0.0625	8.118		

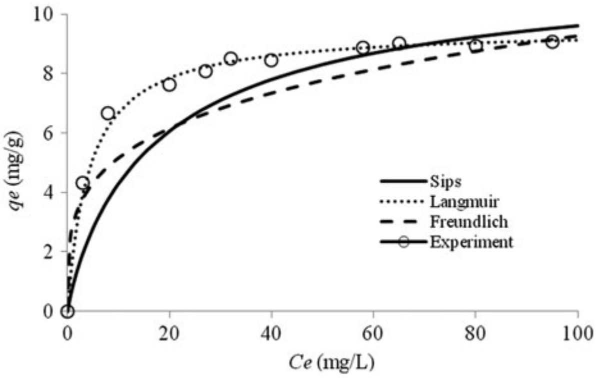

Fig. 5. Non-linear isotherm of CR adsorption onto rubber seed (contact time 90 min, dosage 100 g/L particle size 100 μm and pH 6).

other Freundlich constant K_f indicates the adsorption capacity of the adsorbent.

Sips model is a combination of Langmuir and Freundlich models, having features of both Langmuir and Freundlich equations. It is expressed as:

$$q_e = \frac{q_m \cdot K_{eq} \cdot C_e^n}{1 + K_{eq} \cdot C_e^n} \tag{7}$$

where K_{eq} $[(\mathrm{L/mg})^n]$ represents the equilibrium constant of the Sips equation and q_m (mg/g) is the maximum adsorption capacity. The Sips isotherm model is characterized by the heterogeneity factor, n, and specifically when $n = 1$, the Sips isotherm equation reduces to the Langmuir equation which implies a homogenous adsorption process [2,21,22,35,40].

As shown in Fig. 5, the Langmuir isotherm model showed a better fit to the experimental isotherm data than the Freundlich and Sips isotherm models, indicating that the adsorption of CR on rubber seeds is a monolayer adsorption. Based on the Langmuir isotherm model, the maximum adsorption of CR on rubber seeds at pH 7 and 25˚C was found to be 9.82 mg/g (Table 3).

3.7. Adsorption kinetics

The adsorption kinetics data can predict the rate of CR adsorbed on rubber seeds and provide valuable data for understanding the mechanism of adsorption. The kinetics of CR adsorption on rubber seeds was tested with respect to pseudo-first-order, pseudo-second-order, intra-particles diffusion, and Boyd models. The pseudo-first-order equation can be written as follows:

$$\log\,(q_e - q_t) = \log q_e - k_1/2.303 \cdot t \tag{8}$$

where q_e and q_t are the amounts of CR (mg/g) adsorbed on adsorbents at equilibrium and at time t, respectively, and k_1 is the rate constant (min^{-1}). The value of k_1 was obtained from a slope of the linear plots of log $(q_e - q_t)$ against t. If the plot were found to be linear with good correlation coefficient, it would indicate that equation is appropriate to CR adsorption on rubber seeds. So, the adsorption process is a pseudo-first-order process. The pseudo-first-order rate constants for this study were calculated from slopes of the plots (Fig. 6) of Eq. (8). The values of k_1 and calculated q_e were listed in Table 4.

The pseudo-second-order kinetic model can be represented in the following form:

$$t/q_t = 1/k_2 \cdot q_e^2 + \mathrm{t}/q_e \tag{9}$$

where q_e and q_t are the amounts of CR (mg/g) adsorbed on sorbent at equilibrium and at time t, respectively, and k_2 is the rate constant (g/mg min^{-1}). If pseudo-second-order kinetics is applicable, the plot of t/q_t against t of Eq. (9) should give a linear relationship from which the constants q_e and k can be determined. The plot of t/q_t against t pseudo-second-order model under different adsorbent dosages is shown in Fig. 7. The calculated R^2 values for the pseudo-second-order kinetic model are shown in Table 4.

As shown in Fig. 6, the plot of log $(q_e - q_t)$ against t did not give a linear relation, suggesting that the pseudo-first-order kinetic model cannot describe the CR adsorption process over rubber seeds well. In contrast, the linear plots of t/q_t against t with R^2 higher than 0.99 were obtained for CR adsorption to rubber seeds (Fig. 7). Also from Table 4, all the q_e determined from the model along with correlation coefficients indicate that the calculated q_e value is very close to experiment q_e. This suggests that CR adsorption process obeys pseudo-second-order kinetics. Similar kinetic results have also been reported for the adsorption of CR onto chitosan hydrogel beads [2], N,O-CMC [3], jujuba seed [5], bentonite [8], Ca-bentonite [9], montmorillonite [10], eggshell [12], pine cone powder [13], Eucalyptus wood saw dust [14], sugarcane bagasse [15], clay [17], and Australian kaolins [18].

Adsorption kinetics is usually controlled by different mechanisms; the most general of which is the diffusion mechanism. To investigate the mechanism of adsorption, the intra-particle diffusion and Boyd kinetic models are used. The intra-particle diffusion model can be defined as:

Table 3
Langmuir, Freundlich and Sips constants for CR adsorption*

Langmuir model			Freundlich model			Sips model			
b (L/mg)	q_m (mg/g)	R^2	n	K_f (mg/g)	R^2	q_m (mg/g)	K_{eq} (mL/g)	n	R^2
0.024	9.82	0.999	3.93	2.88	0.962	9.30	0.095	0.088	0.984

*Contact time: 90 min, dosage 2 g/L, pH 6, particle size 100 μm, and temp 25℃.

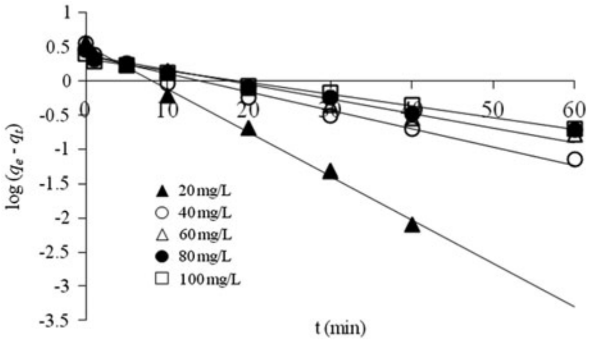

Fig. 6. Pseudo-first-order for adsorption of CR on rubber seed (dosage 100 g/L, particle size 100 μm and pH 6).

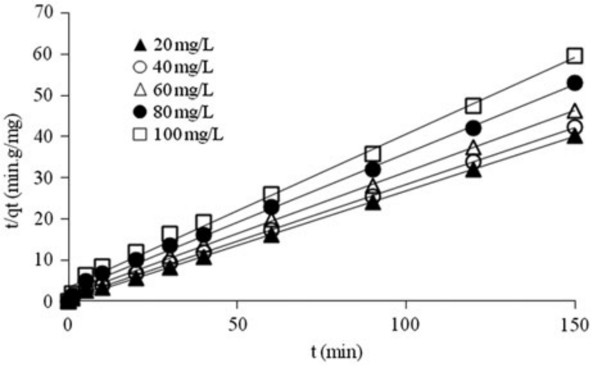

Fig. 7. Pseudo-second-order for adsorption of CR on rubber seed (dosage 100 g/L, particle size 100 μm and pH 6).

$$q_t = k_d \cdot t^{1/2} + C \tag{10}$$

where k_d and C are an intra-particle diffusion rate constant (mg/g min$^{1/2}$) and a constant, respectively. The k_d is obtained from the slope of linear plot of q_t vs. $t^{1/2}$. If the plot of q_t vs. $t^{1/2}$ gives a straight line, the sorption process is controlled by intra-particle diffusion only. However, if the data exhibit multilinear plots, then two or more steps influence the sorption process.

From the plot of q_t against $t^{1/2}$ (figure not shown here), it can be seen that these plots generally have a dual nature, i.e. an initial curved portion and a final linear portion. The initial curved portion represents boundary layer diffusion effects, while the final linear portions are results of intra-particle diffusion effects. Extrapolating the linear portion of the plot to the ordinate produces the intercept (C), which is proportional to the extent of boundary layer thickness. The values of k_{d1} and k_{d2} as obtained from the slopes of the two straight lines are listed in Table 5. The thickness of the boundary layer in the second portion that corresponds to the intra-particle diffusion (C_2) is larger than that of the first portion that concerned the film diffusion (C_1). Consequently, the values of the intra-particle diffusion rates k_{d2} are smaller than the film diffusion rates k_{d1} [12,33,35]. This gives the prediction that the CR removal process may be controlled by intra-particle diffusion [12,33,35]. The value of C_2 for adsorption of

Table 4
The pseudo-first order and second-order kinetic parameters for CR adsorption*

	Pseudo-first-order			Pseudo-second-order			
Concentration (mg/L)	k_1 (min^{-1})	q_e, cal (mg/g)	R^2	k_2 (min^{-1})	q_e, cal (mg/g)	R^2	q_e, exp (mg/g)
20	0.147	3.31	0.994	0.156	3.79	0.999	3.74
40	0.062	2.38	0.969	0.087	3.62	0.999	3.54
60	0.050	2.39	0.969	0.056	3.35	0.998	3.21
80	0.045	2.25	0.976	0.048	2.97	0.996	2.85
100	0.040	2.12	0.989	0.043	2.68	0.993	2.53

*Dosage 10 g/L, pH 6, particle size 100 μm, and temp 25℃.

Table 5
The intra-particle-diffusion model parameters for CR adsorption*

Concentration (mg/L)	k_{d1} (mg/g min$^{1/2}$)	C_1	R_1^2	k_{d2} (mg/g min$^{1/2}$)	C_2	R_2^2
20	0.692	0.628	0.949	0.007	3.661	0.719
40	0.565	0.565	0.960	0.018	3.333	0.773
60	0.425	0.458	0.998	0.055	2.610	0.895
80	0.347	0.343	0.988	0.047	2.308	0.714
100	0.298	0.234	0.986	0.043	2.042	0.662

*Dosage 10 g/L, pH 6, particle size 100 μm, and temp 25℃.

CR on rubber seeds decreased with increasing dye concentration. This suggests that the effect of intra-particle diffusion on the adsorption of CR from aqueous solution is probably more considerable at low concentrations.

In order to determine the actual rate controlling step involved in the CR adsorption process, the kinetic data as obtained by the batch method were further analyzed using the Boyd kinetic model:

$$B_t = -0.4977 - \ln(1 - F) \tag{11}$$

where B_t is a mathematical function of F and F is the fraction of solute adsorbed at different times, t (min), which is calculated as follows:

$$F = q_t/q_\alpha \tag{12}$$

where q_α represents the amount sorbed (mg/g) at infinite time. The calculated B_t values were plotted against time t (min); thus, the linearity of the plots can be used for distinguishing between film diffusion and intra-particle diffusion rates of adsorption [12,25,33,36,41,42]. A straight line passing through the origin is indicative of sorption processes governed by particle diffusion mechanisms. Otherwise, they are governed by film diffusion or chemical reaction [36,41,42]. The calculated B values are used to calculate the effective diffusion coefficient, D_i (cm^2/s) using the relation:

$$B = \pi^2 D_i/r^2 \tag{13}$$

where r represents the radius of the sorbent particle (cm) by assuming spherical particles. From the plot of B_t against t (Fig. 8), it was observed that the plots are linear with high correlation coefficients at all dye concentrations and pass through origin, confirming the particle diffusion-controlled mechanisms.

The calculated D_i value at different initial dye concentrations are provided in Table 6. If film diffusion is to be the rate determining step, the value of D_i should be in the range of 10^{-6}–10^{-8} cm^2/s; whereas, if particle diffusion is the rate determining step, the D_i value should be in the range of 10^{-11}–10^{-13} cm^2/s [25]. The D_i values obtained from this work were in the range of 10^{-11}–10^{-13} cm^2/s, confirming that the slowest step in CR adsorption on rubber seed was particle diffusion.

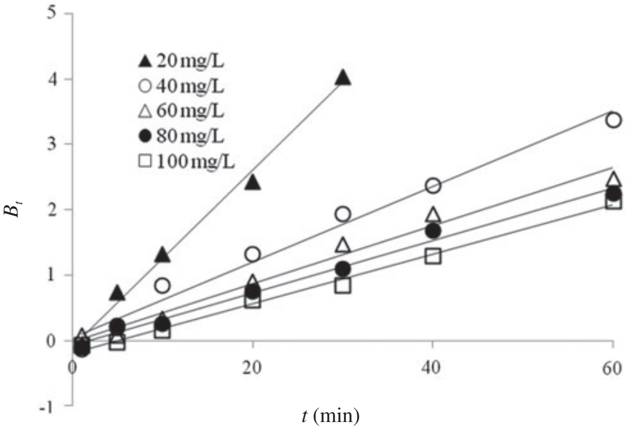

Fig. 8. Boyd kinetic model for adsorption of CR on rubber seed (dosage 10 g/L, particle size 100 μm and pH 6).

Table 6
The Boyd kinetic model parameters for CR adsorption*

Concentration (mg/L)	R^2	$D_i \times 10^{-11}$ cm^2/s
20	0.993	3.42
40	0.980	1.47
60	0.978	1.13
80	0.988	1.01
100	0.995	0.96

*Dosage 10 g/L, pH 6, particle size 100 μm, and temp 25℃.

Table 7
Comparison of adsorption capacity of various adsorbent for CR removal

	q_m (mg/g)	References
Chitosan hydrogel beads impregnated with CTAB	433.12	[2]
N,O-carboxmethyl-chitosan	330.62	[3]
Pyropyllite	4.00	[4]
Jujuba seeds	55.56	[5]
Activated carbon prepared from sawdust	183.8	[6]
Bentonite (acid and thermal activation)	75.75	[7]
Natural bentonite	158.7	[8]
Ca-bentonite	107.41	[9]
Surfactant-modified montmorillonite	351.0	[10]
Powdered eggshell	95.25	[11]
Acid treated pine cone	40.19	[13]
Alkaline treated Eucalyptus wood sawdust (30°C)	31.25	[14]
Sugarcane bagasse	38.20	[15]
Bottom ash (physical activated)	106.61	[16]
Kaolin	5.44	[17]
White firing kaolin	7.27	[18]
Tamarind fruit shell	10.48	[19]
Jute stick powder	35.7	[20]
Chitosan hydrogel bead-SDS	186.02	[21]
Chitosan hydrogel beads impregnated with carbon nanotubes	450.40	[22]
Rubber seeds	9.82	This study

3.8. Comparison of CR adsorption with other adsorbents reported in literature

Several studies have investigated the adsorption or removal of CR in aqueous solution using low-cost adsorbents. Table 7 summarizes the adsorption capacity of different types of adsorbents for CR. The adsorption capacity varies, and it depends on the surface properties and affinity of the individual adsorbent [17], the extent of surface/surface modification and the initial concentration of the adsorbate [43], range of molecular size fraction of adsorbate, and degree of ionization per unit weight of the adsorbate [44]. Rubber seeds show promising potential in CR adsorption when compared to other biosorbent materials, especially when process costs are taken into account. Furthermore, rubber seeds can be obtained from nature without problems.

4. Conclusion

Rubber seeds, an agricultural solid waste, can be effectively used as an adsorbent for the CR adsorption from aqueous solution. The CR adsorption increases with increasing adsorbent dosage. The CR adsorption was found to decrease with increasing pH from 3 to 12. The effect of temperature on CR adsorption could not be neglected. Thermodynamic parameters data indicated that the CR adsorption process was non-spontaneous and endothermic under the experimental conditions, with the Gibbs free energy (ΔG°) in the range of 9.13–8.12 kJ/mol, and enthalpy (ΔH°) and entropy (ΔS°) of 14.15 kJ/mol and 16.85 J/mol, respectively. The equilibrium adsorption data of CR on rubber seeds shows that the Langmuir isotherm model fit to the experimental data better than the Freundlich and Sips isotherm models. Based on the Langmuir isotherm model, the maximum monolayer adsorption capacity is 9.82 mg/g. The adsorption kinetic of CR adsorption on rubber seeds obeyed a pseudo-second-order model with a rate constant in the range of 0.043–0.156 g mg/g min^{-1}. The results from assessing intra-particle and Boyd kinetic models revealed that particle diffusion mechanism mainly governs the CR adsorption process onto rubber seed. The results of this study show that rubber seeds, an agricultural solid waste, are useful as a promising adsorbent for the removal of CR dye in wastewater treatment.

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