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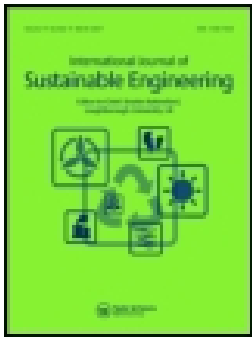
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Combating dye pollution using cocoa pod husks: a sustainable approach

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ABSTRACT

The adsorptive potential of activated carbon prepared by chemical activation of Cocoa pod husk (CPHAA) to remove Congo red (CR) dye from its aqueous solution was investigated in this study. CPHAA was characterised using Energy Dispersive X-Ray, Scanning Electron Micrograph and Fourier Transform Infrared Spectroscopy techniques. The effects of contact time, initial dye concentration, pH and solution temperature were studied. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The equilibrium data were best represented by Langmuir isotherm model, with maximum monolayer adsorption capacity of 43.67 mg/g. The kinetic data were fitted to Pseudo-first-order, Pseudo-second-order, Elovich and Intraparticle diffusion models; the pseudo-second-order kinetic model provided the best correlation. Thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°) were evaluated. The thermodynamic study showed that the process is endothermic, spontaneous and feasible. The mean free energy of adsorption shows that the mechanism is by physisorption. CPHAA was found to be an effective adsorbent for the removal of CR dye from aqueous solution.

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Introduction

Water pollution is one of the most serious ecological threats we face today that requires urgent solution. Water bodies are contaminated by organic and inorganic substances. Inorganic compound is the heavy metals and is classified under anthropogenic and natural sources of water pollution. Organic compounds pollutants include detergent, organochlorine, organophosphorous, polycyclic aromatic compounds, aromatic compounds from petroleum and dyes. Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Textile industry uses dyes and pigments to colour their product. There are more than 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff are produced annually (Robinson et al. 2001; Solomon et al. 2009; Baban, Yediler, and Ciliz 2010). The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibres and from the dyeing and finishing steps. Given the great variety of fibres, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity, which are not adequately treated in conventional wastewater treatment Plant (Wang et al. 2005). Dyes are classified into three broad categories: (1) anionic – direct, acid and reactive dyes; (2) cationic – all basic dyes; and (3) nonionic – dispersed dyes (Mishra and Tripathy 1993). Dyes usually have complex aromatic molecular structures, which make them more stable and difficult to biodegrade (Amin 2008a). Synthetic dyes, classified by their chromophores,

have different and stable chemical structures to meet various colouring requirement and are not often degraded or removed by conventional physical and chemical processes. Effluents from these industries must be treated to reduce the concentration of dyes present within permissible limits before discharge into water bodies, as required by environmental regulations (Namasivayam, Radhika, and Suba 2001; Bhattacharyya and Sharma 2004; Aksu 2005). Coming to term with the menace of pollution has been a major worry for the dyers in face of increasing pressure from strict environmental laws. Dyes are moderately resistant to light and oxidation agents, thus they cannot be completely removed by the conventional methods of anaerobic digestion (Seshadri, Bishop, and Agha 1994). Methods used to treat colour effluents are coagulation and flotation (Panswed and Wongehaisuwan 1986), ozonation (Malik and Saha 2003), membrane separation (Ciardelli, Corsi, and Marucci 2000) and adsorption by activated carbon (DeoMall et al. 2005). However, the single conventional treatment is unable to remove certain forms of colour, particularly those arising from reactive dyes as a result of their high solubility and low biodegradability (Vijayaraghavan, Won, and Yun 2009). The adsorption process is an attractive alternative treatment for dye removal from wastewater and is employed mainly for its efficiency and economy (Namasivayam, Yamuna, and Jayanthi 2003; Gurses et al. 2006). Activated carbon is the most common adsorbent for the removal of many organic contaminants. Commercial activated carbons are expensive and therefore, there is a need to search for effective adsorbents for

economical wastewater treatment. Utilising wastes and biowastes of the environment as adsorbents for the removal of dyes from wastewater is of interest. Different materials such as coconut coir, bagasse pith, rice husk, neem tree leaves and orange peel have been used to prepare carbon from agricultural wastes as low-cost adsorbent materials for the removal of dyes from wastewater (bamboo-based activated carbon) Hameed, Ahmad, and Aziz 2007; activated palm ash (Hameed, Din, and Ahmad 2007a); palm shell (Adinata, Wan Daud, and Aroua 2007); durian peel (Hameed and Hakimi 2008); ackee apple (Bello, Auta, and Ayodele 2013), guava leaf (Ojedokun and Bello 2017a), corn cob (Ojedokun and Bello 2017b).

In this study, Cocoa pod husk (CPH), a nonconventional agricultural waste material, which forms over 70% (w/w) of the whole matured cocoa fruit, i.e. over 700 kg of waste per each ton of cocoa fruit, is a major by-product from cocoa industry but is currently under-utilised. In Nigeria, more than 1.5 million tons of CPH are wasted annually, and some of the CPH is used as organic fertilizer, soap making and animal feed production (Bello and Ahmad 2012). Disposal of agricultural wastes like Cocoa pod husk is a problem for the farmers, and dumping of Cocoa pod husks without scientific methodology of management is a source for mosquito growth (Chethana 2014). However, to further utilise this cheap and abundant agricultural waste, CPH was converted to activated carbon for the removal of Congo red (CR) dye from aqueous solution.

Materials and methods

Adsorbate

The adsorbate used in this study is Congo red (CR) dye. It is the sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid; molecular formula, $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight, 696.66 g/mol; CI number, 22 120; λ_{max} , 497 nm. It is a secondary diazo dye. CR was obtained from M/s Merck, and its solution was prepared by dissolving accurately weighed the amount of dye in distilled water. Different concentrations (20–100 mg/L) were prepared by serial dilution with distilled water.

Preparation of activated carbon from cocoa pod husk

Cocoa pod husks were collected from cocoa farms in three locations within Ogbomoso metropolis (8°07'N, 4°16'E) in south-western part of Nigeria where they were deposited as a waste agricultural product. They were thoroughly washed with distilled water to remove dust and other impurities and dried under the sun until constant weight was attained. Dried Cocoa pod husks were ground, sieved into different sizes and stored in an airtight plastic container and labelled as CPHR for further use. A carefully weighed 25.0 ± 0.01 g grounded cocoa pod husk was placed in a beaker containing 500 cm³ of 0.3 mol/dm³ ortho-phosphoric acid (H_3PO_4). In the present study, we prepared ACs from CPH by activation with H_3PO_4 , the optimum CPH/PA weight/volume ratio allowing complete activation of CPH was evidenced when 25.0 ± 0.01 g grounded CPH impregnated with 500 cm³ of 0.3 mol/dm³ ortho-phosphoric acid (H_3PO_4). The best yield was obtained using this weigh/volume ratio. Alteration in the ratio of CPH/PA did not produce

good yield during pyrolysis (Fierro et al. 2005). Hence, this ratio was used for the acid activation. Ortho-phosphoric acid (PA), H_3PO_4 is a common activating agent whose use has been extensively reported for preparing activated carbons from agricultural products (Diao, Walawender, and Fan 2002; Girgis and El-Hendawy 2002; Vernersson et al. 2002; Guo and Lua 2003). PA promotes bond cleavage in the biopolymers and dehydration at low temperatures. This process results in extensive cross-linking that binds volatile matter into the carbon products, leading to increase in carbon yield. Benaddi et al. (1998) showed that the mechanism of PA activation of biomass feedstock occurs through various steps: cellulose de-polymerisation, biopolymer dehydration, formation of aromatic rings and elimination of phosphate groups. This produces activated carbon with good yields and high surface areas. Activation conditions thus depend on the nature of the precursor, i.e. on the relative amounts of cellulose, hemicelluloses, lignin and ashes.

The content of the beaker was thoroughly mixed and heated until it formed a paste. The paste was then transferred to an evaporating dish, which was placed in a furnace and heated at 300 °C for thirty minutes. This was allowed to cool and washed with distilled water to a pH of 6.78, oven dried at 105 °C for 4 h to constant weight. It was then ground to a powder with a 106 nm mesh to obtain a fine powdered fluted activated carbon, which was kept in airtight plastic container and labelled as CPHAA for further use.

Characterisation of CPHAA

Fourier Transform Infrared

Fourier transform infrared (FTIR) spectroscopic analysis was performed (FTIR-2000, Perkin Elmer). The FTIR spectra give information about the characteristic functional groups on the surface of the sample. The spectra were measured from 4000 to 400 cm⁻¹. The surface morphology of the samples was examined using a scanning electron microscope (SEM; Model VPFESEM Supra 35VP). Elemental analysis of both raw- and acid-activated cocoa pod husks were carried out by energy dispersive X-ray (EDX) to determine the component elements present in the samples.

Batch equilibrium method

Batch adsorption process of Congo red dye removal from its aqueous solution was carried out by agitating 0.1 g of CPHAA with 100 mL of various concentrations of CR dye solution in 250 mL conical flasks. This was done by setting the samples into a water bath shaker, and the samples were shaken for 5 h at 303, 313 and 323 K, respectively, until equilibrium was reached. About 10 mL of the supernatants was taken using a syringe and analysed using UV-visible spectrophotometer (model A Analyst 800; Perkin Elmer) at a wavelength of 497 nm to determine the amount of CR dye adsorbed on cocoa pod husk. The amount of CR dye removed was calculated using Equations (1).

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

where q_e is the amount of CR dye adsorbed, C_0 is the initial dye concentration, C_e is the initial dye concentration at equilibrium,

V is the volume of adsorbate used (dm^3) and W is the weight of the adsorbent (g).

Effect of initial CR dye concentration, contact time and solution temperature

In order to study the effect of initial dye concentration and contact time on CR dye uptake, 100 mL of CR dye solution with initial concentrations of 20–100 mg/L was prepared in a series of 250-mL Erlenmeyer flasks. An equal mass of 0.10 g of CPHAA was added to each flask, covered with glass stopper, and the flasks were placed in an isothermal water bath shaker (Model Protech, Malaysia) at 303 K and a rotation speed of 120 rpm until equilibrium was reached. The effect of solution temperature on the CR dye adsorption process was examined by varying the adsorption temperature to 303, 313 and 323 K by adjusting the temperature controller of the water bath shaker.

Batch kinetic studies

For the batch kinetic studies, the same procedure was followed, but the aqueous samples were taken at preset time intervals. The concentrations of CR dye were similarly measured. The CR dye uptake at any time, q_t (mg/g), was similarly calculated.

Results and discussion

Characterization of adsorbent

Energy Dispersive X-Ray

Elemental analysis of CPHAA is shown in Table 2. Elemental analyses of the samples were carried out using energy dispersive X-ray to determine the component of elements present. Tables 1 and 2 show the various elements present in CPHR and CPHAA samples, respectively. Table 2 shows the presence of C, O, Mg and K; carbon has the highest percentage weight when compared with other elements present in the sample. The high percentage weight of carbon is an indication that cocoa pod husk is a good and suitable precursor for preparing activated carbon. It was also observed that there is an increase in the weight percentage of carbon content from 60.55 to 80.53% and a decrease in oxygen content from 29.86 to 13.02% comparing CPHR and CPHAA. This was as a result of activation using H_3PO_4 and carbonisation at 300 °C for thirty minutes (Tables 1 and 2).

Scanning Electron Micrograph

Scanning electron micrograph (SEM) of CPHR and CPHAA is shown in Figures 1(a) and (b), respectively. From these figures, it is clear that CPHR surface was rough and the pores were not properly developed, whereas, in Figure 1(b), there are several pores formed on the CPHAA. This shows that H_3PO_4 was

effective in creating well-developed pores on the surface of the precursor, thus, leading to activated carbon with large surface area and porous surface structure. These pores provided a good surface for CR dye to be trapped and adsorbed (Amin 2008a, 2008b).

FTIR analyses

Table 3 shows the spectra of both raw- and acid-activated cocoa pod husk. In Table 3 (CPHR), the band at 3253 cm^{-1} is assigned to O–H stretching of alcohol or carboxylic group, and that at 2919 cm^{-1} is assigned to C–H stretching of an alkane. A sharp absorption at 1603 cm^{-1} is assigned to C=C stretching of aromatic, and a broad absorption at 1375 cm^{-1} is assigned to C–H bending of an alkane. A sharp prominent absorption at 1023 cm^{-1} is also assigned to C–O stretching vibration of ether. In the CPHAA spectrum, some of the functional groups have shifted to lower wave number (O–H stretching of alcohol, C–H stretching of alkane and C=C stretching of aromatic) or higher wave number (C–H bending of alkane and C–O stretching vibration of ether). These are due to the result of high temperature in activation process that broke some intermolecular bonds, i.e. forces holding molecules together (Gong et al. 2005; Tan, Ahmad, and Hameed 2008). The changes in spectra confirm the effect of the acid activation resulting in a reduction, broadening, disappearance or appearance of new peaks after acid activation (Figures 2 and 3).

Effect of contact time initial CR dye concentration and solution temperature

Effect of contact time

The effect of contact time on CR dye adsorption onto CPHAA at different concentrations is shown in Figure 4. The particle size of the sample used is 106 nm. CR dye adsorption increases as the initial concentration increases. Figure 4 shows that the adsorption of CR dye was in two phases: (1) an initial rapid phase in which adsorption capacity increased sharply within the first 150 min due to rapid surface adsorption (external surface adsorption) and (2) a slower phase whose contribution to the total amount of dye adsorption was relatively small (internal surface adsorption) (Rais and Rajeev 2010). Adsorption equilibrium was achieved within 240 min, after which the amount of dye adsorption becomes negligible. At the beginning, the adsorption rate was fast as the dye ions were adsorbed by the external surface of the activated carbons. When the adsorptions of the external surface reached saturation, the dye molecules are trapped in the pores of the adsorbent particles and were adsorbed by the internal surface of the particle. This phenomenon takes a relatively long contact time. (Chang and Juang 2005; Mall et al. 2005).

Table 1. Energy dispersive X-ray percentage elemental composition of CPHR.

Elem	Wt %	At %	K-Ratio	Z	A	F
C	60.55	70.38	0.3987	1.0139	0.6494	1.0002
O	29.86	26.06	0.0575	0.9970	0.1930	1.0000
Mg	0.64	0.37	0.0040	0.9570	0.6431	1.0006
K	8.95	3.19	0.0827	0.9040	1.0231	1.0000
Total	100.00	100.00				

Table 2. Energy dispersive X-ray percentage elemental composition of CPHAA.

Elem	Wt %	At %	K-Ratio	Z	A	F
C	80.53	86.81	0.4156	1.0074	0.5122	1.001
O	13.02	10.54	0.0222	0.9906	0.1720	1.0000
Al	0.34	0.16	0.0026	0.9232	0.8445	1.0028
Si	0.56	0.26	0.0049	0.9503	0.9235	1.0046
P	4.69	1.96	0.0414	0.9113	0.9697	1.0004
Ca	0.86	0.28	0.0081	0.9193	1.0207	1.0000
Total	100.00	100.00				

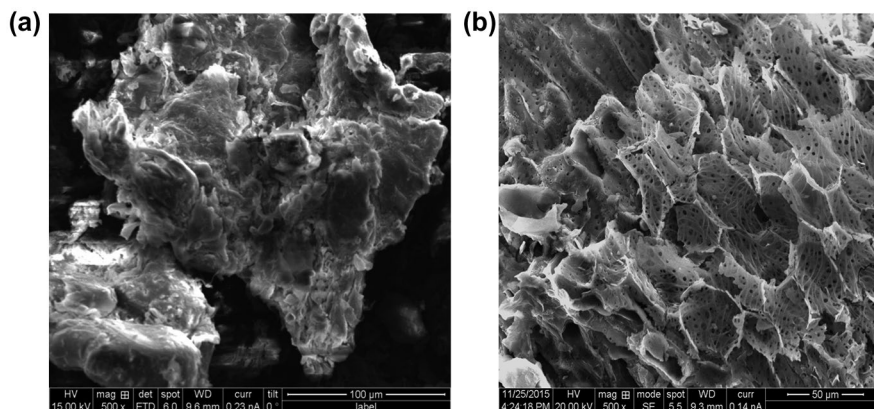


Figure 1. SEM micrographs of (a) CPHR (magnification = 500×) and (b) CPHAA (magnification = 500×).

Table 3. FTIR spectra characteristics of raw and acid activated Cocoa pod husk (CPH).

I.R Peaks	Wave numbers (cm ⁻¹)			Band assignments
	CPHR	CPHAA	Differences	
1	3253	3238	-15	O-H stretching vibration of alcohol or carboxylic acid
2	2919	2910	-9	C-H stretching of alkane
3	1603	1602	-1	C=C stretching vibration of aromatic
4	1375	1436	+61	C-H bending of alkane
5	1023	1073	+50	C-O stretching vibration of ether

Effect of initial CR dye concentration

Five different concentrations, 20, 40, 60, 80 and 100 mg/L, were selected to investigate the effect of CR dye concentration on CPHAA and CPHR, respectively. As shown in Figure 4, with increasing initial dye concentrations from 20 to 100 mg/L, the amount of dye adsorbed by CPHAA increases from 13.14 to 37.2 mg/g. The amount of CR dye adsorbed is a function of the initial concentration of the adsorbate. The adsorption of CR dye is fast at the initial stage and then becomes slower near equilibrium. This is as a result of a large number of vacant surface sites that are available for adsorption during the initial stages, after some time, the remaining vacant surface sites are difficult to occupy because of repulsive forces between the CR dye adsorbed on the surface of CPHAA and the solution phase. It is evident that the adsorption process is highly dependent on the initial dye concentration of the solution.

Solution temperature

The increase in the equilibrium adsorption of CR dyes on CPHAA with temperature shown in Figure 5 revealed that higher temperature favours CR dye removal via adsorption onto CPHAA. As temperature increases, the mobility of dye molecules increases. Increased mobility of as a result of increased temperature results

in higher CR dye adsorption (Alkan and Dogan 2003; Hameed, Ahmad, and Aziz 2007).

Effect of pH on CR dye adsorption

The pH of the aqueous solution is an important controlling parameter in the adsorption process (Jain and Sikarwar 2014). The effect of initial solution pH on the adsorption of CR from aqueous solution was investigated in the pH range between 3.0 and 9.0 (which was adjusted with 0.1 M HCl or 0.1 M NaOH). As shown in Figure 6, when the pH was varied from 3 to 10, the percentage adsorption decreased from 96.4 to 28.2%. The maximum adsorption of CR dye was observed at pH 3.0 (96.4%). At pH 3.0, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye resulting in the higher amount of dye adsorbed. As the pH of the system increases, the number of negatively charged sites increases, and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of the dye anions due to the electrostatic repulsion. Similarly, lower adsorption at higher pH may be due to the abundance of OH⁻ ions, causing ionic repulsion between the negatively charged surface and the anionic dye molecules. Therefore, there are no more exchangeable ions on the outer surface of the adsorbent at higher pH due to increase the number of negatively charged sites. This brings about electrostatic repulsion; consequently, there is a decrease in percentage dye adsorption (28.2%). Similar trends were reported for the adsorption of the dye using different adsorbents (Vijayakumar et al. 2009; Torkian et al. 2012; Munagapati and Kim 2016).

Kinetics of CR dye adsorption

Pseudo-first-order kinetic model

The model assumes that the rate of change the adsorption of solute with time is proportional to the difference in saturation concentration and the amount of solid uptake with time (Lagergren and Svenska 1898). It is generally expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

The values of k_1 and q_e can be obtained from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ vs. t .

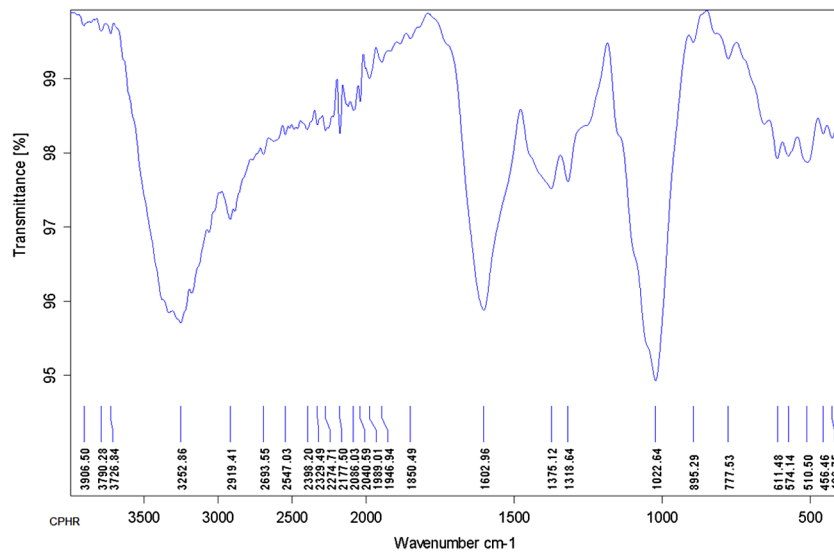


Figure 2. FTIR of spectrum CPHR.

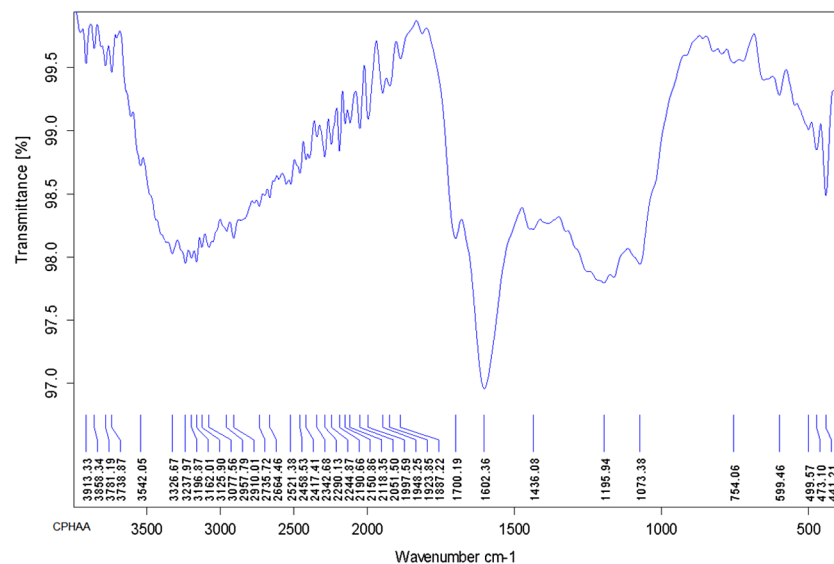


Figure 3. FTIR spectrum of CPHAA.

Pseudo-second-order kinetic model

The pseudo-second-order kinetic model (Ho and McKay 1999) is based on the adsorption capacity onto a solid phase. It is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

The slope and intercept of the plot of t/q_t vs. t give the values of q_e and k_2 , respectively.

The pseudo-first-order kinetic model was used to test the adsorption data. A plot of $\ln(q_e - q_t)$ against t at various concentrations and temperatures resulted in linear graphs with negative slopes (figure not shown). k_1 and q_e are calculated from the slopes and intercepts, respectively. The pseudo-second-order equation was also used to test the adsorption data. Plots of t/q_t vs. t gave linear graphs from which q_e and k_2 were estimated from the slopes and intercepts of the plot (Figure 7) for temperatures

ranging from 303 to 333 K. The values of the regression coefficient calculated (Table 4) from the second-order kinetic plots show that it has the highest R^2 value, best fitted with the experimental data and can be used to describe the adsorption of CR dye onto CPHAA.

The Elovich model

The Elovich equation is suitable in describing the kinetics of adsorption on heterogeneous solids. The Elovich model (Aharoni and Ungarish 1976) is expressed by Equation (4):

$$q_t = \left(\frac{1}{\beta} \right) \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (4)$$

where α is the initial sorption rate (mg/g min), β is the extent of surface coverage and activation energy for chemisorption (g/mg), The slope and intercept of the plot of q_t vs. $\ln t$ can be used

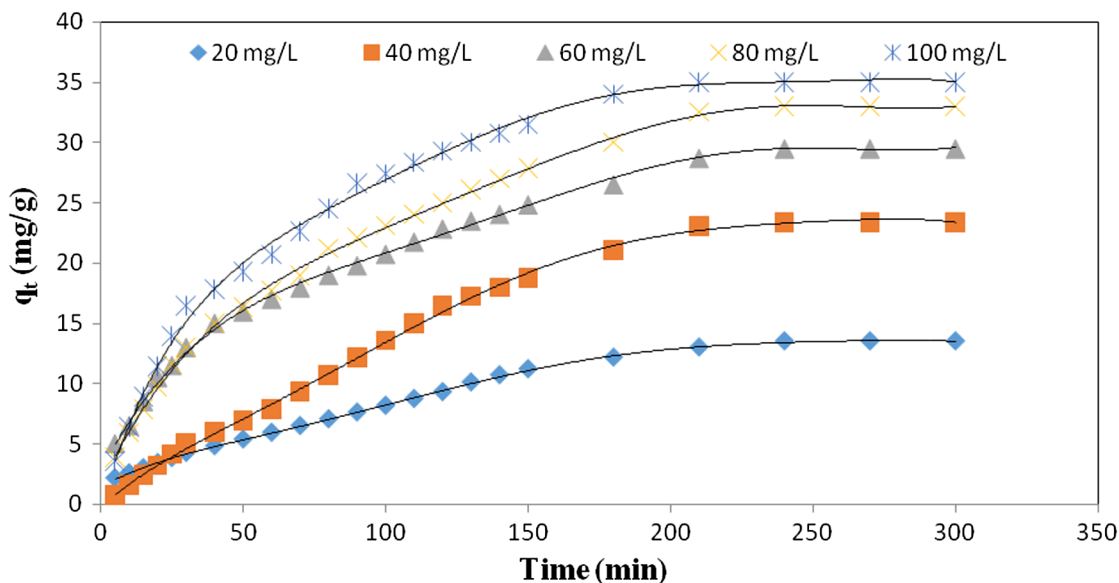


Figure 4. Effect of initial dye concentration on the adsorption of CR dye by CPHAA at 50 °C.

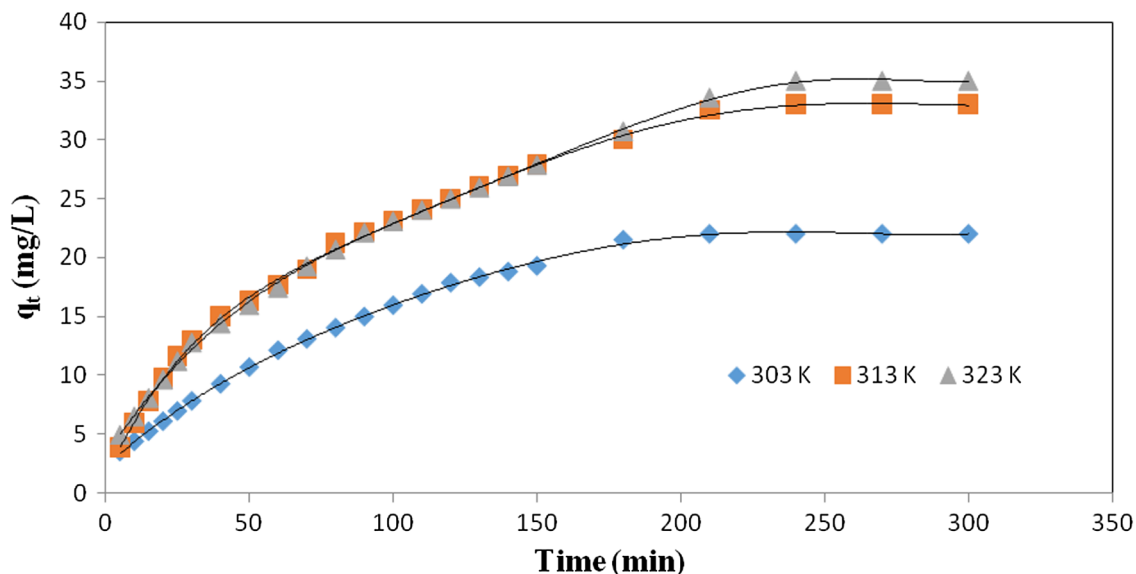


Figure 5. Effect of solution temperature on the adsorption of 100 mg/L CR dye onto CPHAA.

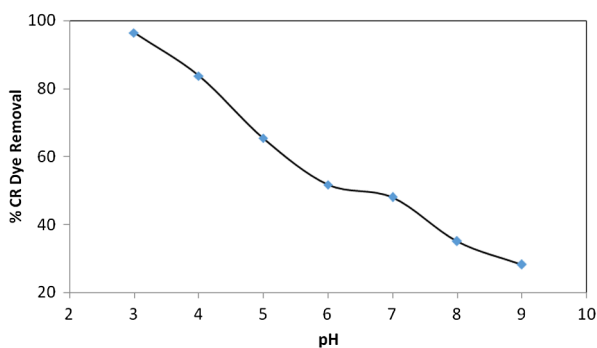


Figure 6. Percentage of CR dye adsorbed at different pH.

to calculate the values of the constants α and β , respectively. Adsorption data were also tested using Elovich model (plot of q_t vs. $\ln t$) yields a linear relationship with a slope of $1/\beta$ and intercept of $(1/\beta) \ln(\alpha\beta)$ (figure not shown). The slope and intercept were used to calculate the values of the constants α and β as shown in Table 4. There was increased in initial adsorption rate α and decreased in desorption constant β with an increase in initial dye concentration. A similar result was reported by Bello and Ahmad (2012).

Intraparticle diffusion model

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental

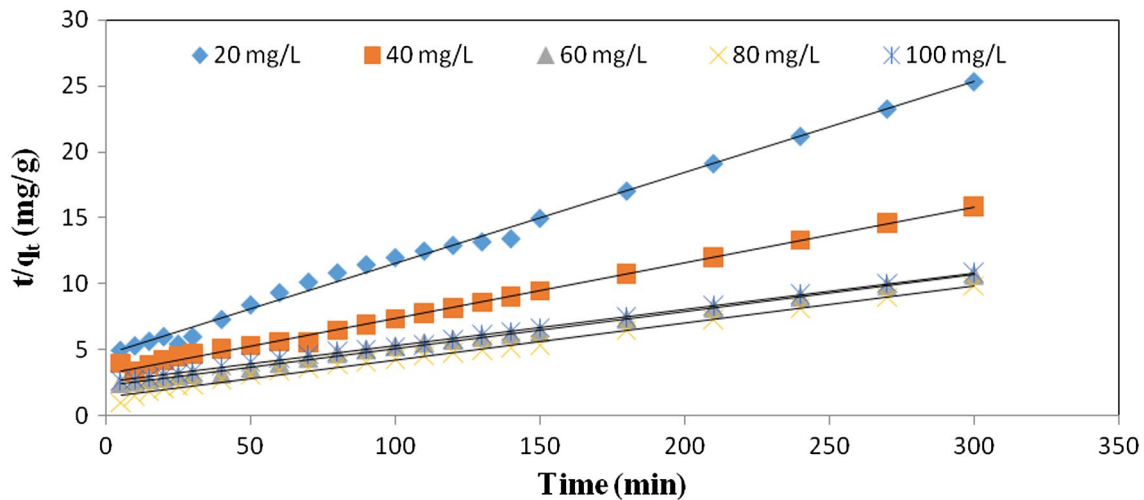


Figure 7. Plot of pseudo-second-order kinetic model for CR dye adsorption onto CPHAA at 50 °C.

Table 4. Parameters of different kinetic models of CR dye adsorption onto CPHAA at 50 °C.

Kinetic models	Parameter	Initial dye concentration				
		20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L
Pseudo-first-order	k_1 (min ⁻¹)	0.007	0.011	0.007	0.009	0.007
	$q_{e(cal)}$ (mg/g)	11.95	24.70	26.02	31.22	35.91
	$q_{e(exp)}$ (mg/g)	14.5	24.80	31.15	35.00	36.99
	R^2	0.982	0.988	0.989	0.991	0.989
Pseudo-second-order	$k_2 \times 10^{-4}$ (g/mg min)	30.354	4.315	3.353	4.743	2.86
	$q_{e(cal)}$ (mg/g)	14.71	24.39	35.71	35.71	37.04
	$q_{e(exp)}$ (mg/g)	14.5	24.80	31.15	35.00	36.99
	R^2	0.994	0.996	0.998	0.993	0.998
Elovich	a (mg/g min)	0.3549	0.5630	0.8531	1.0258	0.6872
	B	0.2236	0.1140	0.1111	0.0954	0.0789
	R^2	0.938	0.986	0.969	0.980	0.948
Intra-particle	k_{diff} (mg/g min ⁻¹)	0.8717	1.8912	1.9424	2.3208	2.4545
	C	0.1491	-3.3029	0.0012	-0.3771	-4.6104
	R^2	0.979	0.993	0.996	0.999	0.992

results were fitted to Weber's intraparticle diffusion (Weber and Morris 1963). It is expressed as:

$$q_t = k_{diff} t^{1/2} + C \quad (5)$$

where q_t is the amount of the adsorbate adsorbed at time t , k_{diff} is the intraparticle diffusion rate constant (mg/g min^{1/2}), C is the intercept. The kinetic results were analysed by the intraparticle model to elucidate the diffusion mechanism. The values of q_t correlated linearly with the values of $t^{1/2}$ (Figure not shown), and the rate constant k_{diff} was directly evaluated from the slope of the regression line. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step. The calculated intraparticle diffusion coefficient k_{diff} values are listed in Table 4. If the regression of q_t vs. $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin. This indicates that there is an initial boundary layer resistance, and the intraparticle diffusion was not only a rate controlling step. The deviation from the origin or near saturation might also be due to the difference in the mass transfer rate in the initial and final stages of adsorption (Mohanty, Das, and Biswas 2005).

Adsorption isotherms

The Langmuir equation is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites and with the negligible interaction between adsorbed molecules. The linearised form of Langmuir adsorption model (Langmuir 1916) is expressed as

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o K_L} \quad (6)$$

where C_e is the dye concentration in the solution at equilibrium (mg/L), q_e is the dye concentration on the adsorbent at equilibrium (mg/g), q_o is the monolayer adsorption capacity of adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L mg⁻¹). A plot of C_e/q_e vs. C_e gave a straight line with a slope $1/q_o$ and an intercept of $1/q_o K_L$ (Figure 8a). The R^2 values for the Langmuir isotherm, when compared with the Freundlich, Tempkin and other isotherms, indicate that the adsorption of CR dye onto CPHAA fits the Langmuir isotherm most. Values of q_o and K_L are calculated from linear plots (figure not shown) and reported in Table 5. Table 6 shows that CPHAA is a promising adsorbent for CR dye. The value of q_o obtained was compared

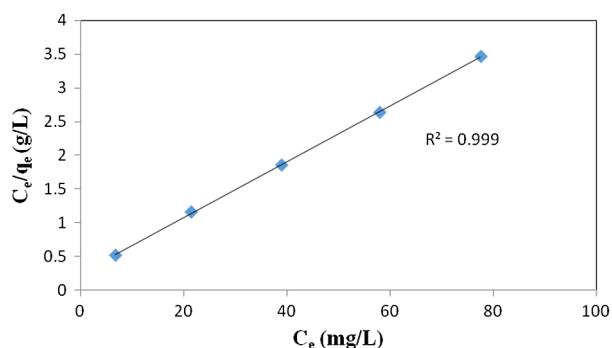


Figure 8a. Langmuir isotherm plot for the adsorption of CR dye on CPHAA at 50 °C.

Table 5. Isotherm model statistical parameters for the adsorption of CR dye onto CPHAA at different temperatures.

Models	Temperature (K)		
	303	313	323
<i>Langmuir isotherm</i>			
q_0 (mg/g)	24.21	42.55	43.67
R_L	0.057	0.120	0.102
K_f (L/mg)	0.073	0.110	0.165
R^2	0.9998	0.9999	0.9999
<i>Freundlich isotherm</i>			
K_f (mg/g)	8.835	6.654	7.986
n	4.441	2.402	2.579
R^2	0.96	0.96	0.97
<i>Temkin isotherm</i>			
K_T (mol/g)	0.587	0.675	0.892
b_T (mol/kJ)	0.641	0.274	0.286
R^2	0.979	0.994	0.995
<i>D-R isotherm</i>			
q_0 (mg/g)	21.41	31.79	33.30
β (mol ² /K ²)	4.2312	6.367	4.252
R^2	0.938	0.930	0.918
E_0 (kJ/mol)	0.3438	0.2802	0.3429

Table 6. Comparison of the maximum monolayer adsorption capacities of CR dye onto various adsorbents.

Adsorbent	q_0 (mg/g)	References
Activated carbon (laboratory grade)	1.88	Mall et al. (2005)
Aspergillus niger biomass	8.19	Fu and Viraraghavan (2002)
Bagasse fly ash	11.89	Mall et al. (2005)
Coir pith	6.70	Namasivayam and Kavitha (2002)
Neem leaf powder	41.20	Bhattacharyya and Sharma (2004)
Acid-activated red mud	7.08	Tor and Cengeloglu (2006)
Aniline propylsilica xerogel	22.62	Pavan et al. (2008)
4-Vinyl pyridine grafted poly(ethylene) terephthalate fibres	18.1	Arslan (2010)
Cashew nut shell	5.184	Kumar et al. (2010)
Montmorillonite	12.7	Wang and Wang (2007)
Cocoa pod husk acid activated	43.67	This work

with values for other adsorbents (Table 6). Table 6 compares the maximum monolayer coverage of CR dye onto different adsorbents. The reason why the value obtained for CPHAA is higher than others is inherent in the porosity and the surface area of the adsorbent. The pores are well developed (Figure 1(b)), resulting in increased surface area which enhances higher adsorption.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant, R_L called equilibrium parameter. The nature of the adsorption process could be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values obtained here are listed in Table 5. The fact that all the R_L values for the adsorption of CR onto CPHAA are in the range 0.057–0.120 shows that the adsorption process is favourable. A similar result was obtained for the adsorption of CR dye onto ackee apple seed (Bello, Auta, and Ayodele 2013).

The linearised form of Freundlich model is expressed as (Freundlich 1906).

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), k_f and n are constants incorporating the factors affecting the adsorption capacity and the degree of nonlinearity between the solute concentration in the solution and the amount adsorbed at equilibrium, respectively. Plots of $\log q_e$ vs. $\log C_e$ gave linear graphs (Figure 8b) with high R^2 values. Comparing the R^2 values with those obtained from Langmuir isotherms, the adsorption data do not fit the Freundlich isotherm well (Table 5). Values of k_f and n obtained from the slopes and intercepts of the graph reported in Table 5 shows the different isotherm parameters, as well the possibility of multilayer adsorption of CR dye through the percolation process; values of $n > 1$ indicate that the adsorption is favourable.

The Temkin isotherm model has been developed on the concept of chemisorption. It assumes that the heat of adsorption of the molecules of the adsorbate linearly decreases with adsorbent layer coverage due to adsorbate–adsorbent interactions. The Temkin model (Temkin and Pyzhev 1940) is expressed as:

$$q_e = B(\ln K_T C_e) \quad (8)$$

This can then be further rearranged to:

$$q_e = B \ln K_T + B \ln C_e \quad (9)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), $B = RT/b_T =$ constant related to the heat capacity (L/mg), R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), K_T is the equilibrium binding constant (L/mg), C_e is the equilibrium concentration of adsorbate (mg/L).

A plot of q_e vs. $\ln C_e$ for the Temkin isotherm yields a linear graphs (Figure 8c). The constants K_T and b_T are shown in Table 5. K_T increase as the temperature increases, inferring that the adsorbate interaction with adsorbent increased with increasing temperature, hence, a higher rate of sorption was observed as energy increases. A similar trend was reported by Bello and Ahmad (2012).

The Dubinin-Radushkevich (Dubinin and Radushkevich 1947) is expressed as:

$$q_e = q_0 \exp(-B\varepsilon^2) \quad (10)$$

where

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (11)$$

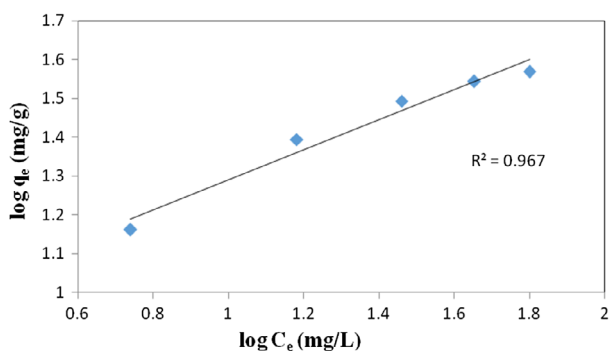


Figure 8b. Freundlich isotherm plot for the adsorption of CR dye on CPHAA at 50 °C.

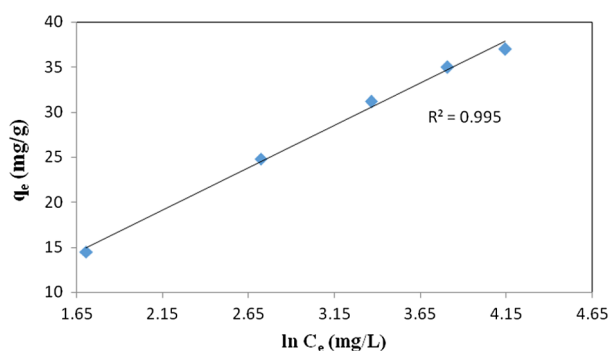


Figure 8c. Temkin isotherm plot for the adsorption of CR dye on CPHAA at 50 °C.

where q_e is the amount of adsorbate adsorbed at equilibrium, q_o is the maximum adsorption capacity, B is the Dubinin-Radushkevich constant, R is the universal gas constant, T is the absolute solution temperature, C_e is the equilibrium concentration of adsorbate. Therefore, a plot of $\ln q_e$ against ξ^2 will give a straight line with slope of B and intercept of $\ln q_o$ (Figure 8d). Also, from the value of B , the free energy of sorption per molecule of the adsorbate, E_a , can be determined by using the equation:

$$E_a = \frac{1}{\sqrt{2B}} \quad (12)$$

The adsorption energy E_a helps in determining the nature of adsorption. The adsorption is physical if E_a ranges from 1 to 8 kJ/mol. If the value of E_a ranged between 9 and 16 kJ/mol, it is

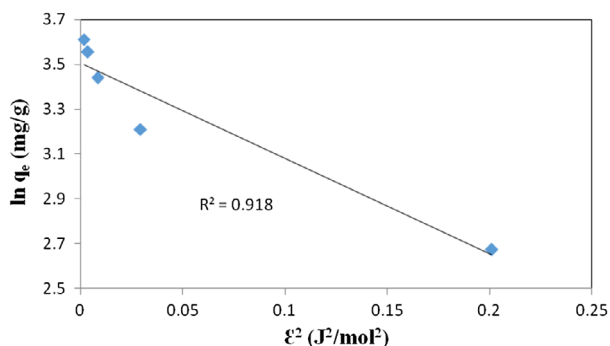


Figure 8d. D-R isotherm plot for the adsorption of CR dye on CPHAA at 50 °C.

chemical adsorption. As presented in Table 5, the value of E_a lies in the range 0.18–0.34 kJ/mol. Since $E_a < 8$ kJ/mol, it suggests that the adsorption mechanism is physical in nature (Onyango et al. 2004).

Adsorption thermodynamics

Thermodynamic parameters are used to reveal the energy changes that occur in an adsorption process. In order to investigate the adsorption process, three thermodynamic parameters were evaluated. They include: standard enthalpy change (ΔH°), standard entropy change (ΔS°) and standard free energy change (ΔG°). These values can be calculated by using Equation (13):

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

where K_L is the Langmuir adsorption constant (L/mg), ΔS° is the change in standard entropy (kJ/mol K), R is the universal gas constant (8.314 J/mol K), ΔH° is the change in standard enthalpy (kJ/mol K), T is the absolute temperature (K). Hence, a plot of $\ln K_L$ against $1/T$ yields the values of both ΔH° and ΔS° from the slope and intercept of the graph, respectively. Fundamentally, a positive ΔH° value indicates that an adsorption process is endothermic in nature while a negative value represents exothermic reaction. A positive value of ΔS° signifies an increase in randomness at the solid/solution interface that occurs in the adsorption process besides reflecting the affinity of the adsorbent towards the adsorbate. Furthermore, a negative ΔG° value indicates that an adsorption process is a spontaneous process at the study temperature and vice-versa. ΔG° can be calculated using the following relation:

$$\Delta G^\circ = -RT \ln K_L \quad (14)$$

The calculated values of ΔH° , ΔS° and ΔG° are listed in Table 7. The Van't Hoff plot (Equation (13)) for the adsorption of CR dye onto CPHAA gave linear graphs (Figure 9). As shown in Table 7, the negative values of ΔG° indicated the feasibility of the process

Table 7. Thermodynamic parameters for the adsorption of CR dye adsorption onto CPHAA at different temperatures.

Temp (K)	K_L (L/mg)	$K_L \times 10^4$ (L/mol)	ΔG° (kJ/mol)	ΔH°_{ads} (kJ/mol)	ΔS° (kJ/mol K)	E_a (kJ/mol)
303	0.073	5.09	-27.30	33.57	0.20	36.09
313	0.110	7.69	-29.28			36.17
323	0.165	11.5	-31.29			36.26

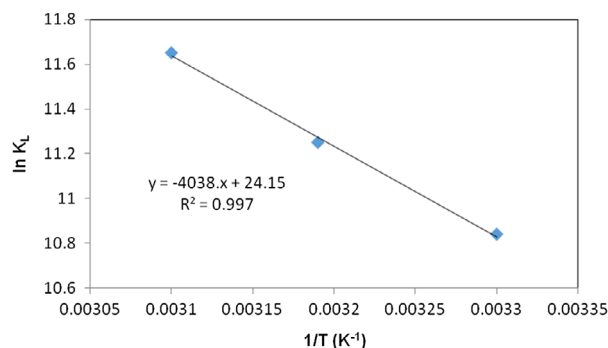


Figure 9. Van't Hoff plot of CR dye adsorption onto CPHAA.

and the spontaneous nature of the adsorption with a high preference of CR dye onto the prepared activated carbon. Values of ΔH° and ΔS° were positive, showing that the adsorption process is endothermic and there was increased randomness between the adsorbent/adsorbate interfaces during the adsorption of CR dye onto CPHAA.

Conclusions

The present investigation shows that activated carbon prepared from cocoa pod husk was a promising adsorbent for the removal of Congo red dye from aqueous solutions over a wide range of concentrations. FTIR, SEM and EDX revealed the adsorptive features of this novel adsorbent. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms, and the equilibrium data were best described by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 43.67 mg/g at 50 °C. The adsorption performance of the cocoa pod husk acid activated was comparable to the commercial activated carbon and some other adsorbents reported in earlier studies. The adsorption kinetics was found to follow closely the pseudo-second-order kinetic model. The negative value of free energy change indicated the spontaneous nature of sorption. The positive values of ΔH° indicated that the adsorption process was endothermic in nature. The mean free energy obtained from D–R isotherm showed that the adsorption process is physically controlled. Results from this study have shown that cocoa pod husk can be used as a low-cost, readily available and easily prepared sorbent for the effective removal of CR dye from aqueous solution.

Disclosure statement

No potential conflict of interest was reported by the authors.

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