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## ORIGINAL ARTICLE

# Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution



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## KEYWORDS

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**Abstract** Adsorption of methylene blue from aqueous solution onto coconut coir dust (CCD) a low cost agricultural waste material in a batch process was investigated. Adsorption was studied as a function of amount of adsorbent, pH and concentration with time. It was found that percentage adsorption varied linearly with the amount of adsorbent and concentration with time but varies non-linearly with pH. Adsorption equilibrium data were represented by isotherm, kinetics and thermodynamics models. Three isotherm models namely Langmuir, Freundlich and Temkin were tested and adsorption was found to fit well into these models with  $R^2 \geq 0.90$ . The kinetic data were well described by the pseudo-second order kinetic model. The adsorption process was endothermic with a mean change in enthalpy ( $\Delta H$ ) ( $+17.87 \text{ KJ mol}^{-1}$ ) and spontaneous with a mean free energy change ( $\Delta G$ ) ( $-9.69 \text{ KJ mol}^{-1}$ ). FTIR analyses of the adsorbent suggest that adsorption of the dye was through a chemical interaction of the functional groups on the surface of the adsorbent. © 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Removal of dye from effluents of chemical industries such as plastics, dyestuffs, textile, pulp and paper has remained a problem of increasing concern to the environmentalists. It is estimated that 2% of dyes produced annually are discharged as effluents from manufacturing operations whilst 10% are discharged from textile and associated industries (Easton, 1995). Most of these dyes are of synthetic origin and toxic in nature with suspected carcinogenic and genotoxic effects (Chatterjee

et al., 2005; Daneshvar et al., 2007). The presence of these dyes even at a very low concentration is highly observable and undesirable. Therefore dye removal has been a very important but challenging area of wastewater treatment (Hu et al., 2006). The effluents containing dyes are highly coloured and cause serious water pollution. Many health related problems such as allergy, dermatitis, skin irritation, cancer, and mutations in humans are associated with dye pollution in water (Bhattacharyya and Sharma, 2004). Today there are more than 100,000 dyes with different chemical structures available commercially (Robinson et al., 2001). Dyes are broadly classified as anionic, cationic and non-ionic depending on the ionic charge on the dye molecules. Cationic dyes are more toxic than anionic dyes (Hao et al., 2000). From the environmental stand point, it is challenging to treat dye effluents because of their synthetic origins and their mainly aromatic structures, which are biologically non-degradable and may be toxic to health. In order to remove dye from industrial effluents, several processes have

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been adopted by researchers worldwide. Among several chemical and physical methods available, the adsorption process is one of the effective techniques that have been successfully employed for colour removal from wastewater.

Several adsorbents have shown good promise for dye removal from wastewater. Activated carbon is an effective but expensive adsorbent due to its high costs of manufacturing. Similarly polymers have proven to be efficient in dye adsorption due to their high regeneration capacity but lack economy in terms of cost. In view of these many natural adsorbents have been tested to reduce dye concentrations from aqueous solutions (Deniz and Saygideger, 2011; Yagub et al., 2011). Among the natural materials used as adsorbents for synthetic dyes, biomass and agricultural wastes are considered to be low-cost products. They have proved very efficient for dye removal from waste water due to high ligno-cellulose material which is part of their constituent (Annadurai et al., 2002; Chen et al., 2011; Sen et al., 2011; Wang and Yan, 2011). These wastes are renewable, available in large amounts and less expensive as compared to other materials used as adsorbents. They are better than other adsorbents because the agricultural wastes are usually used without or with a minimum of processing (washing, drying, grinding) and thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment (Franca et al., 2009). Different low cost sorbents have been explored by various researchers for dye removal from wastewater. These include Palm kernel fibre (El-Sayed, 2011), rice husk (Gupta et al., 2006; Lakshmi et al., 2009), sawdust (Batzias and Sidoras, 2007; Khattri and Singh, 2009), tea waste (Uddin et al., 2009), peanut shell (Tanyildizi, 2011), orange peels (Khaled et al., 2009; Arami et al., 2008), wheat shell (Bulut and Aydin, 2006), pineapple stem (Hameed et al., 2009), and coconut based sorbent; babassu coconut mesocarp (Vieira et al., 2009), coconut husk (Jain and Shrivastava, 2008; Low and Lee, 1990; Gupta et al., 2010), coconut shell fibre (de Sousa et al., 2010; Babel and Kurniawan, 2004), coconut copra meal (Ho and Ofomaja, 2006), coconut coir pith (Namasivayam et al., 2001), coconut bunch waste (Hameed et al., 2008) to mention a few.

In the extraction of coir fibre from the coconut husk and in the production of finished materials from the extracted fibre, a large amount of coir dust is produced. Coconut coir dust is described as that brown, spongy particle of low weight which falls out when the fibre is shredded from the husk. The coir dust is about 70% of the weight of the coconut husk (Tejano, 1985). Coir dust is rich in lignins and tannins. It is reported to be composed of cellulose, pentosan, furfural, and lignin (Gonzales, 1970; Joachim, 1930). Whilst a great deal has already been learned about the solid parts of the coconut, coir dust has, up to now, the least use and is still considered waste and nuisance for which no important industrial uses have been developed, and they are normally incinerated or dumped without control (Meerow, 1997; Vidhana Arachchi and Somasiri, 1997). It is known to have no commercial importance except, may be, in applications where sawdust is used in a very limited amount. However, in an effort to find an immediate solution to the perennial problem of coir dust disposal, several product development activities were undertaken that may bring about large scale utilization of this waste material. For sometime, coir dust was used in the tropics as a locally available material for preparing soilless growing media for containerized crop production (Reynolds, 1973; Chweya et al., 1978). Only during

the past few years has this material become commercially popular and it is now being successfully used in different parts of the world as an environmentally sound peat substitute for container-grown ornamental plants (Offord et al., 1998; Noguera et al., 1998).

Researchers who have utilized coconut-based adsorbents for water treatment used them in modified forms as reported in a review work by Bhatnagar et al. (2010). The present study is undertaken to investigate the efficiency of raw coconut coir dust (without physical/chemical modification or activation) as a low cost adsorbent for the removal of methylene blue from aqueous solution. The effect of contact time, concentration of the dye, amount of adsorbent, pH and temperature on MB adsorption was studied. Adsorption isotherm and kinetics parameters were also evaluated, presented and discussed.

## 2. Experimental methods

### 2.1. Materials

The adsorbent, coconut (*Cocos nucifera* L.) coir dust was obtained from a local coconut processing mill in Ukanafun Local area of Akwa Ibom State. Methylene blue (MB) was purchased from Smerck fine chemicals, Onitsha, Nigeria. MB has molecular formula  $C_{16}H_{18}N_3ClS$  (Mol. wt. 319.85 g/mol). It was used without further purification. Other reagents include concentrated  $H_2SO_4$  and dilute NaOH solutions. All reagents were of analytical grade. De-ionized water was used throughout the experiment. Instruments employed for the work include UV-visible spectrophotometer (Unicam He $\lambda$ 105 model), FTIR spectrophotometer (model 8400S), electric (platform shaker 20-880), mottle P165 weighing balance, pH-meter-16, and 10 ml clinical syringe and sieves of about 50–100 $\mu$ m size.

### 2.2. Preparation of adsorbent

Coconut coir dust was soaked in de-ionized water for 3 days and washed several times with water until all the coloured extract was removed and clean water obtained. It was oven dried at 60 °C for 24 h. It was sieved using a 50–100  $\mu$ m sieve to obtain particles in this range. This was stored in a plastic container prior to use for adsorption studies. No chemical or physical treatments were performed prior to adsorption experiments.

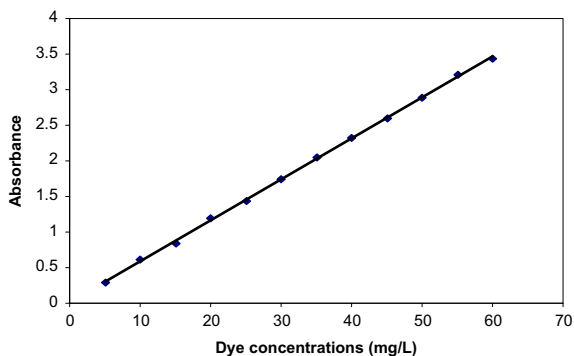
### 2.3. Preparation of adsorbate

The dye stock solution was prepared by dissolving 1.0 g of dye in deionized water in a 1 litre volumetric flask and made to a concentration of 1 g L<sup>-1</sup>. The working solutions were obtained by diluting the dye stock solution in accurate proportions to needed initial concentrations (5–60 mg L<sup>-1</sup>) and were used to obtain a calibration curve (Fig. 1).

### 2.4. Adsorption experiments

#### 2.4.1. Time optimization

For the optimization of shaking time, 50 mL of aqueous solutions 50 mg L<sup>-1</sup> of methylene blue was taken in a 250 ml conical flask and a fixed amount of adsorbent (0.1 g) was added. The absorbance of the residual dye solution was recorded at  $\lambda_{max}$  (650 nm) at different time intervals. It was observed that



**Figure 1** Standard curve of methylene blue at concentration range from 5 to 60 mg L<sup>-1</sup> at room temperature.

the adsorption of dye increased with increasing shaking time and attained a constant value at equilibrium after a specific time (20 min). It was also observed that the uptake of the dye was fast at the initial stages of contact time and thereafter becomes slower near equilibrium and reached a steady value at equilibrium.

#### 2.4.2. Adsorption process

Batch adsorption experiments were carried out in 250 mL flasks and the total volume of the reaction solution was kept at 50 mL. The flasks were shaken at 200 rpm for an equilibrium time of 20 min on a mechanical shaker. The effect of adsorbent dosage on the removal of MB was studied with different adsorbent dosages (0.05–0.20 g) in a 50 mL dye solution of 20 mg L<sup>-1</sup> concentration, pH 6.0 and shaken till equilibrium time. The effect of pH on the removal of MB was investigated over the pH range of 2.0–10.0 with 0.1 g of the adsorbent for 20 min in a dye solution concentration of 20 mg L<sup>-1</sup>. The initial solution pH was adjusted using 0.1 M H<sub>2</sub>SO<sub>4</sub> or 0.1 M NaOH. Effect of contact time and initial concentration was studied by shaking 0.10 g of the adsorbent at ambient temperature and pH of 6.0 at different time intervals and different initial concentrations. Adsorption kinetic experiments were done by contacting 0.10 g of adsorbent with 50 mL of MB aqueous solution of (10–50) mg L<sup>-1</sup> in a series of 250 mL flasks, maintained at ambient temperature and optimum conditions. The flasks were taken out at some intervals. After adsorption, the adsorbent and the supernatants were separated by centrifugation at 4000 rpm for 10 min and samples for analyses (5 mL) withdrawn with a clinical syringe and analysed for residual dye concentration using a UV–Visible Spectrophotometer by monitoring the absorbance changes at λ<sub>max</sub> 650 nm. The amount of dye adsorbed per gram of adsorbent (*q<sub>e</sub>*) is given as:

$$q_e = \frac{V}{m}(C_o - C_e) \quad (1)$$

and the percentage removal (*R*) was calculated using Eq. (2)

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where *C<sub>o</sub>* and *C<sub>e</sub>* are the initial and equilibrium MB concentrations, respectively (mg L<sup>-1</sup>), *V* is the MB solution volume (L), *m* is the mass of the adsorbent (g).

The effects of temperature on the adsorption data were studied by performing the adsorption experiments at various

temperatures (30, 40, 50 and 60 °C) with 0.1 g of the adsorbent and other conditions remaining constant. The equilibrium data were analysed using the Langmuir, Freundlich and Temkin isotherms and the characteristic parameters for each isotherm were determined.

#### 2.5. Spectral analyses

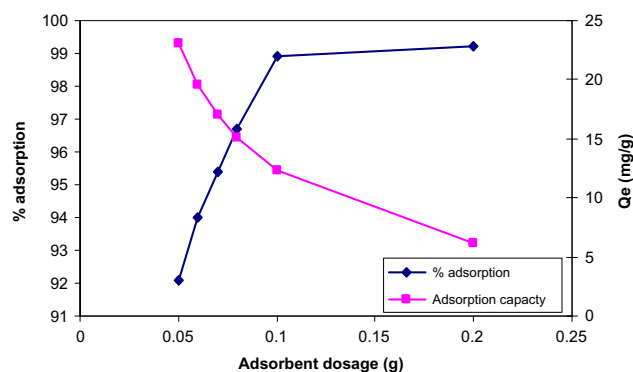
The spectra of raw CCD and dye loaded CCD were recorded by a FTIR spectrophotometer (FTIR 8400S) in the range of 4500–500 cm<sup>-1</sup> using a KBr disc containing 1% of finely ground sample. The mixture was pressed into a KBr wafer under vacuum conditions and used as such for IR studies.

### 3. Results and discussion

#### 3.1. Effect of operational variables on dye removal

##### 3.1.1. Adsorbent dosage

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution. The effect of coconut coir dust (CCD) dosages on the amount of dye adsorbed was investigated by contacting 50 mL of dye solution with an initial dye concentration of 50 mg L<sup>-1</sup> for the adsorbent, for a contact time of 20 min at a temperature of 27 ± 0.5 °C, a shaking speed of 200 rpm and optimum pH of 6.0. Different amounts of adsorbents (0.05, 0.06, 0.07, 0.08, 0.1 and 0.2 g) were added. After equilibrium, the samples were allowed to settle for some time after which the supernatant solutions were collected and analysed. Fig. 2 shows the effect of adsorbent dosages on the dye removal by CCD. The percentage of dye removal increased with an increase in adsorbent dosage. For instance an increase from 92.1% to 99.5% was observed when the dosage increased from 0.05 to 0.20 g. When the adsorbent dosage was doubled from 0.10 to 0.20 g, dye removal was only 0.3% indicating that adsorption was almost complete with 0.10 g of the adsorbent. The increase in adsorption with adsorbent dosage can be attributed to an increase in the adsorption surface and availability of more adsorption sites (SenthilKumar et al., 2010). However, if the adsorption capacity was expressed in mg g<sup>-1</sup> of material, the capacity decreased with increasing



**Figure 2** Effect of adsorbent dosage on the adsorption of MB onto CCD at room temperature; pH = 6.0; 20 mg/L<sup>-1</sup>; stirring speed = 200 rpm and time = 20 min.

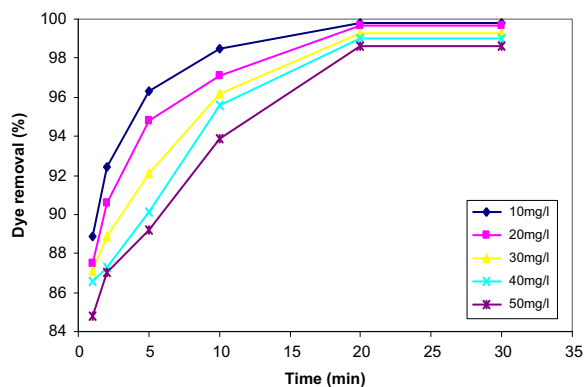
amount of adsorbents. This may be explained as a result of overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorption surface area available to the dye and an increase in the diffusion path length. A similar trend was reported by El-Sayed (2011) in his studies of removal of methylene blue and crystal violet from aqueous solution by palm kernel fibres.

### 3.1.2. Initial dye concentration/time effect

The percentage of dye removal is highly dependent on the initial amount of dye concentration. The effect of the initial dye concentration factor depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface. Generally the percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface (Salleh et al., 2011) and the adsorption capacity increased with an increase in the initial concentration of the dye. At low concentrations there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will not be available (Kannan and Sundaram, 2001). The effect of the initial concentration of MB/time of adsorption on the percentage of dye removal is given in Fig. 3. It was found that more than 80% of the dye was removed in the first minute of adsorption and increased slowly to maximum at equilibrium. Also, the percentage of adsorption decreased with an increase in the initial concentration and increased as the contact time prolonged. However, the increase in the initial dye concentration caused an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial dye concentration (Bulut and Aydin, 2006). In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of the initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of the initial concentration.

### 3.1.3. Effect of pH

pH factor is very crucial in adsorption studies especially dye adsorption. The pH of a medium controls the magnitude of electrostatic charges which are imparted both by the ionized

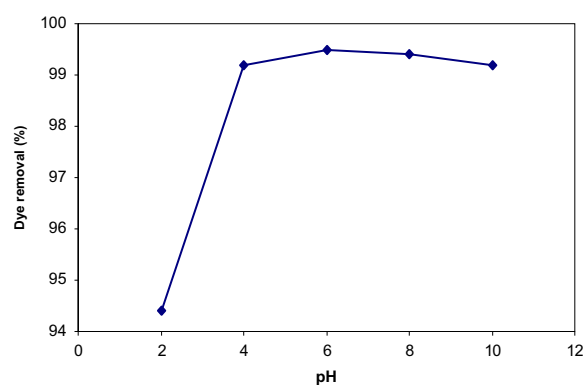


**Figure 3** Time/concentration effect of MB adsorption onto CCD at room temperature; dosage = 0.1 g; pH = 0.6; and stirring speed = 200 rpm.

dye molecules and the charges on the surface of the adsorbent. As a result, the rate of adsorption will vary with the pH of an aqueous medium (Önal et al., 2006). Fig. 4 shows the effect of pH on the adsorption efficiency of coconut coir dust. Percentage dye removal increased from 94.4 at pH 2.0 to 99.2 at pH 6.0. This value is close to the neutral pH and can therefore not be assumed as adsorption at low pH. However, percentage adsorption had a slight difference up to pH 10.0. Similar observations have been reported for the adsorption of methylene blue (El-Sayed, 2011; Ponnusami et al., 2009). Lower adsorption of MB at highly acidic pH may be due to the presence of excess  $H^+$  ions competing with dye cations and the functional groups such as the amine ( $NH_2^+$ ) group in CCD for the adsorption sites (SenthilKumar et al., 2010). As the solution pH increased, the number of negatively charged surface sites on the adsorbent increased, which may result in the increase in adsorption of cationic dye molecules due to the electrostatic attraction (Amin, 2009). The percentage adsorption had only a slight change when pH was within the range of 4–10 (Fig. 4), which indicated that the electrostatic mechanism was not the only mechanism for dye adsorption in the solution but was also affected by the chemical reaction between the adsorbent and dye molecules (Al-Degs et al., 2008).

### 3.2. Adsorption isotherms

Adsorption isotherm provides important models in the description of adsorption behaviour. It describes how the adsorbate interacts with the adsorbent and offers explanation for the nature and mechanism of the adsorption process. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of adsorbate molecules between the solid phase and the liquid phase (Tan et al., 2008). Equilibrium isotherm data obtained from the different models provide important information on adsorption mechanisms and the surface properties and affinities of the adsorbent (Santhi et al., 2010). Therefore it is essential to establish the most appropriate correlation of equilibrium curves to optimize the conditions for designing adsorption systems. In this present work, Langmuir, Freundlich and Temkin isotherms were employed to investigate the adsorption behaviour and was found that all three could be used to explain adsorption behaviour.



**Figure 4** pH effect of Methylene blue adsorption onto CCD at room temperature, adsorbent dosage = 0.1 g; time = 20 min; initial dye concentration = 50 mg  $L^{-1}$  and stirring speed = 200 rpm.

First, the Langmuir isotherm model proposed by Langmuir (1916) is based on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. It explains monolayer adsorption which lies on the fact that the adsorbent has a finite capacity for the adsorbate i.e. at equilibrium; a saturation point is attained where no further adsorption can occur. The equation below shows the Langmuir isotherm expressions:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

This can be linearized to:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (4)$$

where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g),  $q_{\max}$  is the theoretical maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $K_L$  is the Langmuir isotherm constant ( $\text{L mg}^{-1}$ ). The values of  $K_L$  and  $q_{\max}$  can be determined from the slopes and intercepts of the linear plots of  $C_e/q_e$  against  $C_e$  (Fig. 5). The values of  $R^2$ ,  $K_L$  and  $q_{\max}$  are listed in Table 1 from the Langmuir isotherm. The value of  $q_{\max}$  obtained in the present study is within the range of the values reported in the literature for the adsorption of MB onto various agricultural wastes as listed in Table 2. Values of  $K_L$  increase as the temperature increases which indicates an increase in the binding forces of the adsorbate onto the adsorbent.

Second, the Freundlich isotherm model is another most widely applied isotherm in explaining adsorption. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules. It assumes that adsorption energy exponentially decreases on the completion of the sorptional centres in the adsorbent (Crini and Badot, 2008). The Freundlich equation is given as:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where  $q_e$  is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g),  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ),  $K_F$  is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ ) and  $n$ , a dimensionless constant, which can be used to explain the extent of adsorption and the adsorption intensity between the solute concentration and adsorbent respectively. A linear form of the Freundlich equation is generally expressed as:

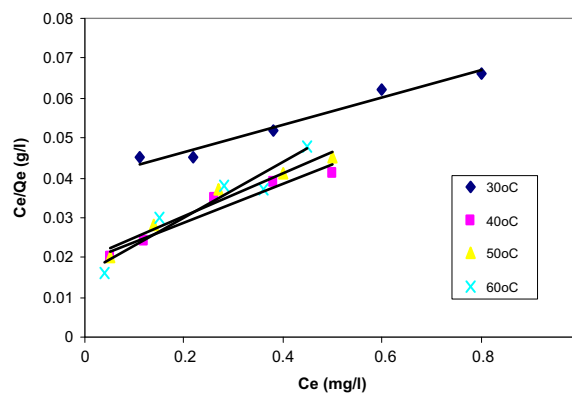


Figure 5 Langmuir isotherm plots for the adsorption of MB onto CCD at different temperatures.

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (6)$$

The values of  $K_F$  and  $n$  are calculated from the intercepts and slopes of the plot of  $\log q_e$  versus  $\log C_e$ . Fig. 6 shows the Freundlich plots and the isotherm parameters derived from Freundlich plots are listed in Table 1. It is evident from the table that the value of  $n$  is greater than one for the adsorption of the dye at all temperatures and decreases with increase in temperature. This explains that the amount of dye adsorbed increased with a rise in temperature (Iqbal and Ashiq, 2007). The larger value of  $K_F$  for the dye adsorption as the temperature increased suggests enhanced adsorption at high temperatures and further confirmed the endothermic nature of the adsorption process.

The Temkin isotherm model takes into account adsorbent–adsorbate interactions (Temkin and Pyzhev, 1940). This model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The linear form of Temkin isotherm is given as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (7)$$

where  $B_1$  is the Temkin constant related to the heat of adsorption and is given as:  $B_1 = \frac{RT}{b}$ , where  $B_1$  is related to the heat of adsorption.  $K_T$  is the equilibrium binding constant ( $\text{L mg}^{-1}$ ). The values of  $K_T$  and  $B_1$  obtained from the intercepts and

Table 1 Isotherm parameters for the adsorption of Methylene blue onto CCD.

Isotherm model	Parameters	Temperature (°C)			
		30 ± 0.5	40 ± 0.5	50 ± 0.5	60 ± 0.5
Langmuir	$q_{\max}$ ( $\text{mg g}^{-1}$ )	29.50	21.14	20.41	20.16
	$K_L$ ( $\text{L mg}^{-1}$ )	0.85	2.31	2.18	2.26
	$R^2$	0.968	0.938	0.960	0.922
Freundlich	$K_F$ ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ )	13.62	22.83	23.45	27.41
	$n$	1.37	1.17	1.11	1.00
	$R^2$	0.98	0.90	0.95	0.97
Temkin	$K_T$	14.75	17.42	15.70	14.42
	$B_1$	4.43	5.38	5.59	6.08
	$R^2$	0.99	0.96	0.98	0.96

**Table 2** Maximum monolayer adsorption capacities of different agricultural waste towards Methylene blue.

Adsorbents	Monolayer adsorption capacity (mg/g)	References
Pine leaves	126.58	Yagub et al. (2011)
Pine cone biomass of <i>Pinus radiata</i>	109.89	Sen et al. (2011)
Raw beech sawdust	9.78	Franca et al. (2009)
Palm kernel fibre	95.4	El-Sayed (2011)
Wheat shell	16.56	Bulut and Aydin (2006)
Coir pith carbon	5.87	Kavitha and Namasivayam (2007)
Thermally activated coconut activated carbon	20.62	Sharma and Uma (2009)
Orange peel	18.6	Annadurai et al. (2002)
Cocoa waste	1.21	McKay et al. (1986)
Oak saw dust	29.94	Ferrero (2007)
Raw coconut coir dust	29.50	Present study

slopes of the plots of  $q_e$  versus  $\ln C_e$ , respectively (Fig. 7) are summarized in Table 1. From the table, the values of  $K_T$  were not regular and cannot be used to predict the behaviour of the dye in terms of heat energy.  $B_1$  increases as the temperature increases and has reached the maximum at 60 °C which indicates the endothermic reaction proposed earlier by the Freundlich model in the present study.

All the three isotherm models showed a good correlation coefficient with the experimental data ( $R^2 > 0.90$ ) (Table 1), which suggests that the adsorption data obtained in the present

study could be said to fit the three isotherm models. However, Temkin isotherm had the highest correlation coefficient range ( $R^2$ : 0.96–0.99), thus could be considered as the best of the models although others can also be used to account for the adsorption process. Reports of fit of adsorption experimental data to more than one isotherm can be found in the literature (Santhi et al., 2010; Wang and Yan, 2011; Malana et al., 2010).

### 3.3. Adsorption equilibrium kinetics

The dynamics of the adsorption can be studied by the kinetics of adsorption in terms of the order of the rate constant (Gómez et al., 2007). In order to design a fast and effective model, investigations were made on adsorption rate using pseudo first order and pseudo second order kinetic models. The pseudo-first order model though has a good correlation coefficient for dye concentrations  $> 10 \text{ mg L}^{-1}$  with experimental data has deviated from theory since it fails to predict the amount of dye adsorbed (Crini and Badot, 2008).

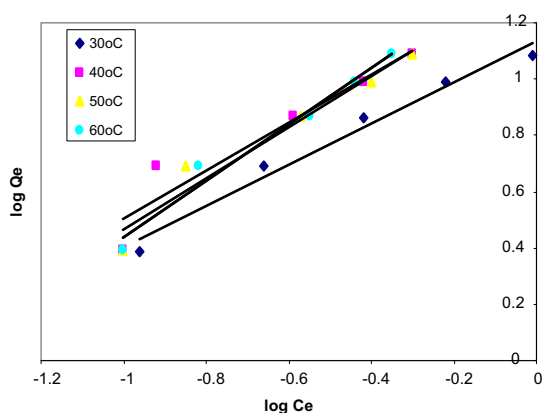
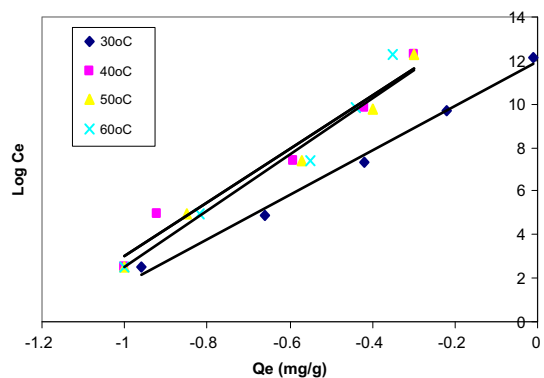
The pseudo second order model is based on the adsorption capacity (as pseudo first order) and predicts the behaviour for the adsorption process for all dye concentrations. It can also be used to predict chemisorption processes. The pseudo second order kinetic model is represented with the expression (Ho and McKay, 1998):

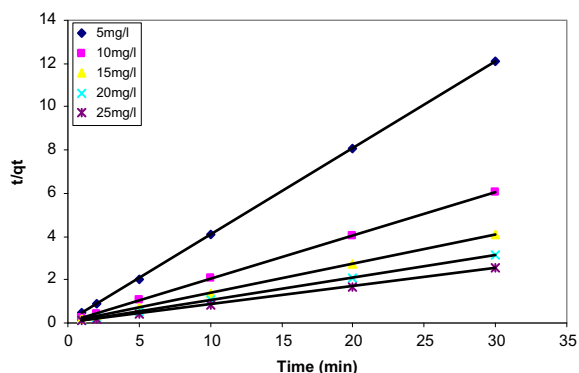
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where  $k_2$  is the rate constant of pseudo-second order adsorption ( $\text{g mg}^{-1} \text{ min}^{-1}$ ). Fig. 8 shows pseudo-second order plots for the adsorption process for five different concentrations of the dye.  $K_2$  and  $q_e$  values were determined from the intercepts and slopes of the linear plots respectively. Table 3 shows the pseudo-second order kinetic data for the adsorption of MB onto CCD. Values of the experimental data obtained showed negligible difference with that of theory. The correlation coefficient ( $R^2$ ) value for the dye concentration range studied was unity indicating a perfect fit of the process to the second-order kinetic model and its applicability in explaining adsorption data. The initial adsorption rate is given as:

$$h = k_2 q_e^2 \quad (9)$$

The increase in values of the initial adsorption rates ( $h = 19.64, 25.79, 35.75, 40.91$  and  $107.62 \text{ mg/g min}$ ) for ( $C_0 = 10, 20, 30, 40$  and  $50 \text{ mg/L}$ ) respectively with an increase in the initial dye concentration could be attributed to

**Figure 6** Freundlich isotherm plots for the adsorption of MB onto CCD at different temperatures.**Figure 7** Temkin isotherm plot for the adsorption of MB onto CCD at different temperatures.



**Figure 8** Pseudo-second order kinetic plot for the adsorption of MB onto CCD.

the increase in the driving force for mass transfer, allowing more dye molecules to reach the surface of the adsorbents in a shorter period of time (Ho and McKay, 1998; Ho and McKay, 1998).

### 3.4. Thermodynamic studies

The values of thermodynamic parameters including change in the enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), and Gibbs free energy ( $\Delta G$ ) obtained from the experimental data can be used to predict the feasibility of the adsorption process. In the present study, the effect of temperature on adsorption was studied at four different temperatures (30, 40, 50 and 60 °C) and for five different concentrations of the dye.  $\Delta H$  and  $\Delta S$  were obtained from the slopes and intercepts of the linear plots of  $\log K_L$  against  $1/T$  (not presented) in the linear expression (Eq. (10)):

$$\text{Log } K_L = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (10)$$

where  $K_L = \frac{q_e}{C_e}$ , and is the equilibrium constant obtained for each temperature from the Langmuir model,  $R$  is the molar

gas constant (8.314 J/mol K);  $T$  is the absolute temperature. The values of Gibbs free energy ( $\Delta G$ ) were calculated using the equations:

$$\Delta G = -RT \ln K_L \quad (11)$$

The obtained thermodynamic parameters are given in Table 4. Positive  $\Delta H$  suggests an endothermic reaction. Similarly a positive value of  $\Delta S$  suggests the increased randomness at the solid/liquid interface during the adsorption process so that increased entropy induces the replacement of hydrated dye ions for water molecules around adsorbent particles (Messina and Schulz, 2006). Similar results of adsorption of dyes onto different adsorbents with a positive change in entropy and enthalpy have been reported (Kavitha and Namasivayam, 2007; Zhong et al., 2011; Kuo et al., 2006). The negative values of  $\Delta G$  imply the spontaneous nature of the adsorption process. Further, the decrease in the values of  $\Delta G$  with a rise in temperature indicates that the adsorption is more spontaneous at higher temperatures. The enthalpy change in the ranges of 20–40 kJ/mol and 80–400 kJ/mol, indicates physisorption and chemisorption respectively (Bansal and Goyal, 2005). The values of  $\Delta H$  obtained in this study (Table 4) are within the ranges of the physisorption mechanism (14.97–25.69 kJ/mol).

### 3.5. Spectral analyses

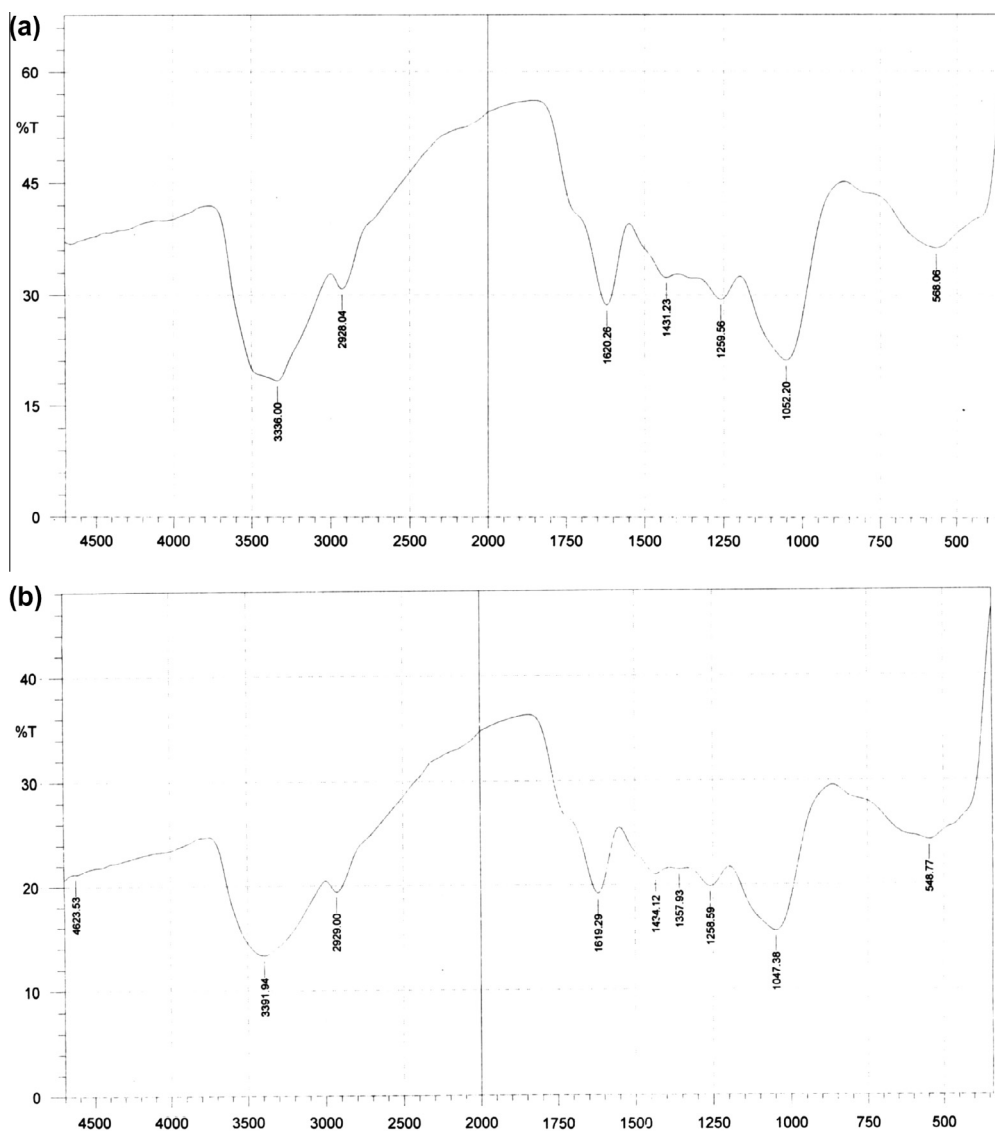
FTIR spectroscopy provides structural and compositional information on the functional groups presented in the samples. The functional groups present in the proximate composition of the CCD were investigated by Fourier transform infrared (FTIR) spectroscopy. Fig. 9(a) and (b) shows IR spectra of raw CCD and dye loaded CCD respectively. The adsorption capacity of adsorbents depends upon porosity as well as chemical reactivity of functional groups at the surface. This reactivity creates an imbalance between forces at the surface when compared to those within the body, thus leading to molecular adsorption by the van der Waals force (SenthilKumar et al., 2010). The adsorption spectra displayed a number of

**Table 3** Kinetic parameters for the adsorption of Methylene blue onto CCD.

Conc. of dye (mg g <sup>-1</sup> )	$q_{e, \text{exp}}$ (mg g <sup>-1</sup> )	Pseudo-first order			Second-order order		
		$K_1$ (min <sup>-1</sup> )	$q_e, \text{cal}$ (mg g <sup>-1</sup> )	$R^2$	$K_2$ (g/mg min)	$q_e, \text{cal}$ (mg g <sup>-1</sup> )	$R^2$
10	2.48	0.29	0.24	0.74	3.41	2.49	1.00
20	4.94	0.20	0.63	0.99	1.04	4.98	1.00
30	7.31	0.25	1.08	0.98	0.66	7.36	1.00
40	7.63	0.31	1.71	0.92	0.69	7.70	1.00
50	11.84	0.33	1.54	0.95	0.76	11.90	1.00

**Table 4** Thermodynamic parameters for the adsorption of Methylene blue onto CCD.

Conc. of dye (mg L <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )			
			30 ± 0.5 °C	40 ± 0.5 °C	50 ± 0.5 °C	60 ± 0.5 °C
10	25.69	112.2	-7.80	-10.15	-10.47	-11.43
20	18.40	55.3	-7.80	-9.68	-9.56	-9.66
30	17.73	51.1	-7.43	-8.69	-8.89	-9.05
40	12.55	65.6	-7.03	-8.46	-8.59	-9.16
50	14.97	73.0	-6.83	-8.33	-8.59	-9.16



**Figure 9** FTIR spectra of (a) raw coconut coir dust and (b) dye loaded coconut coir dust.

absorption peaks, indicating the complex nature of the CCD. The exhibition of broad band at  $3391.94\text{ cm}^{-1}$  is an indication of the presence of the stretch vibration of bonded hydroxyl groups on the coconut coir dust. The broad absorption peak at  $2929\text{ cm}^{-1}$  is evidence of alkyl stretch vibration of  $-\text{CH}_3$ . The strong absorption peak at  $1619.29\text{ cm}^{-1}$  is attributed to the presence of conjugate C–C bond of diene. The vibration at  $1434.12\text{ cm}^{-1}$  is due to a possible C–C (in ring) stretching from an aromatic group. The strong band at  $1357.93\text{ cm}^{-1}$  is characteristic of weak vibration of the aliphatic N–O group. The existence of C–O of carboxylic acid groups gave rise to the peak at  $1258.59\text{ cm}^{-1}$ . The peak shown at  $1047.38\text{ cm}^{-1}$  is associated with the strong and broad band of C–O of zprimary alcohol and medium vibration of primary amine ( $-\text{NH}_2$ ) in the structure. The stretched adsorption peak at  $548.77\text{ cm}^{-1}$  could be assigned to the presence of alkyl halide (C–X) and disulphide groups. As presented in Fig. 9b, after adsorption, the non prominent peak at  $4623.53\text{ cm}^{-1}$  which could not be attributed to any functional group and the peak

at  $1357.93\text{ cm}^{-1}$  disappeared completely. However, all other peaks show a shift to a new wavelength which is an indication of the involvement of the functional groups in the adsorption process.

#### 4. Conclusion

Results obtained from this work revealed that coconut coir dust (CCD) is an effective low cost adsorbent for the removal of MB dye from aqueous solutions. The adsorbent had good adsorption capacity for methylene blue and showed strong adsorption as the initial concentration of the dye was increased. Adsorption parameters calculated from Langmuir, Freundlich and Temkin isotherms are useful for the explanation of the mechanisms of the adsorption process as indicated by the good linear correlation coefficient values. The adsorption kinetic data were best described by the pseudo-second order kinetic model. Thermodynamic studies show the adsorption process to be endothermic and spontaneous.



Adsorption capacity of CCD is found to be comparable to those of other agricultural waste materials hence CCD could find industrial applications for the treatment of industrial wastewater containing dyes.

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