The Performance of Coconut Husk and Shell for the Removal of Methyl Red from Aqueous Solution: Adsorption Equilibrium and Kinetic Study

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Abstract: Removal of methyl red from aqueous solution onto coconut husks and coconut shell, a low cost agricultural waste material in a batch process was investigated. Adsorption and removal was studied as a function of amount of adsorbent (0.02-0.08 g), pH (2.0-12.0) and initial concentration (200-800 mg L^{-1}). Adsorption data were modeled using Langmuir, Freundlich and Tempkin adsorption isotherm models. Equilibrium data of the biosorption process fitted very well into Langmuir isotherm model. The maximum adsorption capacity was approximately 71 mg g^{-1} for both coconut husks and coconut shell at an optimum pH 12. Adsorption kinetic was verified by pseudo-first order and pseudo-second order kinetic models. The results indicated that the dye uptake process followed the pseudo-second order which suggest that adsorption of the dye was through a chemical sorption. From the removal experiments, the results indicated that coconut husks and coconut shell could not effectively be employed as a low-cost adsorbent for the removal of basic dyes (methyl red) from aqueous solution as its removal is concentration dependent.

Key words: Adsorption, methyl red, coconut husk, coconut shell, equilibrium, isotherm, kinetics

INTRODUCTION

Removal of dye from effluents of chemical industries such a s 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 discharge from textile and associated industries. Most of these dyes are already known to be suspected carcinogenic and genotoxic to human and nature. The presence of these dyes even at very low concentrations is highly observable and undesirable. Thus, dye removal has been a very important and challenging task of wastewater treatment. Many health related problems such as allergy, dermatitis, skin irritation, cancer and mutations in humans are associated with dye pollution in water. They impart colour to water which is visible to human eye and therefore highly objectionable on aesthetic grounds. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem. Further the dyes have a tendency to sequester metal and may cause micro toxicity to fish and other organisms.

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods such as coagulation and flocculation, adsorption, ozonation, electrochemical techniques and fungal decolorization. Among these methods adsorption has gained favour in recent years due to proven efficiency in the removal of pollutants from effluents. Activated carbon as an adsorbent has been widely investigated for the adsorption of dyes but its high cost limits its commercial application. In recent years, there has been growing interest in finding inexpensive and effective alternatives to carbon such as rice husks, chitin, orange waste, lemon peel, raw barley straw, coconut coir pith, durian seed and etc., (Namasivayam *et al.*, 2001; Ho *et al.*, 2005; Azhar *et al.*, 2005; Ofomaja and Ho, 2007; Xue *et al.*, 2008; Lakshmi *et al.*, 2009; Tamez-Uddin *et al.*, 2009; Amin, 2009; Ahmad *et al.*, 2015).

Methyl Red (MR) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products. It may cause eye and skin sensitization and pharyngeal or digestive tract irritation if inhaled or swallowed. Furthermore, MR is mutagenic under aerobic conditions and it undergoes biotransformation into 2-aminobenzoic acid and N-N'-dimethyl-p-phenylene diamine. Of latter, there has been increasing interest to

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develop low-cost means of reducing amount as well as removing completely of MR in wastewater before being discharged into receiving water body (Ahmad *et al.*, 2015).

In Malaysia, coconut is the fourth important industrial crop after oil palm, rubber and paddy in terms of total planted area. It is also one of the oldest agro-based industries. As an industry, coconut contributes very little to the overall economy of Malaysia. However, coconut still plays an important role in the socio-economic position of the Malaysian rural population. About 63% of coconut production is for domestic consumption and 37% is for export and industrial processing. In terms of exports, the country has seen an increase in the export of end-products of coconut such as desiccated coconut, coconut milk powder and also activated carbon. As the husks and shells are readily available, we investigated the potential of such material in removing dyes from solution. Thus, in this study, the adsorption characteristics of methyl red-coconut husk system and methyl red-coconut shells system on a laboratory batch scale has been investigated. Parameters studied included adsorptive equilibrium as function of dye concentration, adsorbent dosage and pH as well as the adsorption kinetics study.

MATERIALS AND METHODS

The adsorbents, coconut (*Cocos nucifera* L.) husks and shell was obtained from a local coconut processing mill in Kuantan area of Pahang, Malaysia. Methyl red (MR) was purchased from Sigma Aldrich Ltd. Other reagents include Sodium Hyroxide (NaOH) and Hydrochloric acid (HCl). All reagents were of analytical grade. Deionised water was used throughout the experiment. Other instruments employed for the work include UV-visible spectrophotometer (Model DR5000), weighing balance and pH-meter.

Preparation of adsorbent: The coconut husks and shell were soaked in deionized water for 3 day and washed several times with water until all the colored extract was removed and clean water obtained. Both materials were oven dried at 80 and 120°C, respectively until a constant weight was obtained. The resulting material was ground and sieved using a 50-300 μm sieve to obtain particles in this range. These were stored in a plastic container prior to use for adsorption studies.

Preparation of adsorbate: Methyl Red (MR) dye was used as adsorbate to determine the adsorption performance of the prepared activated carbon. The properties of MR dye used are listed in Table 1.

Table 1: Properties of methyl red

Properties	Values
Chemical name	4-Dimethylamino azobenzene-2-carboxylic acid
Common name	Methyl red
Generic name	Acid red 2
CAS number	493-52-7
Color indexed number	25,019
Ionization	Acidic
Maximum wavelength	410 nm
Empirical formula	$C_{15}H_{15}N_3O$
Molecular weight	269.3 g mol^{-1}

The dye stock solution was prepared by dissolving 1.0 g of dye in deionised water in a 1 L volumetric flask and made to a concentration of 1 g L^{-1}. The working solutions were obtained by diluting the dye stock solution in accurate proportions to needed initial concentrations (50-100 mg L^{-1}) and were used to obtain a calibration curve.

Adsorption experiment

Adsorption capacity and removal efficiency of dye: Standard solution of methyl red in distilled water was prepared at 1000 mg L^{-1} concentrations and was subjected to spectrophotometer. Its absorbance value at 1000 mg L^{-1} concentration was recorded. The coconut husk and coconut shell granules weighing 0.1 g was first placed in glass centrifuge tubes. The 10 mL of a standard methyl red solution at a concentration of 1000 mg L^{-1} was added to the tubes. The mixtures were shaken continuously at 160 rpm in a controlled room temperature and left to settle before samples were taken after 30 and 60 sec, 15 and 30 min, 1-5, 12 and 24 h, respectively. The concentrations of methyl red in the samples were measured using UV-Visible spectrophotometer. The adsorption capacity and removal efficiency of methyl red by coconut husk and coconut shell activated carbons could be expressed as follows:

$$AC = \frac{(C_i - C_f)V}{Wg} \quad (1)$$

$$RE(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

Where:

AC = The adsorption capacity of methyl red

RE (%) = The removal efficiency of methyl red

C_i and C_f (mg L^{-1}) = The concentration of methyl red before and after adsorption experiments

V(L) = The solution volume of methyl red

W_g (g) = The dosage of coconut husk and coconut shell activated carbon

Adsorption process: Batch adsorption experiments were carried out in 27 mL of glass centrifuge tube equipped with a Teflon lined screw cap. The centrifuge tubes were shaken at 160 rpm for an equilibrium time of 1 and 3 h on a mechanical shaker. The effect of adsorbent dosage on the removal of Methyl Red (MR) was studied with different adsorbent dosages (0.02-0.08 g) in a 1000 mg L^{-1} of concentration, shaken till equilibrium time. The effect of pH on the removal of MR was investigated over the pH range of 2-12 with 0.1 g of the adsorbent for 1 and 3 h in a dye solution concentration of 1000 mg L^{-1}. The initial solution pH was adjusted using 0.1 M H_2SO_4 or 0.1M NaOH. Effect of contact time and initial concentration was studied by shaking 0.1 g of the adsorbent at room temperature (27°C) and pH of 6.6 at different time intervals and different initial concentrations. Adsorption kinetic experiments were conducted by contacting 0.10 g of adsorbent with MR aqueous solution of the concentration 200-800 mg L^{-1}, maintained at room temperature and optimum conditions. The centrifuge tubes were taken out at some intervals. After adsorption, the adsorbent and the supernatants were separated by centrifugation at 2000 rpm for 10 min and samples for analyses withdrawn with a clinical syringe and analysed for residual dye concentration using a UV-Visible Spectrophotometer by monitoring the absorbance changes at λ_{max} 500 nm. The amount of dye adsorbed per gram of adsorbent (q_e) is given as:

$$q_e = \frac{v}{(m)(C_e - C_g)} \qquad (3)$$

and the percentage Removal (R) was calculated by using Eq. 4:

$$\%R = \frac{(C_e - C_g)}{C_e} \times 100 \qquad (4)$$

Where:

C_o and C_e = The initial and equilibrium Methyl Red (MR) concentrations, respectively (mg L^{-1})
V = The MR solution volume (L)
m = The mass of the adsorbent (g)

The equilibrium data were analysed using the Langmuir, Freundlich and Tempkin isotherms and the characteristics parameters for each isotherm were determined.

RESULTS AND DISCUSSION

Effect of operational variables on dye adsorption capacity and removal

Adsorbent dosage: The adsorbent dose is a pertinent parameter in adsorption studies because it determines the
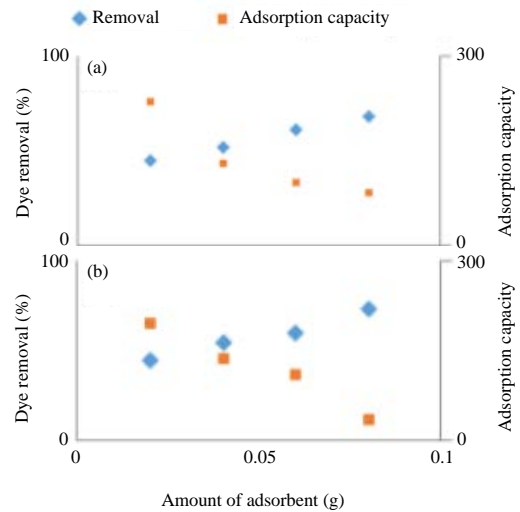

Fig. 1: The effect of adsorbent dosages on dye removal and adsorption capacity of methyl red: a) Coconut Husk (CH) and b) Coconut Shell (CS)

capacity of adsorbent for a given initial concentration of dye solution. The effect of adsorbent dosages on the amount of dye adsorbed was investigated by contacting initial dye concentration of 1000 mg L^{-1} with different amounts of adsorbents (0.02-0.08 g) for a contact time of 1 and 3 h of coconut husk and coconut shell, respectively at a temperature of 27±0.5°C and shaking speed at 160 rpm. After equilibrium, the samples were allowed to settle by centrifugation at 2000 rpm for 10 min after which the supernatant solutions were collected and analysed. Generally, the Adsorption Capacity (AC) of coconut husk and shell was exceptional with 99.87 and 99.26%, respectively.

Figure 1 shows the effect of adsorbent dosages on dye removal by Coconut Husk (CH) and Coconut Shell (CS) as well the adsorption capacity of methyl red by those materials. The percentage age of dye removal increased with an increase in adsorbent dosage. The increase in removal%age with adsorbent dosage can be attributed to an increase in the adsorption surface and availability of more adsorption sites (Kumar *et al.*, 2010). However, the adsorption capacity decreased with increasing amount of adsorbents. This may be explained as a result of overlapping of adsorption sites resulting in the total adsorption surface area available to the dye. A similar trend was also reported by El-Sayed (2011) in his study of dye removal from the aqueous solution by palm kernel fibres and (Etim *et al.*, 2012) in his study regarding dye removal by coconut coir dust.

Initial dye concentration: The percentage age of dye removal is highly dependent on the initial amount of dye concentration.
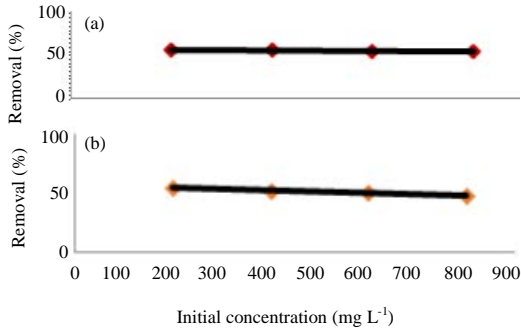
Fig. 2: The percentage age of dye removal with an increase of initial dye concentration: a) Coconut shell and b) Coconut husks
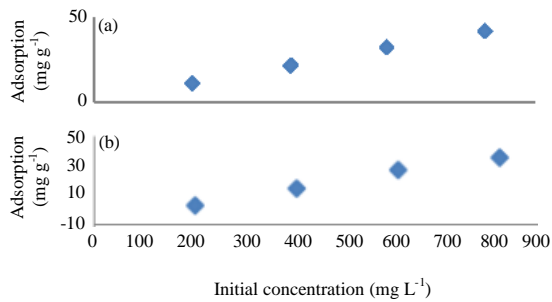

Fig. 3: Effect of initial concentration on adsorption of methyl red onto: a) Coconut Shell and b) Coconut husks

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. In this study as shown in Fig. 2 the percentage age of dye removal decreases with an increase of initial dye concentration which may be due to the saturation of adsorption sites on the adsorbent surface and the adsorption capacity increased with an increase in the initial concentration of the dye (Salleh *et al.*, 2011). In addition to that at low concentrations the active sites of the adsorbent surface is unoccupied while as the initial concentration increases the active sites required for adsorption of the dye molecules is unavailable (Kannan and Sundaram, 2001).

In Fig. 3, the effect of initial concentration of Methyl Red (MR) on the adsorption capacity is illustrated. It shows that the equilibrium adsorption capacity increase with an increase of initial dye concentration and this shows that the dye removal is highly concentration dependent. The increase in adsorption capacity may due to the high driving force for mass at high initial dye concentration (Bulut and Aydin, 2006).
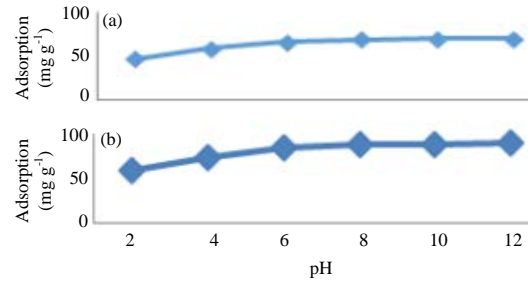

Fig. 4: Effect of pH on adsorption of methyl red onto: a) Coconut shell and b) Coconut husks

pH: The pH of the dye solution is crucial in adsorption studies. The rate of adsorption will vary with the pH of an aqueous medium. It is mainly due to the role of medium pH which controls the magnitude of electrostatic charges which are imparted both by ionised dye molecules and the charges on the surface of the adsorbent. Figure 4 shows the effect of pH on the adsorption of both materials. The dye adsorption capacity was found to increase with increasing pH 2-9 from 34.48-70.78 mg g^{-1} for coconut husks while from 47.64-71 mg g^{-1} for coconut shell.

The latter prevents adsorption of dye cations on to the binding sites of adsorbent through repulsion. As the 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; Ahmad *et al.*, 2015; Low and Lee, 1990). However, the percentage of adsorption was observed to be almost constant thus indicated that electrostatic attraction was not the dominant mechanism for dye adsorption but may be affected by the chemical reaction between adsorbent and adsorbate and might explained by presence of nearly equal concentrations of H_3O^+ and OH^- ions in the bulk solution that affect the polarity of adsorbent making it almost too neutral to adsorb more ions.

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 the equilibrium state, the adsorption isotherm can indicate the distribution of adsorbate molecules between the solid phase and the liquid phase. Equilibrium isotherm data obtained from the difference models provide important information on adsorption mechanisms and the surface properties and affinities of the adsorbent (Weber and Chakravort, 1974).

Thus, it is essential to establish the most appropriate correlation of equilibrium curves to optimise the conditions for designing adsorption systems. In this
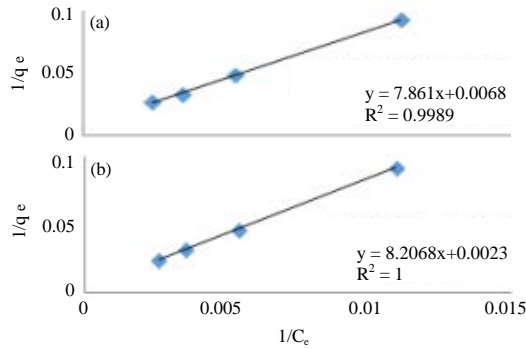
Fig. 5: Langmuir isotherm plots for the adsorption of methyl red onto: a) Coconut husk and b) Coconut shell

present work, Langmuir, Freundlich and Tempkin isotherms were employed to investigate the adsorption behaviour. The Langmuir isotherm model proposed by Langmuir is based on the assumption that adsorption occurs at specific homogeneous sites within the adsorbent. It explains monolayer adsorption which lies on the fact that the adsorbent has a finite capacity for the adsorbate. For example, at equilibrium; a saturation point is attained where no further adsorption can occur. The Langmuir isotherm is expressed in Eq. 5:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \qquad (5)$$

and this can be linearised to:

$$\frac{1}{q_e} = \frac{1}{Q_0 K_L C_e} + \frac{1}{Q_0} \qquad (6)$$

Where:

C_e = The equilibrium concentration (mg L^{-1})

q_e = The amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1})

Q_0 = The theoretical maximum monolayer adsorption capacity (mg g^{-1})

K_L = The Langmuir isotherm constant (L mg^{-1})

The values of and can be determined from the slopes and intercepts of the linear plot of against as shown in Fig. 5. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter which is a dimensionless constant referred to as separation factor or equilibrium parameter (Weber and Chakravort, 1974) value indicates the adsorption nature ($R_L > 1$ unfavourable; $R_L = 1$ linear; $0 < R_L < 1$ favourable and $R_L = 0$ irreversible):

Table 2: Isotherm parameters for the adsorption of methyl red onto coconut husk and coconut shell

Isotherm model	Parameters	Coconut husk (Temp: 27±0.5°C)	Coconut shell (Temp: 27±0.5°C)
	Q_0 (mg g^{-1})	147.059	434.783
Langmuir	K_L	0.0009562	0.0002803
	R^2	0.9989	1
	n	1.184	1.056
Freundlich	K_F	0.242	0.152
	R^2	0.9942	0.9998
	B_1	18.020	21.241
Tempkin	K_T	0.019	0.017
	R^2	0.9818	0.9684

$$R_L = \frac{1}{1 + (1 + K_L C_e)} \qquad (7)$$

Where:

C_0 = The initial concentration

K_L = The the constant related to the energy of adsorption (Langmuir constant)

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:

$$q_e = K_F + C_e^{\frac{1}{n}} \qquad (8)$$

Where:

q_e = The amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1})

C_e = The equilibrium concentration (mg L^{-1})

K_f = The Freundlich adsorption constant related to the adsorption capacity of the adsorbent (mg$^{1-1/n}$L$^{1/n}$g^{-1})

n = A dimensionless constant which can be used to explain the extent of adsorption and the adsorption intensity between the solute (adsorbate) concentration and adsorbent, respectively

A linear form of Freundlich equation is generally expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (9)$$

The values of and n are calculated from the intercepts and slopes of the plot of $\log q_e$ versus $\log C_e$ as shown in Fig. 6. The isotherm parameters derived from Freundlich plots are listed in Table 2. K_F is the Freundlich constant that shows the adsorption capacity of an adsorbent and is a constant which shows the strength of the relationship between adsorbate and adsorbent (Magdy and Daifullah, 1998). The value of for coconut husks and coconut
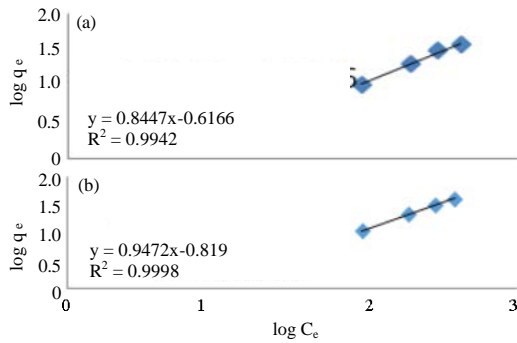
Fig. 6: Freundlich isotherm plots for the adsorption of methyl red onto: a) Coconut husk and b) Coconut shell

shells are 0.242 and 0.152, respectively. It is generally stated that the values of n in the range of 1-10 represent good adsorption. In the present research, the exponent, n was <n<10 indicating favaourable adsorption.

The Tempkin isotherm model takes into account adsorbent-adsorbate interactions. 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 characterised by a uniform distribution of binding energies, up to some maximum binding energy. The linear form of Tempkin isotherm is given as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \qquad (10)$$

where, B_1 is the Tempkin constant related to the heat of adsorption and is given as:

$$B_1 = RT/b$$

Where:
B_1 = Related to the heat of adsorption
K_T = The equilibrium binding constant (Lm g^{-1})

The values of K_T and B_1 obtained from the intercepts and slopes of the plots of q_e versus $\ln C_e$ as in Fig. 7 are summarised in Table 2.

The isotherm data were calculated from the least square method and related correlation coefficients (R^2 values) are given in Table 2. The Langmuir isotherm fits the experimental data very well. In addition to that, the calculated, R_L is greater than 0 but <1 indicating that Langmuir isotherm favourable. The value of Q_0, K_L and R^2 obtained in this study for both material for Langmuir isotherm is also shown in Table 2. With the R_L values between 0-1 for both adsorbent indicating that the equilibrium sorption was favourable and the R^2 value of
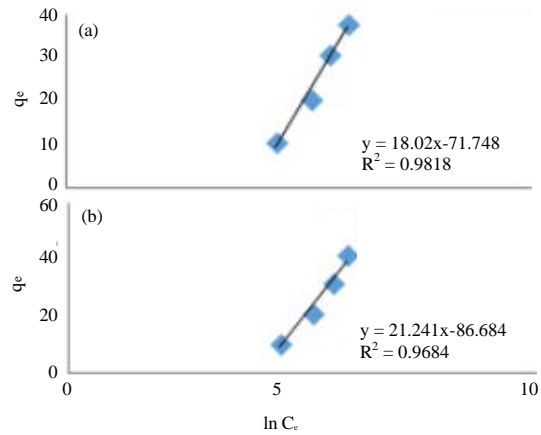

Fig. 7: Tempkin isotherm plots for the adsorption of methyl red onto: a) Coconut husk and b) Coconut shell

0.9989 and 1 for coconut husk and coconut shell proving that the sorption data fitted well to Langmuir Isotherm Model. The fact that the Langmuir isotherm fits the experimental data may be due to the homogeneous distribution of active sites onto the coconut husks and shells surfaces.

As seen in Table 2, it can be said that all the data was fitted well into Langmuir and Freundlich isotherm models. The R^2 values indicate that both Langmuir and Freundlich isotherm models represent adsorption of methyl red onto both coconut husks and coconut shell. Although, in general Langmuir isotherm assumes monolayer coverage on a homogeneous surface with identical adsorption sites, these assumptions are valid for gas adsorption on solid surfaces. In solution-solid system, the condition becomes dynamic and complicated due to several factors such as the hydration forces and mass transport effects thus, the isotherms adequacy might seriously affected. However, in the present study, it can be said that the adsorption data was very well fitted into Langmuir isotherm model.

Adsorption kinetics: The dynamics of the adsorption can be studied by the kinetics of adsorption in term of the order of the rate constant (Gomez *et al.*, 2007). The study of adsorption kinetics describes the solute uptake rate which controls the residence time of adsorbate uptake at the solid solution interface. The kinetics of methylene red adsorption on the coconut husks and coconut shell were analysed using pseudo first-order and pseudo-second order kinetic models. The linear pseudo-first-order equation is given as follows:
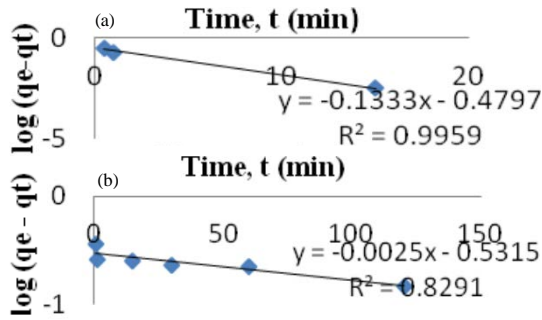
Fig. 8: Pseudo-first order kinetics plot of adsorption of methyl red on: a) Coconut husks and b) Coconut shell
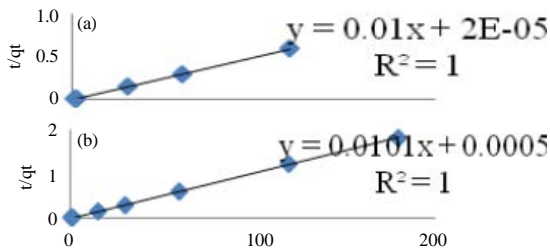

Fig. 9: Pseudo-second order kinetics plot of adsorption of methyl red on: a) Coconut husks and b) Coconut shell

Table 3: Kinetics parameter for biosorption of methyl red on coconut husk and coconut shell

	Pseudo-first order			Pseudo second order		
Variables	q_e	K_1	R^2	q_e	K_1	R^2
CH	0.331	0.307	0.9959	100	5.0	1
CS	0.294	0.006	0.8291	99.01	0.204	1

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1 t}{2.303} \qquad (11)$$

Where:

q_e and q_t = The adsorption capacity at equilibrium and at time t, respectively ($mg\ g^{-1}$)

K_1 = The rate constant of the pseudo first-order adsorption (min^{-1})

A plot of log (q_e-q_t) against t-test should give a linear relationship from which K_1 and (q_e-q_t) can be determined from the slope and intercept of the plot, respectively as shown in Fig. 8. The linear Pseudo-second order equation is given as follows K_2:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (12)$$

where, k_2 is the rate constant of pseudo-second order adsorption ($g\ mg^{-1}$ min). Figure 9 shows pseudo-second order plots for the adsorption process of methyl red onto coconut husks and coconut shell. The k_2 and q_e values were determined from the intercepts and slopes of the linear plot, respectively. Table 3 shows the pseudo first order and pseudo second order kinetic data for the adsorption of methyl red onto coconut husks and coconut shell.

As can be seen, the correlation coefficients (R^2) are unity for the pseudo-second order model and less for pseudo-first order model, indicating a better fir with the pseudo-second order model. The calculated q_e values also agree very well with the experimental data. These results indicate that the adsorption system studied for both adsorbate belongs to the second-order kinetic model, thus indicates that the reaction is more inclined towards chemisorption.

CONCLUSION

The adsorption of methyl red from aqueous solution onto coconut husks and coconut shell has been studied. Adsorption experiments were carried out as a function of adsorbent dosage, initial dye concentration and pH. The adsorption experiments indicated that coconut husks and coconut shell were not effective in removing basic dyes such as methyl red from aqueous solution. The removal percentage decreased with the increasing initial dye concentration and increased with the increasing adsorbent dosage. As the equilibrium adsorption capacity increased with an increased of initial dye concentration, this further shows that the dye removal is highly concentration dependent. The adorption data was well described by both Freundlich and Langmuir isotherm models however the Langmuir isotherm can be said as the most best isotherm model that can be fitted by the this experimental adsorption data, may due to the complexity of solid-solution system that may affected the isotherm adequacy. The rate of sorption were found to conform to pseudo-second order kinetics with good correlation for both coconut husks and coconut shell. The present study concludes that coconut husks and coconut shell could not effectively be employed as a low-cost adsorbent for the removal of basic dyes (methyl red) from aqueous solution as its removal is concentration dependent.

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