ADSORPTION OF RHODAMINE B BY PLAM KERNEL SHELL ADSORBENTS

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ABSTRACT

This study was aimed at evaluating the adsorptive removal of rhodamine B dye (RhB) by palm kernel shell adsorbents. The precursor was mixed with potassium hydroxide solution, and the mixture was further heated using furnace (FC) and microwave (MC). Microwave-assisted water (steam) treatment (MH) of palm kernel shell char was also performed for comparison. The adsorbents were characterized according to the specific surface area, surface morphology and surface functional groups. Result indicates that the RhB removal by adsorbent is in the order: MC>FC>MH, that is in agreement with the surface chemistry of the adsorbents. The adsorption of RhB by palm kernel shell adsorbents agreed well with the Redlich-Peterson model, suggesting the monolayer coverage on the heterogeneous surface. Kinetics study demonstrates that MC obeyed the pseudo-first-order model, and signifies that the external diffusion to overcome the adsorbent mass transfer resistance as the rate-determining step.

KEYWORDS: *Adsorbent; adsorption; chemical treatment; microwave-assisted process; palm kernel shell; rhodamine B dye*

1.0 INTRODUCTION

Dye is composed of organic compound with an unsaturated aromatic structure that can absorb certain wavelength of light. The absorption of light by chromophores and auxochromes atoms explains why dyes are coloured. However, the chemicals used to synthesize dye are highly toxic and carcinogenic. Effluent laden with dyes that are released from various fabrics, textile and other related industries is the main contributor to the colour in the wastewater. The presence of dyes in water hinders the light penetration that would upset the photosynthetic activity, and may also result in micro-toxicity in aquatic organisms due to the accumulation of chelate metal ions. Dyes are difficult to be removed from water due to the fact that they are stable towards biological degradation (Ming-Twang et al., 2015a).

Rhodamine B (RhB) is among the widely used dyes in textile industry. It is a basic dye under the family of xanthene (fluorescent dye) that is toxic and highly water soluble (Hou et al., 2011). The fluorescent of RhB is obvious at low concentration, while it is capable of damaging the whole water bodies at high concentration. In addition, RhB

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contains stable aromatic groups that are less prone to biodegradation. The exposure to RhB dye can cause injury to eye, rhinorrhea and sore throat (Grant, 1986), skin irritation (Dire & Wilkinson, 1987), phototoxic and photo allergic reactions (Zenz, 1988), and risk of tumors (Dharmawardene, 1991). Therefore, the treatment of effluents containing RhB from water is of utmost importance due to the environmental and health issues.

Though many physico-chemical and biological methods are proven to be quite effective in removing RhB, the processes are known to require definite equipment, high energy consumption and additional treatment to dispose the sludge by-product (Panneerselvam et al., 2012; Ming-Twang et al., 2015a, 2015b). Adsorption has been a preferred method to treat dyes-laden wastewater owing to the excellent surface chemistry and textural characteristics of the adsorbent. Moreover, adsorption is a sludge-free process, easy to operate and has been proven to be able to efficiently remove dyes even in dilute solution (Ming-Twang et al., 2015b). However, the widely used adsorbent, i.e., activated carbon is at the disadvantage because of expensive precursor and difficult regeneration of spent adsorbent for subsequent adsorption cycles. Therefore, search for abundantly available and inexpensive adsorbent precursor has continue in gaining considerable attention by many researchers.

Malaysia is among the largest producers of palm oil. From the extraction of oil from oil palm fruit, nearly 4.6 million tons of palm kernel shell (PKS) are produced every year (Mohammadi et al., 2010). PKS is an agricultural waste that can be converted into adsorbent because of its abundance, even though certain portion of the waste has been used as fuel in the milling process (Mohammadi et al., 2010). PKS is an excellent adsorbent candidate due to its hard granular structure, high carbon content, insolubility in water, chemically stable, insensitive towards toxicity, mechanically durable and locally available at almost costless (Panneerselvam et al., 2012; Ming-Twang et al., 2015b).

The present study aims to investigate the removal of RhB using adsorbents derived from palm kernel shell. The adsorption data were analyzed and interpreted using the commonly used isotherm models. The rate of adsorption was performed for adsorbent showing the highest RhB removal. The results were compared with the previous studies, and the removal mechanisms were discussed.

2.0 MATERIALS AND METHODS

2.1 Materials

Palm kernel shell (PKS) was obtained from FTA palm oil mill located at Johor state of Malaysia. Rhodamine B (abbr.: RhB; molecular formula: $C_{28}H_{31}ClN_2O_3$; molecular weight: 479.02 g/mol) was purchased from R&M Chemicals Essex, UK. RhB is a cationic and xanthenic dye (colour and index number, C.I.: 45170) that is soluble in water (solubility: 50 g/L) and produces pink or bluish-red solution. The chemical structure of RhB is shown in Figure 1. Other chemicals such as potassium hydroxide, (KOH) hydrochloric acid (NaOH), sodium hydroxide and phenolphthalein are of analytical reagent grade.

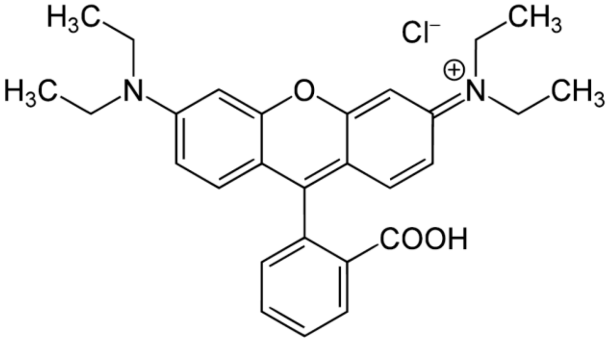

Figure 1. Chemical structure of rhodamine B

2.2 Preparation of Adsorbents

Three adsorbents were prepared from PKS. The PKS was mixed with potassium hydroxide solution at a ratio (weight KOH/weight PKS) of 0.5. The sample was then treated using two different heating methods. The first adsorbent was prepared using muffle furnace at 550°C for 1.5 hours, hereinafter is designated as FC, while the other one was heated using microwave at 70% power intensity for 0.5 h, hereinafter is designated as MC. The third adsorbent was also prepared for comparison. The PKS was heated in muffle furnace at 250°C for 1.5 hours to produce PKS char. The PKS char was immersed in distilled water, and then was heated using the same conditions as for MC. The adsorbent was labelled as MH. All adsorbents were soaked in 3 M HCl for removing the leachable minerals, and then were thoroughly washed with distilled water to pH 4. The adsorbents were dried in oven at 110°C overnight prior to be used for characterization and adsorption studies.

2.3 Characterization of Adsorbents

The adsorbents were characterized using a Pulse Chemi Sorb 2705 surface area analyzer at liquid N_2 temperature of 77 K for specific surface area. A simple titration analysis was used to determine the surface acidity of adsorbents, assuming that sodium hydroxide would neutralize most of the acidic groups present on the activated carbon such as carboxyl and lactone groups (Boehm, 1994; Liu et al., 2010). About 0.3 g of adsorbent was brought into contact with 15 ml 0.1 M NaOH solution, and the mixture was allowed to equilibrate using orbital shaker for 48 h. Then 5 ml aliquot from the mixture was back-titrated with 0.05 M of HCl, and the neutralization end-point was observed using phenolphthalein solution.

The surface functional groups of adsorbents was qualitatively determined using a Perkin Elmer Spectrum One (FTIR) spectrometer over the frequency range of 400-4000 cm^{-1}. High resolution images of adsorbents surface were obtained using a SUPRA 35 VP field emission scanning electron microscope (FESEM) at magnifications of 1000 and 5000 times. The FESEM instrument is equipped with an energy dispersive X-ray (EDX) spectrometer for surface elemental composition.

2.4 Adsorption Studies

Batch adsorption was performed for equilibrium and rate of adsorption. For equilibrium adsorption, about 50 mg adsorbent was brought into intimate contact with 50 mL RhB dye solution of varying concentrations between 5 and 50 mg/L. The mixture was allowed to equilibrate in orbital shaker at 120 rpm and 25°C for 72 h. The RhB concentration was measured using visible spectrophotometer (Biochrom Libra S6) at a wavelength of 494 nm. The correlation was determined as concentration (in unit of mg/L) is equal to 16.529 multiplied by absorption unit (a.u.) for the upper limit of 15 mg/L with R^2 of 0.9917. The removal of RhB dye, q_e (in mg dye over g of adsorbent) was calculated using material balance,

$$q_e = \frac{C_o - C_e}{m} V \tag{1}$$

where C_o and C_e are respectively the initial and final equilibrium concentrations (mg/L), V is the volume of dye solution (L), and m is the mass of adsorbent (g). The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The Langmuir model represents monolayer adsorption on a homogeneous surface is expressed as (Langmuir, 1916, 1918),

$$q_e = \frac{QK_L C_e}{1 + K_L C_e} \tag{2}$$

where Q (mg/g) is theoretical maximum removal and K_L (L/mg) is the Langmuir constant that reflects the affinity of adsorption. The Freundlich model indicates surface heterogeneity of the adsorbent as well as multilayer coverage on the surface. The Freundlich equation is expressed as (Freundlich, 1906),

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F (mg/g (L/mg)$^{1/n}$) and n are the Freundlich constants that are related to the adsorption capacity and intensity, respectively. The $1/n$ value ranging from 0 to 1 signifies the surface heterogeneity, while the n value ranging between 2 and 10 represents a favourable adsorption. Redlich-Peterson model is a hybrid isotherm that combines both features of the Langmuir and Freundlich equations, and is given as (Redlich & Peterson, 1959),

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{4}$$

where A, B and g are the Redlich-Peterson constants, and $0 < g < 1$. The equation reduces to Henry's law when g is equal to zero, while it becomes the Langmuir model when g is equal to one.

The rate of adsorption study was performed for adsorbent that showed the highest RhB removal in equilibrium study. About 0.2 g of adsorbent was added to conical flasks containing 200 mL RhB solution with concentrations of 10 and 50 mg/L, respectively.

At different time intervals, the liquid sample was withdrawn from the conical flask and the residual concentration was measured using a Biochrom Libra S6 visible spectrophotometer. The amount of RhB adsorbed per unit mass of adsorbent at time t, q_t (mg/g) was calculated as,

$$q_t = \frac{C_o - C_t}{m} V \tag{5}$$

where C_t (mg/L) is the liquid-phase concentrations of dye at time, t (h). The experimental data were fitted into the pseudo-first order and pseudo-second order models. The pseudo-first-order model is given as (Lagergren, 1898),

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{6}$$

where q_e (mg/g) is the predicted equilibrium adsorption by the model, k_1 (h^{-1}) is the rate constant of pseudo-first-order model and t (h) is the adsorption time. The applicability of the pseudo-first-order model indicates that the external diffusion is a significant step. The pseudo-second-order equation is based on chemical related adsorption, and is expressed as (Ho & McKay, 1998),

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{7}$$

where k_2 (g/mg.h) is the rate constant of pseudo-second-order model. The initial adsorption rate, h (mg/g.h), of the pseudo-second-order as t approaching zero is given as,

$$h = k_2 q_e^2 \tag{8}$$

All constants in isotherm and kinetics models were solved using *Solver* add-in of MS Excel, given the condition where the sum of squared error (*SSE*) is the least rendering the optimum R^2 value.

3.0 RESULTS AND DISCUSSION

3.1 Characteristics of Adsorbents

Table 1 shows the characteristics of the precursor and the derived adsorbents. The moisture content of PKS is 12%. In general, the yield of adsorbent decreased after the treatment procedures. Potassium hydroxide (KOH) treatment has resulted in a much lower yield of adsorbents (FC and MC). The attached potassium ions on the carbon surface could act as the catalyst to accelerate the gasification of organic substances, and consequently would result in the weight loss due to the carbon burning-off (Guo & Lua, 2002; Foo & Hameed, 2009). The decreasing order of specific surface area of adsorbents is given as: FC > MC > MH. FC demonstrates a greater specific surface area of 336 m^2/g, nearly 120 times higher than that of the precursor. This is in agreement with other reported results from literature (Tay et al., 2001; Martin et al., 2003; Wang et al., 2008). On the other hand, no appreciable difference in surface area was observed for other prepared adsorbents even though there was a decrease in yield.

Table 1. Characteristics of palm kernel shell adsorbents

Characteristics	**PKS**	**Adsorbent**		
		MH	**MC**	**FC**
Yield (%)	-	75.5	26.3	16.8
Specific surface area (m^2/g)	2.76	1.17	3.79	336
Surface acidity (mmol/g)	0.017	0.70	1.05	0.40
Carbon content (%)	50	63.7	58.3	87
Oxygen content (%)	35	36.3	40.7	13
Ash (%)	1.3	-	1	-

It is likely that the treatment (impregnation) temperature in microwave is not sufficient enough to develop the porous textures of the adsorbent. This could be proven by a slight increase in carbon content of MC and MH after the microwave-assisted treatment. A somewhat greater carbon content in MH could be attributed to the production of char preceding the microwave drying. Therefore, MC and MH could only be regarded as adsorbent (not activated carbon) while FC is successfully converted into activated carbon (Ming-Twang et al., 2015b).

The FTIR spectra of adsorbents are shown in Figure 2, and the respective peak assignments are tabulated in Table 2.

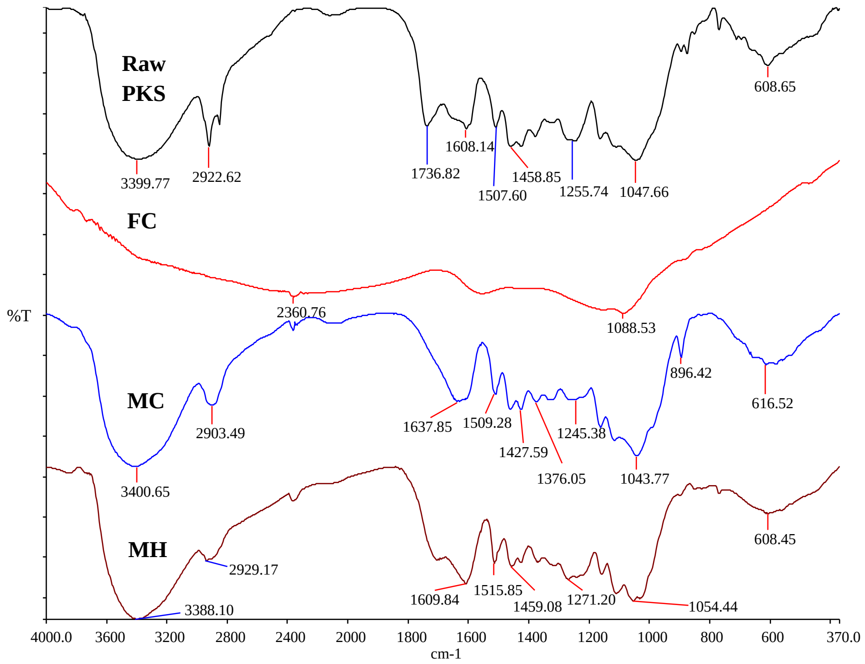

Figure 2. FTIR spectra of palm kernel shell adsorbents

Obviously, most of the functional groups in FC are eliminated after the activation procedure. This is in accordance with the fact that potassium salt is a strong dehydrating agent that accelerates the liberation of functional groups at elevated temperature. On the other hand, PKS, MC and MH share a similar pattern of FTIR spectra. This again confirms that the aforementioned adsorbents (MC and MH) are not activated, and reflects that they possess a similar surface functional groups. From Figure 2 and Table 2, the presence of oxygen-containing surface functional groups in adsorbents could create some degree of polarity for possible interaction with the target contaminants. The acidic (oxygen) groups could easily influence the surface properties and the adsorptive behaviour of the adsorbent (Mohammadi et al., 2010). Figure 3 compares the FTIR spectra of MC and MH according to the difference in the peaks intensity.

Table 2. Peak assignments of FTIR spectra

Wave number (cm^{-1})	**Infrared assignment**	**Functional groups**
3400	O—H (stretching)	Hydroxyl groups
3000-2900	C—H (stretching)	Methylene (CH_2)
2360	C=O (stretching)	Ketone
1600-1700	C=O (stretching)	Quinones; carboxylic anhydrides
1500	C=C (stretching)	Aromatic rings
1425	C—H (bending)	Methylene (CH_2)
1375	C—H (bending)	Tert-butyl
1045-1245	C—O—C (stretching)	Ethers
900	C—O—H (bending)	Ethers
600	C—H (bending)	Benzene derivative

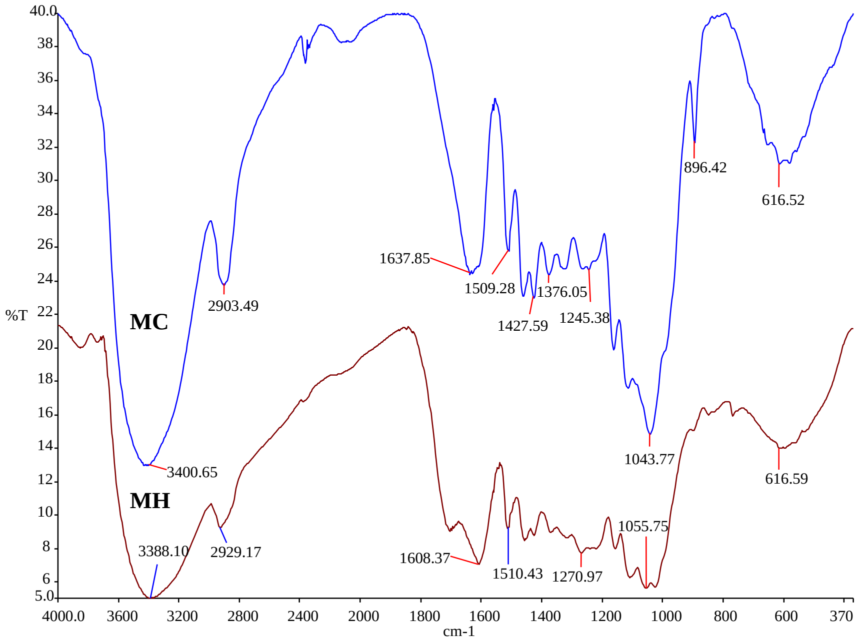

Figure 3. Overlay view of selected FTIR spectra

From Figure 3, MC exhibits a greater peaks intensity than MH especially for the O—H (stretching), C=O (stretching) and C—O—C (stretching) regions. It can be postulated that MC possesses a higher concentration of surface oxygen functional groups than MH (Shin et al., 1997). In addition, the surface acidity of MC (1.05 mmol/g) as shown in

Table 1 is higher than that of MH (0.70 mmol/g). It is also consistent with the variation of oxygen content in the adsorbents studied (Table 1).

Figure 4 displays the surface morphology of adsorbents. The images are directly associated with the development of porous textures and the surface area of adsorbents (Table 1).

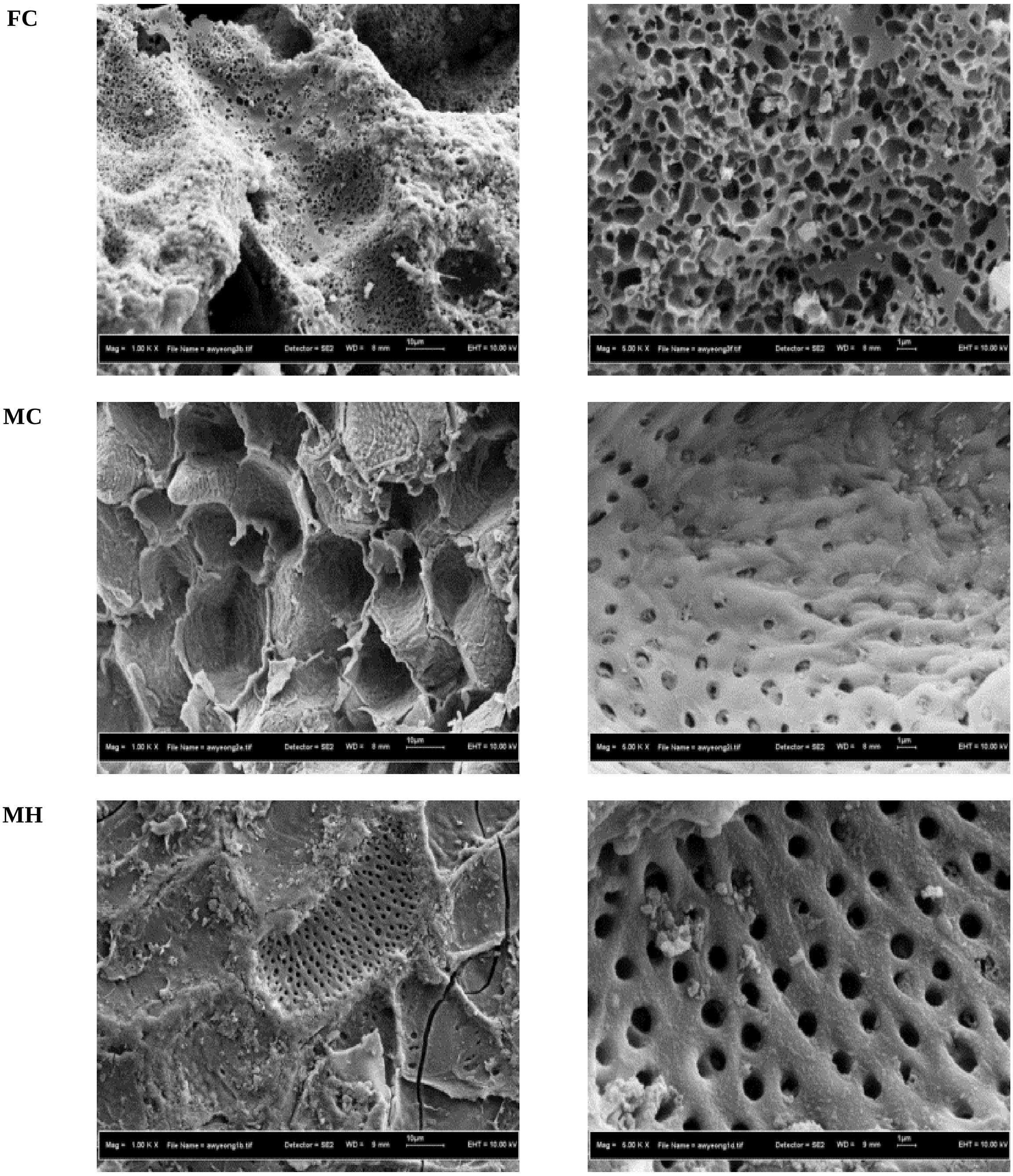

Figure 4. SEM images of palm kernel shell adsorbents

The activated carbon (FC) exhibits a well developed porous networks with exterior opening of about 1 μm, while the adsorbents (MC and MH) demonstrate a rough surface with rudimentary pores (macropores).

3.2 Adsorption Studies

In the batch adsorption of RhB, the mean initial pH was recorded as 5.34 ± 0.76. RhB can exist in three forms, namely in the acidic (cation), basic (zwitterion) and lactone, depending on the solvent used, temperature, pH and concentration. RhB is in the form of lactone (colourless) in non-hydrogen bond donating solvents, while it exhibits colour from bright orange to red when it is in the forms of cation and zwitterion in hydrogen bonding donating solvents (McKay (2007); Chingin et al. (2010)). Because water is a hydrogen bonding donating solvent, the cation is likely to be in equilibrium with the zwitterion. Thus, in carrying out the adsorption studies, the RhB solution was unadjusted, and kept at slightly acidic to avoid the complexity in the two types of equilibrium. According to Hema and Arivoli (2009), the solution pH can also influence the uptake of RhB. At pH greater than 6, the zwitterions predominate, thus increasing the accumulation of RhB dimers due to the electrostatic interaction between the carboxyl group and the xanthene monomer. As a result, the dimmers are unable to pass through the pore channels (Hema & Arivoli, 2009).

Figure 5 illustrates the equilibrium uptake of RhB by different PKS adsorbents. The highest RhB uptake is given by MC (18.1 mg/g), and followed by FC (4.10 mg/g) and MH (0.854 mg/g).

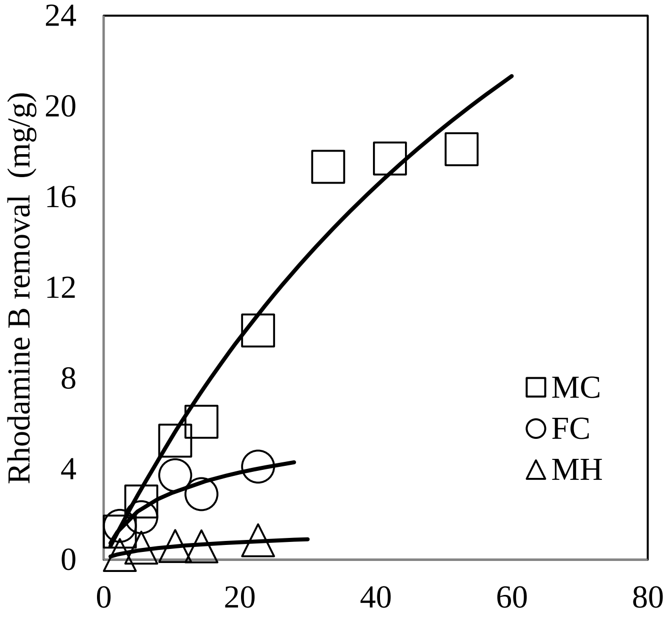

Figure 5. Equilibrium removal of rhodamine B dye by palm kernel shell adsorbents

In general, the removal capacity gradually increased before reaching a plateau, at which the adsorption is said to be at saturation. Increasing the RhB concentration beyond this saturation point will no longer increase the adsorption capacity. The adsorption rate is usually rapid when the initial concentration is low, and decreased with increasing initial concentration. This could be seen from the changes in slope as the equilibrium concentration increases. The concentration gradient is the main driving force for the adsorption process. This is true until the adsorbent surface is saturated, and the equilibrium is attained. At equilibrium, the rate of adsorption is equal to the rate of desorption, thus no further increase in RhB adsorption would be observed.

The decreasing order of RhB removal capacity is given as: MC>FC>MH. Generally, The common attributes of adsorbent that could contribute in the removal of dye molecules are porous textures and surface chemistry. Apparently, the surface of adsorbents is rough with elementary development of macropores (Figure 4). The presence of macroporous channels (pore with width greater than 50 nm) allows the RhB dye molecules (size: 1.8 nm) to pass through and lodge on the pore wall as the minimum requirement for diffusion is about three times the amplification of molecular size (Mohammadi et al., 2010). Although FC exhibits a well developed porous structure with high specific surface area, its ability to remove RhB dye is not as high as that of MC. It is due to the fact that FC is mainly microporous with pore width lesser than 2 nm (Mohammadi et al., 2010; Shu-Hui & Zaini, 2015). Thus, the RhB removal is not specific surface area-sensitive and suggested that the removal of RhB dye by MC is driven by the surface chemistry of the adsorbent. Because RhB is a cationic dye, the negatively charged surface would favour the uptake of this contaminant. The presence of surface acidic (oxygen) functional groups is likely to furnish the adsorbent with negatively charged surface through the dissociation (release) of protons. The surface oxygen groups play an important role in determining the adsorptive characteristics of adsorbent (Ana et al., 2011). In an earlier work, Hema and Arivoli (2009) reported a removal of 49 mg/g RhB using H_2SO_4-activated *Thespusia populinia* bark carbon with high surface acidity (0.381 mmol/g). In a similar development, Gad and El-Sayed (2009) showed a RhB removal of about 20 mg/g (that is nearly five times greater than that of FC, but comparable with that of MC) using KOH-activated bagasse pith carbon (ratio 1.17). Ju and co-workers (2008) reported a somewhat lower removal of RhB (3.44 mg/g) using H_2SO_4-treated dried biomass of activated sludge, while other authors demonstrate a higher RhB uptake using bentonite and iron oxide nanoparticles coated H_2SO_4-activated PKS carbon (Hou et al., 2011; Panneerselvam et al., 2012). In a related study, Mohammadi et al (2010) used NaOH-activated PKS carbon with surface area of 477 m^2/g (68% microporosity) to obtain a maximum RhB removal of 1.40 mg/g. It is obvious that the specific surface area and porous textures of adsorbent may not be the necessary reasons for the effective removal of RhB from water. In this work, we demonstrated a greater removal of RhB using adsorbent prepared through simple microwave-assisted chemical treatment.

The adsorption data were analyzed using isotherm models, and the respective constants are tabulated in Table 3. All isotherm models are adequately fitted with the adsorption data with reasonable values of sum of squared error (SSE) and R^2. The Langmuir model seems to over-predicted the maximum removal of RhB by MC. The applicability of Redlich-Peterson model suggests that the adsorption of RhB is monolayer in nature and happens to be on the heterogeneous adsorbent surface (Gad & El-Sayed, 2009; Kong et al., 2013). It is also interesting to observe that MC exhibits a one order of magnitude lower adsorption intensity (K_L) as compared to FC.

Table 3. Isotherms constants

Isotherm model	Adsorbent		
	MC	**MH**	**FC**
Langmuir isotherm			
Q (mg/g)	52.2	1.08	5.24
K_L (L/mg)	0.012	0.123	0.136
SSE	14.5	0.024	0.944
R^2	0.960	0.888	0.817
Freundlich isotherm			
K_F (mg/g (L/mg)$^{1/n}$)	0.861	0.184	1.02
n	1.26	2.07	2.25
SSE	18.8	0.024	0.965
R^2	0.947	0.889	0.812
Redlich-Peterson isotherm			
A (L/g)	0.601	0.205	0.996
B	0.012	0.456	0.365
G	1.00	0.750	0.814
SSE	14.5	0.022	0.930
R^2	0.960	0.897	0.819

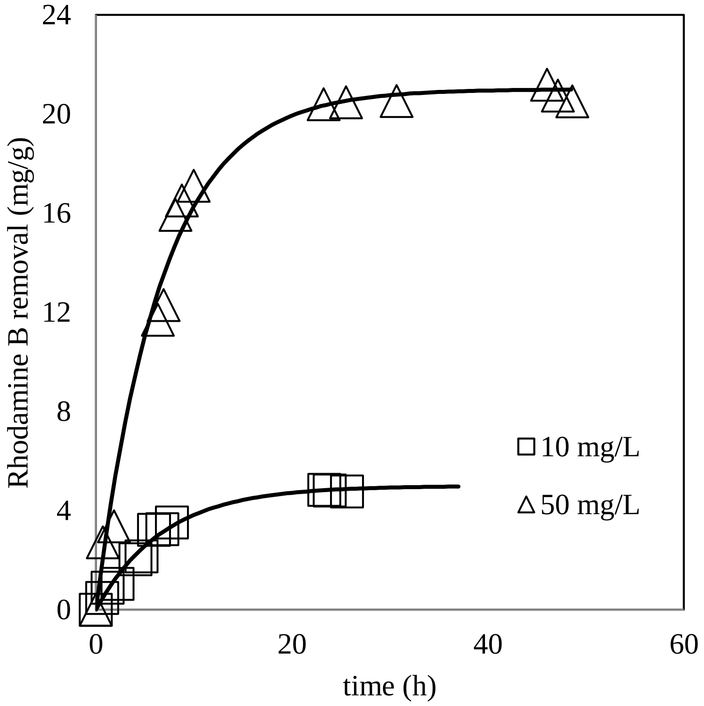

Figure 4. Rate of adsorption for MC adsorbent

Although the adsorptive performance of MC is higher, its affinity especially at lower RhB concentration is rather weak and is not too favourable (*n* value for MC is lesser than 2). This could be due to the adsorbent (MC) that is less porous, hence decreases the interaction probabilities with the cations.

Figure 4 shows the removal patterns for 10 and 50 mg/L of RhB dye solution by MC adsorbent at different time intervals. The adsorption rate is usually high when the dye molecules are initially in contact with the adsorbent, but it decreases with increasing period of time. In addition, a more steep slope for 50 mg/L suggests that the adsorption rate for this adsorption system is faster than that for 10 mg/L.

The adsorption data were evaluated for the rate of adsorption using kinetics models, and the results are tabulated in Table 4. From Table 4, the experimental data using both concentrations are best fitted to the pseudo-first-order model with reasonably better values of SSE and R^2. The predicted q_e values also agreed well with the experimental ones. The applicability of the pseudo-first-order model indicates that the external diffusion of RhB molecules to overcome the adsorbent mass transfer resistance is a significant step in adsorption (Gad & El-Sayed, 2009; Zaini et al., 2013). The model also predicts a similar rate constant, k_1 value for both concentrations used — a common characteristic of a diffusion-controlled adsorption.

Table 4. Kinetics constants

Kinetics model	**Concentration**	
	10 mg/L	**50 mg/L**
Measured q_e (mg/g)	5.25	18.1
Pseudo-first-order model		
Calculated q_e (mg/g)	4.99	21
k_1 (h^{-1})	0.145	0.149
SSE	0.384	10.1
R^2	0.989	0.986
Pseudo-second-order model		
Calculated q_e (mg/g)	6.37	24.1
k_2 (g/mg.h)	0.0211	0.00757
h (mg/g.h)	0.855	4.41
SSE	0.592	21.3
R^2	0.983	0.972

The transport of adsorbate molecules in adsorption usually follows three steps: external (bulk) diffusion, intra-particle diffusion and adsorption. The bulk diffusion is a rate determining step (slow process) when there is no driving force that assists the mixing and to overcome the mass transfer resistance between RhB cations and the adsorbent. In addition, the intra-particle diffusion could also be the rate determining step due to insufficient macro or mesopores in the adsorbent. The adsorption is a rate determining step when there is less driving force (concentration, porous texture, surface functional groups, etc.) for the adsorption to take place.

The mechanisms of RhB adsorption onto MC could be the electrostatic interaction between the surface acidic (oxygen) groups and the dye cations (Mohammadi et al., 2010). Such interaction is likely to form stable complexes on the adsorbent surface. Attempts have also been made to evaluate the desorption of RhB dye from the spent MC adsorbent using 50 mL boiled water for 0.5 h. The results show that out of 50 mg/L of RhB dye used for the fresh adsorption, only 1 mg/L was able to be desorbed. This is true after three adsorption-desorption cycles with average RhB re-adsorption of 6.23 mg/g. It indicates that the complex is stable and the bond formed is relatively strong from desorption using boiled water.

4.0 CONCLUSION

Adsorbents were prepared from PKS for RhB dye removal from water. Despite having a larger surface area, the KOH-activated palm kernel shell carbon (FC) demonstrated a lower removal of RhB as compared to the KOH-treated (impregnated) adsorbent (MC). The surface acidic (oxygen) groups are likely to play a vital role in the removal of RhB by MC. In other words, the RhB adsorption by MC is not surface area-dependent. The adsorption is assumed to be monolayer coverage of adsorbate on the heterogeneous adsorbent surface. In addition, the adsorption is controlled by external diffusion for the RhB cations to overcome the adsorbent mass transfer resistance. Finally, it is postulated that the electrostatic interaction between RhB cations and the surface acidic (oxygen) groups formed stable complexes on the adsorbent surface.

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