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RESEARCH ARTICLE

Physicochemical properties of char derived from palm fatty acid distillate

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Abstract

The present work was aimed to evaluate the physiochemical properties of chars derived from palm fatty acid distillate. The palm fatty acid distillate was heat-treated at 500 °C and 600 °C in a muffle furnace for 0.5 h, and the resultant products were characterized for elemental composition, surface functional groups, thermogravimetric profile and methylene blue adsorption. Results show that the char samples are rich in carbon content with unique surface functional groups that could be useful in the liquid-phase adsorption. The solid chars depict a thermally stable profile with the increase of temperature during the heat treatment. The char demonstrated the maximum removal of methylene blue of 7.6 mg/g and obeyed the monolayer-trend adsorption of Langmuir isotherm. The findings concluded that the palm fatty acid distillate-based char could be an adsorbent candidate for the removal of methylene blue.

Keywords: Adsorption, char, methylene blue, palm fatty acid distillate, physicochemical characteristics

INTRODUCTION

Textile industries use dyes for beautifications, varieties and aesthetic values of their final products. Methylene blue is a commonly used basic dye for dyeing and other industrial applications. In general, dyes are synthetic in nature and possess complex aromatic molecular structures, inert and not biodegradable (Nasuha & Hameed, 2011; Hadi et al., 2015). Therefore, the release of dyes into the water streams has become a serious threat to the aquatic environment and public health.

Adsorption is an effective method for dye removal from water, despite the fact that the process is expensive due to the dilemma revolving around adsorbent recycling (Kharub, 2012). The shortfall of this method has led to the quest for potentially more suitable, economical and effective strategies in dye treatment by adsorption process (Gupta & Suhas, 2009). A number of studies have shown that the industrial by-products such as ash (Woolard et al., 2002), palm oil mill effluent (Yahaya & Lau, 2013), slag (Ali et al., 2012), palm kernel shell (Garcia et al., 2017) and palm fatty acid distillates (Top, 2010) possess the inherent advantages to be exploited as low cost adsorbents for dye removal. These industrial by-products are generally cheap and abundantly available (Musapatika, 2010). Because of that, the spent adsorbent derived form these materials can be disposed off by incineration (Kong et al., 2014).

Malaysia is the world's second largest producer of crude palm oil. The preferred method in processing palm oil is physical refining to produce refined, bleached and deodorized palm oil products. During physical refining, the fatty acids residue, aldehydes and ketones responsible for the unacceptable odour and flavours are removed by steam distillation under low vacuum (less than 10 torr). The fatty acids vapour leaving the deodorizer is then condensed and cooled (Vijay et al., 2016). This residue is known as palm fatty acid distillate.

Palm fatty acid distillate (PFAD) is a by-product from the refining of crude palm oil. PFAD is a light brown semi-solid at room temperature, and melt to a brown liquid on heating. It comprises mainly of free fatty acid (FFA) (>80%) with palmitic acid and oleic acid as the major components. The remaining composition includes triglycerides, partial glycerides and unsaponifiable matters, e.g., vitamin E, sterols, squalenes and volatile substances (Ping et al., 2009; Top, 2010). Because of the sub-standard quality and yet with the continuous production, hence large availability, PFAD opens the opportunity to be exploited as useful char adsorbent for dye removal. Therefore, the present work was aimed at evaluating the physicochemical properties of chars and the potential to be used as adsorbent for methylene blue removal.

EXPERIMENTAL

Materials

The Palm fatty acid distillate (PFAD) was supplied by IFFCO (M) Sdn Bhd. Methylene blue dye powder ($C_{16}H_{18}ClN_3S$, molecular weight = 319.85 g/mol, assay 98.5%) was purchased from HmbG Chemicals.

Preparation of palm fatty acid distillate-based char

Desired amount of PFAD was weighed and placed inside a crucible. Then it was introduced into a muffle furnace for heat treatment at 500 °C and 600 °C for 0.5 h. The resultant products, designated as C1 and C2, respectively, were weighed for yield and were used for physicochemical characteristics and methylene blue adsorption.

Physicochemical properties of char

The resultant char samples were characterized for surface function groups using a Fourier transform infrared (FTIR) spectrometer (Spectrum One, PerkinElmer). The thermal stability of the material with temperature was evaluated from room temperature to 900°C under the flow of N_2 and heating rate of 10°C/min using a thermogravimetric analyzer (Q500, TA Instruments). The elemental composition of PFAD and the resultant chars were determined using elemental analyzer.

Adsorption of methylene blue

The adsorption of methylene blue onto PFAD-based char was performed for the effects of initial concentration and solution pH. Thirty mg of solid adsorbent was brought into intimate contact with 30 mL of methylene blue solution of different concentrations (5 – 50 mg/L). Next, the solution mixture was allowed to equilibrate for 72 h. After that, the residual concentration was measured using visible spectrophotometer (Halo Vis-10) at a wavelength of 615 nm. The adsorption capacity, q_e (mg/g) was calculated as, $q_e=(C_o-C_e)\times V/m$, where C_o and C_e (mg/L) are initial and equilibrium concentrations, respectively, V (L) is the volume of methylene blue solution, and m (g) is the weight of char.

The effect of pH on the removal of 20 mg/L of methylene blue was studied over the pH range of 3 – 12. The pH was adjusted by adding few drops of 0.01 M NaOH or 0.01 M HCl solution. The remaining procedures are the same as described earlier.

RESULTS AND DISCUSSION

Physicochemical properties of PFAD-based chars

Table 1 shows the yield and elemental composition of PFAD and the derived chars. The heat treatment of PFAD significantly decreases the yield of char to less than 1 %. The effect is more pronounced when the treatment temperature was increased to 600 °C. However, the resultant solids (chars) are purely black, with carbon content of about 85 %. It implies the promising application of the material as adsorbent for wastewater treatment.

Table 1 Yield and elemental composition of PFAD-based chars.

Sample	Phase /colour	Yield (%)	Elemental composition (%)				
			C	H	N	S	O*
PFAD	Semi-solid, brown	-	82.2	3.48	0.69	0.11	13.5
C1	Solid, black	< 1	84.4	3.85	0.06	0.19	11.5
C2	Solid, black	< 1	85.7	3.74	0.16	0.06	10.3

* calculated by difference

FTIR spectra of PFAD and chars are shown in Fig. 1. The figure sheds light on the unique functional properties of chars from the peaks at different wave numbers. Generally, both C1 and C2 display the same peaks which indicates that the samples have practically the same composition of functional groups. This simply means that the increase of temperature in the char production provides trivial effect on the surface functional groups, on top of the decrease in yield. The peaks at around 3840 cm^{-1} correspond to the O—H streching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations) such as alcohols, phenols and carboxylic acids. The ˋfree' hydroxyl groups of PFAD could be due to the presence of free fatty acids, while that of the chars could be associated with the bound water and/or O—H functional groups. The peaks at 2840 cm^{-1} are attributed to the symmetric and asymmetric C—H stretching vibrations of aliphatic acids. Obviously, the peaks disappeared upon the heat treatment at high temperature due to the liberation of fatty acids. The peaks observed at 2660 cm^{-1} and 2360 cm^{-1} are due to the asymmetric stretching vibrations of C=O (carbonic group). Also, the peaks noticed at 2370 cm^{-1} and 2330 cm^{-1} could be related to the asymmetric vibrations of triple bond of carbon-to-carbon and carbon-to-nitrogen. The chars also exhibit peaks at 1710 cm^{-1} and 1550 cm^{-1} as a result of the presence of C=O, C=N and C=C groups. The peaks ranging from 1460 cm^{-1} to 1010 cm^{-1} indicate the heavy presence of single bond of various functional groups. The peaks at the fingerprint region with wave number lesser than 1000 cm^{-1} imply the presence of volatile components.

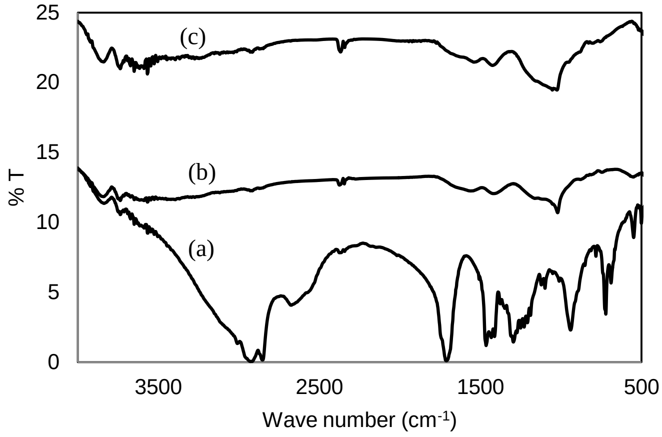

Fig. 1 FTIR spectra of (a) PFAD and PFAD-based chars, (b) C1 and (c) C2.

The thermogravimetric profiles of PFAD and the derived chars are displayed in Fig. 2. PFAD is not thermally stable as it vaporizes at high temperature, and all weight is loss at 500 °C. The sharp peak at 250 °C could be attributed to the liberation of light free fatty acids and volatiles, while the heavier fractions are released at 350 °C to 450 °C. On the other hand, the chars, C1 and C2, that were prepared from PFAD under the controlled environment are more stable with temperature. The degradation of material as corresponds to the peaks ranging from 500 °C to 700 °C is due to the burning off of high density carbon structures. As shown in Fig. 2, the thermal stability of C2 is more pronounced as compared to that of C1. It is suggested that the building block of C2 is composed of high density graphitic structure that can withstand high temperature heating.

Equally, there is no significant difference between the physicochemical properties of chars produced from PFAD. As a result, C1, i.e., the char with a higher yield was considered for further methylene blue adsorption as discussed in the following section.

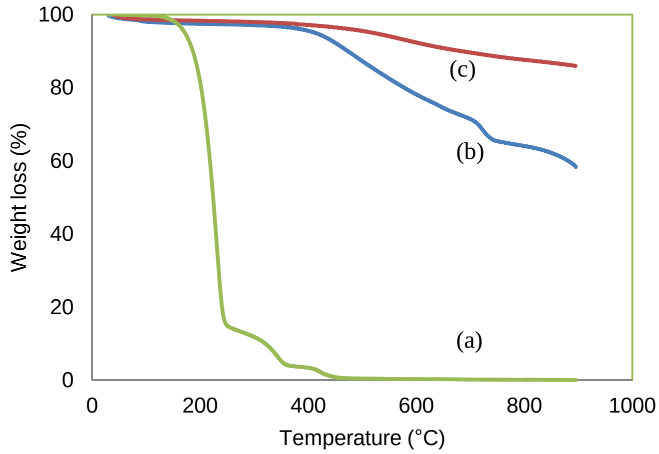

Fig. 2 Thermal profiles of (a) PFAD, (b) C1, (c) C2.

Methylene blue adsorption

Fig. 3 shows the equilibrium adsorption of methylene blue onto C1. The isotherm shows a favourable convex upward adsorptive characteristic with a sharp slope at low C_e values, to a maximum value of 7.62 mg/g and then levelling-off. This pattern is common in the dye removal using adsorbents from agricultural and industrial by-products (Aljeboree et al. 2014; Mahamad et al. 2015). The adsorption of methylene blue onto PFAD-char could be promoted by the π-π interaction (weak interaction between aromatic rings of graphitic structure of char and aromatic rings of methylene blue molecules), and the dissociation of acidic oxygenated functional groups to attract the positively charged methylene blue dye molecules. The adsorption data were analyzed using the commonly used isotherm models namely Langmuir and Freundlich. The Langmuir model is given as $q_e=Qk_LC_e/(1+k_LC_e)$, where Q (mg/g) is the maximum capacity and k_L (L/mg) is the adsorption affinity. The Freundlich model is given as $q_e=k_FC_e^{1/n}$, where k_F and n are the Freundlich constants representing the adsorption capacity and adsorption intensity, respectively. The *Solver*-add in was used to process the data using non-linear regression for the least sum of squared errors (SSE), and the obtained parameters are summarized in Table 2. Clearly, the Langmuir model can adequately describe the adsorption of MB onto C1 with the predicted maximum capacity of 6.61 mg/g at room temperature. The underlying theory of Langmuir equation suggests the monolayer coverage of methylene blue onto the homogeneous surface of C1. The essential characteristic of this model can be expressed in terms of a dimensionless separation factor, $R_L=1/(1+k_LC_o)$ (Mahamad et al., 2015). R_L indicates the shape of the isotherm, either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L=0$). Fig. 4 illustrates the profile of R_L for methylene blue adsorption onto C1. The R_L values are in the range of 0.013 – 0.700, indicating that the adsorption is favorable, in which the process becomes practically irreversible at high initial concentration. The Freundlich model is based on the assumption that the multi-layer coverage onto heterogeneous adsorbent surface. From Table 2 and Fig. 3, it is evident that the Freundlich isotherm shows a lack of fit because of a greater SSE, and a large deviation from the experimental data, hence it can not be used to represent the adsorption data.

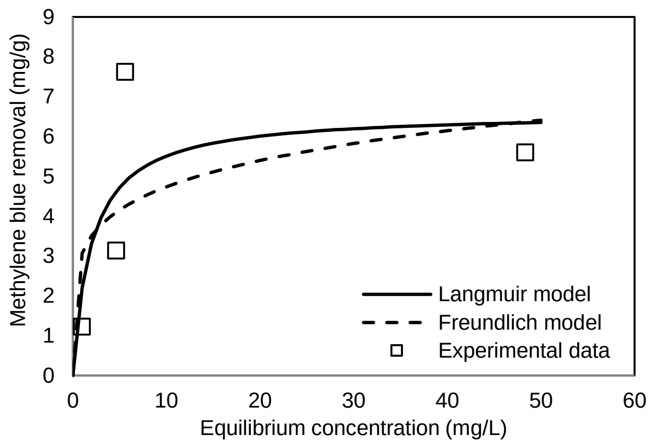

Fig. 3 Adsorption isotherm of methylene blue onto PFAD-based char.

Table 2 Isotherm constants.

Langmuir model	
Q (mg/g)	6.61
k_L (L/mg)	0.50
SSE	11.1
Freundlich model	
k_F (mg/g)(L/mg)$^{1/n}$	3.07
n	5.32
SSE	16.2

Fig. 5 displays the adsorption of methylene blue onto C1 at varying solution pHs. From Fig. 5, there was no appreciable change in the degree of adsorption at acidic range of pH 2 – 7. At this region, the adsorption is restricted, and is apparently to be pH-independent. However, the equilibrium adsorption was found to increase slightly with increasing pH from pH 7 – 11, and the methylene blue removal of 7.60 mg/g was recorded at the pH range of 10 – 11. A methylene blue-deficient adsorption in acidic region is probably due to the presence of excess H^+ ions competing with the methylene blue cations for the adsorption sites. The decrease in protons concentration at higher solution pH enables the dye cations to easily lodge on the active sites (Hameed & El-Khaiary, 2008; Peydayesh & Rahbar-Kelishami, 2015).

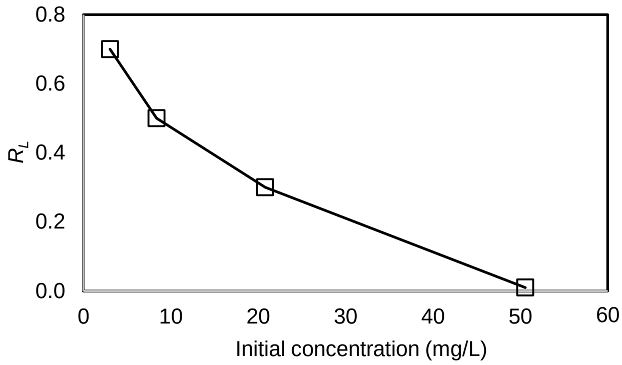

Fig. 4 R_L profile for methylene blue adsorption onto C1.

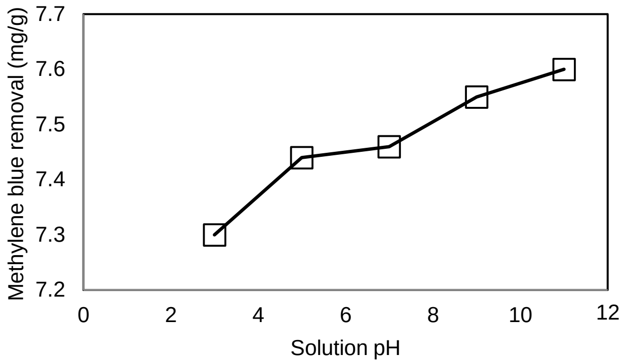

Fig. 5 Adsorption of methylene blue at different solution pHs.

The performance of C1 in the adsorption of methylene blue was compared with other adsorbents formerly employed for the same application. The information are summarized in Table 3.

Table 3 Adsorption of methylene blue by various adsorbents.

Adsorbent	Q (mg/g)	Reference
PFAD-based char	7.62	This work
sulphuric acid-treated deffated algae biomass	7.80	Sarat-Chandra et al. (2015)
KOH-treated palm oil mill effluent sludge	23.5	Zaini et al. (2013)
Fly ash	5.72	Kumar et al. (2005)
Lignocellulosic material	56.5	Low et al. (2011)
Coir pith carbon	5.87	Kavitha & Namasivayam (2007)
Biochar	9.50	Sun et al. (2013)
Marble dust sorbent	16.4	Hamed et al. (2014)
Food processing sludge	23.6	Mahapatra et al. (2012)

The PFAD-based char portrays a comparable monolayer adsorption of methylene blue with the adsorbents listed in Table 3. It may be due to its purity and litle or no ash content that ease the adsorption. On the other hand, the other adsorbents demonstrate dissimilar adsorption capacities. This could be due to the nature of the starting materials, carbonization or treatment procedures and the setting conditions for adsorption. This study shows the feasible conversion of PFAD into char or adsorbent, and paves new way for the exploitation of this material in the removal of dye from wastewater.

CONCLUSION

Palm fatty acid distillate (PFAD) was converted into chars by heat treatment in a muffle furnace at 500 °C – 600 °C for 0.5 h. The physicochemical properties of PFAD and the derived chars were characterized. The chars are thermally stable at higher temperature as compared to its precursor, PFAD. Also, the chars are rich in carbon content which is likely to be in the graphitized structures, and possess unique functional groups that could be useful in the adsorption of dye. The PFAD-based char show a maximum methylene blue adsorption of 7.62 mg/g, and the experimental data fitted adequately well with the Langmuir model with the predicted monolayer capacity of 6.61 mg/g. There is no appreciable change in the adsorption capacity of methylene blue by PFAD-char at acidic region, while it slightly increased in the basic solution. The results of this study show that the industrial by-product, namely PFAD can be converted into char as an alternative adsorbent for dye removal from water.

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