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Palm oil mill effluent sludge ash as adsorbent for methylene blue dye removal

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ABSTRACT

This work was aimed to evaluate the adsorptive nature of palm oil mill effluent sludge ash for methylene blue dye removal in aqueous solution. Two types of palm oil mill effluent sludge collected from different treatment ponds, i.e. anaerobic and biopolishing were burnt to ash, and treated with 5 M HCl. The treated and untreated adsorbents were characterized for surface area and morphology. Methylene blue dye adsorption was carried out in laboratory at room temperature, and the adsorption data were analyzed based on equilibrium isotherm and kinetic models. The surface area of ash-adsorbents was found to increase more than 12 times after HCl treatment. The highest surface area recorded was 218 m^2/g. Equilibrium data of ash-adsorbents obeyed Langmuir isotherm to linear approximation suggesting the monolayer uptake of methylene blue dye. The highest maximum uptake of 50.7 mg/g methylene blue dye (50% removal) was demonstrated by HCl-treated biopolishing ash-adsorbent at initial concentration of 200 mg/L and pH 5.8 ± 0.1. The kinetic data for selected HCl-treated ash-adsorbent were fitted to Ho's pseudo-second-order model, indicating chemisorption process. Results showed that ash obtained from palm oil mill effluent sludge after simple treatment with HCl could be employed as effective adsorbent for the removal of methylene blue dye.

Keywords: Adsorbent; Adsorption; Ash; Methylene blue dye; Palm oil mill effluent sludge

1. Introduction

The release of dyes from textile industries into receiving water resources affects the aquatic creatures because some dyes are highly toxic and carcinogenic [1,2]. Dyes block the passage of sunlight into the stream, thus destroy the life cycle and food chain in the water, and disrupt the biodiversity within. Methylene blue is one example of commonly used dyes in textile and fabric industries [2]. It can cause harmful effects to human health such as eye injury, difficulty in breathing, nausea, vomiting, profuse sweating, Heinz body formation, diarrhea, gastritis, mental confusion, cyanosis, jaundice, tissue necrosis, and methemoglobinemia [2–5].

Methods for dye removal include adsorption, chemical coagulation, ion exchange, biological treatment, and electrolysis [2,3,6]. Of these, adsorption by activated carbon is highly effective to remove dye [7]. However, activated carbon precursors like coal and petroleum pitch are not renewable, while regeneration of spent activated carbon is relatively expensive. This scenario has brought about searches for alternative

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precursors that are abundantly available and low cost [8].

Malaysia is one of the largest palm oil producers in the world with 426 operating mills in year 2011 [9]. Wet palm oil milling is a common process of extracting palm oil, and requires large amounts of steam and water. About 5–8 tonnes of water is utilized for every ton of crude palm oil produced, to which more than 50% of this water ends up as palm oil mill effluent [10]. It is estimated that about 55×10^6 m^3 of palm oil mill effluent is generated from the palm oil industry in Malaysia every year [11]. Of this, about 48,000 mg/L is solids, commonly known as palm oil mill effluent sludge [12].

Sludge of palm oil mill effluent produces bad odor, and is considered as a source contributing to surface and ground pollution [10,12]. There has been a burgeoning concern over the sustainable measures in dealing with sludge, especially when it comes to handling and disposal.

Palm oil mill effluent sludge (PS) originates from leaves, trunk, decanter cake, empty fruit bunches, seed shells, and mesocarp fiber [12]. Due to its higher nutrient content, some researchers suggested composting as an eco-friendly alternative to PS problems [12,13]. However, this option is relatively expensive and to some extent could produce phytotoxic substances such as ammonia, ethylene oxide, and organic acids that are detrimental to plant growth [12].

Larger load of PS could be greatly reduced if it can be converted into value-added product such as adsorbent. Apart from solving the problems related to sludge handling and disposal, the adsorbent produced could become as a source of environmental protection to treat wide range of pollutants present in water [14]. Moreover, the operation costs incurred by palm oil mill in the treatment of the sludge could be greatly reduced if the sludge is reusable for the in-plant operations.

The conversion of sludge into adsorbent is relatively a new route of dealing with sludge.

To date, sewage sludge originated from waste recycling process [15], urban waste water treatment plant [16], and paper mill factory [17] were among the precursors that have been extensively studied. A number of authors claimed that sludge can be converted into activated carbon using activating agents such as CO_2 [15], H_2SO_4 [16], KOH [17,18], and $ZnCl_2$ [18]. It is being observed that some of these studies produced activated carbons with poor surface area due to high ash content of more than 50% in the original sludge precursors [19–21].

Because the content of ash outweighs the organic constituents, it is presumed that inorganic ash may also contribute to the adsorption process by sludge-adsorbents. To date, the adsorptive properties of sludge ash is still lacking in much of the published literature. Therefore, the present work was aimed to characterize the adsorptive properties of ash-adsorbents derived from PS. Methylene blue dye was used as a probe to evaluate the suitability of adsorbent. The equilibrium and kinetic data were analyzed using the established models. Finally, the results and possible mechanisms governing the removal efficiency of methylene blue dye were discussed.

2. Materials and methods

2.1. Materials

Palm oil mill effluent sludge (PS) was obtained from two treatment ponds at Felda Taib Andak palm oil mill, Johor, Malaysia. The two treatment ponds, anaerobic (AP1) and biopolishing (AP2) are the final effluent treatment prior to the discharge. All chemicals used were of analytical grade. Hydrochloric acid (37%) and powder of methylene blue dye (assay 98.5%) were supplied by R & M Chemicals and HmbG Chemicals, respectively.

2.2. Preparation of ash-adsorbent

Excess water was removed from the sludge by conventional oven-drying at 110°C for 24 h. The dried sludge was burnt to ash at 850°C for 2 h in a furnace [22]. Ash content was calculated from the weight of leftover after pyrolysis divided by the dried weight of sludge.

The resultant ash-adsorbents were divided into two parts; treated and untreated. The treated ash-adsorbents were soaked in 5 M HCl overnight, washed in distilled water to a constant pH, and then dried in oven before analysis. The untreated ash-adsorbents were used without further treatment. Ash-adsorbents were designated as AP1, AP2, AP1-H, and AP2-H, where AP1 and AP2 represent the adsorbents from anaerobic and biopolishing treatment ponds, respectively, while H denotes HCl treatment.

2.3. Characterization of ash-adsorbent

Specific surface area of ash-adsorbents was measured with liquid nitrogen at temperature of 77 K by surface area analyzer (Pulse ChemiSorb 2705, Micrometrics). Surface morphology was determined by scanning electron microscopy coupled with EDX (SEM, Gemini SUPRA 35VP).

2.4. Adsorption studies

Adsorbate solution was prepared by dissolving desired weight of methylene blue dye powder in distilled water. Necessary dilution was performed to obtain varying concentrations between 1 and 200 mg/L of the solution. Initial pH of the solution was left unadjusted and measured as 5.8 ± 0.1. Control solution was prepared to determine initial concentration. Batch adsorption was carried out by adding 0.1 g adsorbent in 50 mL methylene blue dye solution, and the mixture was allowed to equilibrate with orbital shaker at 120 rpm, 28 ± 1˚C for 72 h. Then, the solution was filtrated and the residual concentration of dye was measured using Biochrom Libra S6 Spectrophotometer at 690 nm [23,24]. The amount of methylene blue dye adsorbed at equilibrium, q_e (mg/g), was calculated by,

$$q_e = \frac{(C_0 - C_e)}{m} V \tag{1}$$

where C_0 and C_e (mg/L) are initial and equilibrium concentrations, respectively, V (mL) is the volume of the solution and m (g) is the mass of dry adsorbent.

Two isotherm models, namely Langmuir [25,26] and Freundlich [27] were used to describe the adsorption of methylene blue onto sludge-adsorbent. The Langmuir isotherm indicates monolayer adsorption onto a complete homogeneous surface, and is given as,

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 \cdot b} \tag{2}$$

where Q_0 (mg/g) is the maximum uptake per unit mass of adsorbent to form a complete monolayer on the surface of adsorbent, and b (L/mg) is a constant related to the affinity of the binding site. The empirical Freundlich isotherm that describes sorption on a heterogeneous surface is given by,

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{3}$$

where K_F and $1/n$ are the Freundlich constants which are the indicators of maximum adsorption capacity and intensity, respectively. The $1/n$ value ranging from 0 to 1 is considered to represent surface heterogeneity. It is also suggested that the n value ranging between 2 and 10 represents favorable adsorption process. The applicability of the two models was determined based on the coefficient of determination (R^2).

The kinetic studies for the selected ash-adsorbent were performed by measuring the residual concentration of methylene blue dye at different time intervals. Similar settings as for equilibrium adsorption were used, and the initial concentrations were recorded as 50 and 130 mg/L. The kinetic data were evaluated by using two kinetic models, namely pseudo-first-order [28] and Ho's pseudo-second-order models [29]. Pseudo-first-order model is given by,

$$\ln (q_e - q_t) = \ln q_e - k_1 \cdot t \tag{4}$$

where q_t (mg/g) is the amount of methylene blue dye adsorbed at time t (h), and k_1 (h^{-1}) is the rate constant of first order adsorption. Ho's pseudo-second-order equation based on chemical related adsorption is expressed as,

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{5}$$

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

$$h = k_2 \cdot q_e^2 \tag{6}$$

All constants of isotherm and kinetic models were solved using *Solver* add-in of MS Excel, given the condition where the sum of squared error is the least thus yield the optimum value of coefficient of determination (R^2). The R^2 value between the calculated and experimental values was obtained using RSQ function.

3. Results and discussion

3.1. Characteristics of ash-adsorbent

Characterization of adsorbent is crucial to understand the properties that may influence the adsorptive ability of the adsorbent. Table 1 represents elemental composition of ash-adsorbent. In general, these minerals are mainly of oil palm origins because the milling used only physical processes which do not involve any use of chemicals [30].

Table 2 shows the ash content of two sludge precursors and the surface area of ash-adsorbents. The values of ash content were recorded as 32 and 43% for anaerobic sludge and biopolishing sludge, respectively. In a related work, Rio and co-workers [19] reported adsorbent from sewage sludge with 22% ash has

Table 1
Elemental composition of ash from palm oil mill effluent sludge

Element	wt%
Mg	7.45
Al	14.42
Si	10.86
P	4.31
S	1.12
K	0.80
Ca	2.51
Fe	7.11
Cu	0.17
O (oxides)	51.27
Sum	100.00

Table 2
Ash content and specific surface area of ash-adsorbents

Ash-adsorbent	Ash content (%)	Surface area (m^2/g)
AP1	32	15.3
AP1-H	–	218
AP2	43	13.5
AP2-H	–	163

resulted in a small specific surface area of 52 m^2/g. A number of similar findings have also been reported in literature [20,21], suggesting that the inorganic constituents in ash could behave as inert material that impedes the development of pores within the organic substances during the activated carbon preparation. Because of their low carbon content and low surface area, the adsorbents reported in these works [19–21] could not be regarded as activated carbon. However, it is believed that ash may still act as active site for adsorption.

The important parameter that is commonly reported for adsorbent is specific surface area. From Table 2, the non-treated ash-adsorbents, namely AP1 and AP2 demonstrate a trivial surface area, and the values were comparable at about 14 m^2/g. The surface area was found to increase more than 12 times after the HCl treatment and the values were 218 and 163 m^2/g for AP1-H and AP2-H, respectively. In a previous related work, Klasson and co-workers [31] reported a nearly two times increase of surface area after 0.1 M HCl treatment. It shows that HCl treatment is effective to remove surface impurities so as to enhance the accessible surface area for adsorption [31].

Fig. 1 displays the morphology of ash-adsorbents. It can be observed that the surface of untreated ash-adsorbents was dense and planar. After 5 M HCl treatment, the two ash-adsorbents demonstrated scattered and dispersed particles of irregular shape and size.

3.2. Adsorption studies

Methylene blue is a commonly used dye for coloring. However, this substance is toxic and carcinogenic to human and aquatic creatures, and therefore is essential to be removed before entering the receiving water resources. This section describes the adsorptive properties of ash-adsorbents in removing methylene blue dye from aqueous solution. Fig. 2 shows the ability of ash-adsorbents to remove methylene blue dye at different initial concentrations.

Different initial concentrations of methylene blue dye ranging from 1 to 130 mg/L were used to investigate the uptake and percent removal by ash-adsorbents. In general, the uptake efficiency of methylene blue dye by all ash-adsorbents increased along with different initial concentrations. However, the HCl-treated ash-adsorbents showed a greater methylene blue dye removal than the untreated ones due to the formation of higher surface area. For example, the removal of methylene blue dye by anaerobic sludge ash after the HCl treatment has increased from 31 to 72% at initial concentration of 100 mg/L. Clearly, the dye uptake was found to increase more than twice after the treatment of adsorbent at all initial concentrations studied. The increase in surface area is expected to enhance the interaction probabilities between the adsorbate (methylene blue dye) and ash-adsorbent towards a greater removal of methylene blue dye [7,8,32,33].

Fig. 2 illustrates the percent removal decreased with increasing initial concentration. It is clear that the methylene blue dye removal depends on the initial concentration because the mass driving force for separation is larger at higher initial concentration until the surface saturation of adsorbent is reached. However, as the initial concentration increases, only small more fraction of methylene blue dye could be adsorbed onto the adsorbent, and this would leave behind higher residual concentration that leads to lower removal efficiency. For HCl-treated ash-adsorbents, the highest percent removal of more than 90% was recorded with the initial methylene blue dye concentration of 10 mg/L.

3.2.1. Equilibrium adsorption

Adsorption isotherm is useful to describe how the adsorbate molecule distributes between the liquid and solid phases as the adsorption reaches the equilibrium

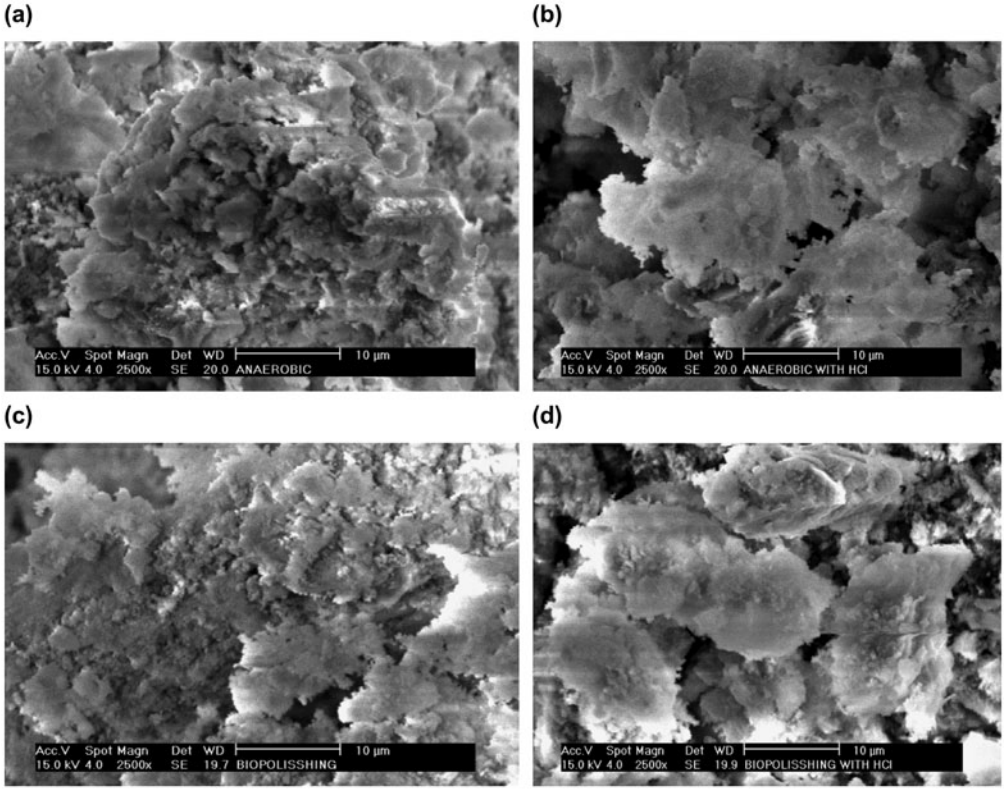

Fig. 1. SEM images for (a) AP1, (b) AP1-H, (c) AP2, and (d) AP2-H.

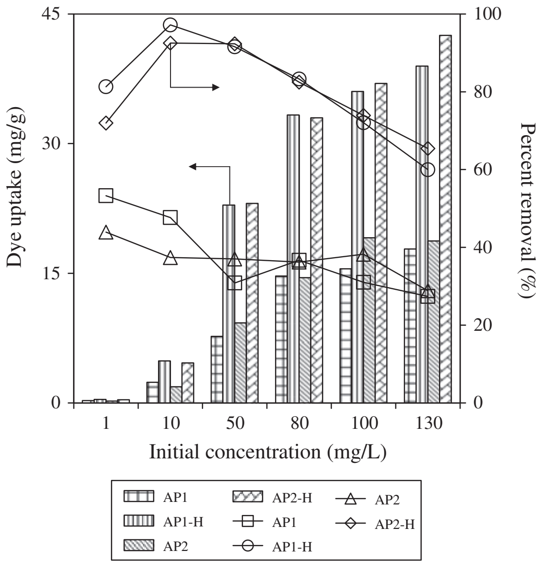

Fig. 2. Removal of methylene blue dye at different initial concentrations.

state. Fig. 3 depicts the equilibrium isotherm of methylene blue dye onto ash-adsorbents, and the respective values of Langmuir and Freundlich constants are tabulated in Table 3.

The convex upward shape demonstrated by the four ash-adsorbents exhibits a strongly favorable adsorption of methylene blue dye. The decolorization of methylene blue was observed to have the following order: AP2-H > AP1-H > AP2 > AP1. It shows that the removal of methylene blue dye was surface area-sensitive [7,33]. Although the uptake significantly increased after HCl treatment, this trend however is not directly in agreement with the respective values of surface area; suggesting that the inorganic constituents in ash could play some contributing role in the removal of methylene blue dye [34–40].

The applicability of isotherm models shown in Table 3 was deduced based on coefficient of determination (R^2). It shows that, Langmuir model fitted the adsorption data better than Freundlich model, although the values of maximum uptake, Q_0 for AP1 and AP2 were overestimated by the Langmuir model. The applicability of Langmuir model suggests the methylene blue dye removal as monolayer adsorption onto the homogeneous surface of ash-adsorbent. The $1/n$ values of Freundlich isotherm varied between 0.2 and 0.4 also implies the homogeneous surface of HCl-treated ash adsorbent. The results agreed to a certain degree with the micrographs shown in Fig. 1. The adsorption affinity, b for methylene blue dye towards

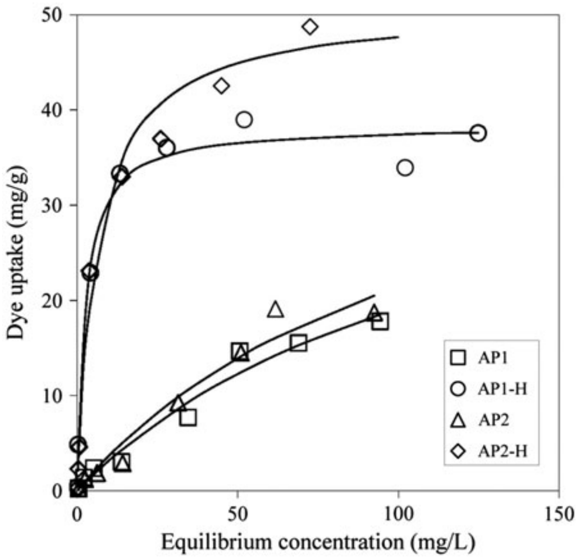

Fig. 3. Equilibrium adsorption of methylene blue dye onto ash-adsorbents.

Table 3
Constants of Langmuir and Freundlich models

	Langmuir model			Freundlich model		
Ash-adsorbent	Q_0 (mg/g)	b (L/mg)	R^2	K_F	$1/n$	R^2
AP1	43.4	0.0079	0.970	0.642	0.745	0.963
AP1-H	38.4	0.387	0.983	14.4	0.222	0.811
AP2	46.1	0.0087	0.960	0.681	0.760	0.944
AP2-H	50.7	0.154	0.984	10.3	0.378	0.937

ash-adsorbent is directly related to the values of surface area. The higher the surface area means the greater the affinity for methylene blue dye removal, particularly at lower equilibrium concentrations [32].

The adsorption data was further analyzed by Langmuir separation factor, $R_L = 1/(1 + b{\cdot}C_0)$, a feature of Langmuir model [41]. The R_L value depicts the nature of adsorption process irrespective of the shape of isotherm. The adsorption is unfavorable if $R_L > 1$; linear if $R_L = 1$; favorable if $0 < R_L < 1$; or irreversible if $R_L = 0$. Fig. 4 shows the R_L profiles of ash-adsorbents at varying initial concentrations.

As it can be seen, these adsorbents displayed the R_L values ranging from 0.01 to 1.0; in accordance to the favorable region of adsorption at all initial concentrations studied. However, the R_L values given by AP1-H and AP2-H were much lower and approaching zero; demonstrating that they were more favorable in adsorption because of higher intensity of methylene blue dye adsorption.

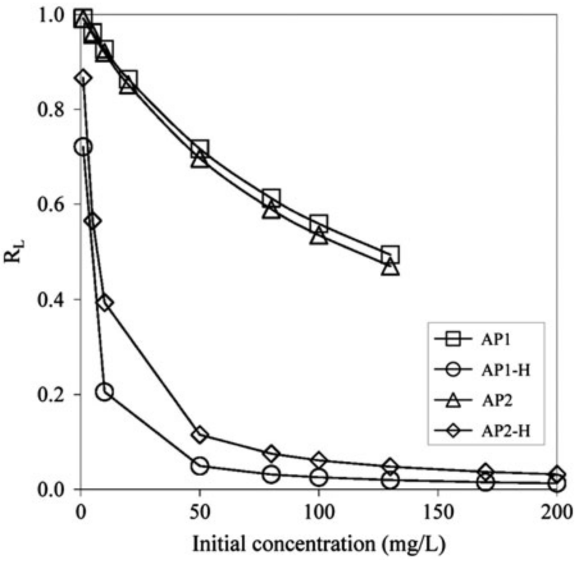

Fig. 4. Langmuir separation factor.

3.2.2. Adsorption kinetics

A better understanding of the mechanism and rate of adsorption is important to design the adsorption process [34,42]. Thus, the pseudo-first-order and Ho's pseudo-second-order models were employed to fit the kinetic data. For this purpose, AP2-H was selected for kinetic evaluation because of its better methylene blue dye removal efficiency compared to the other three ash-adsorbents. Fig. 5 shows the kinetic profiles of AP2-H for two different initial concentrations, and the constants are tabulated in Table 4.

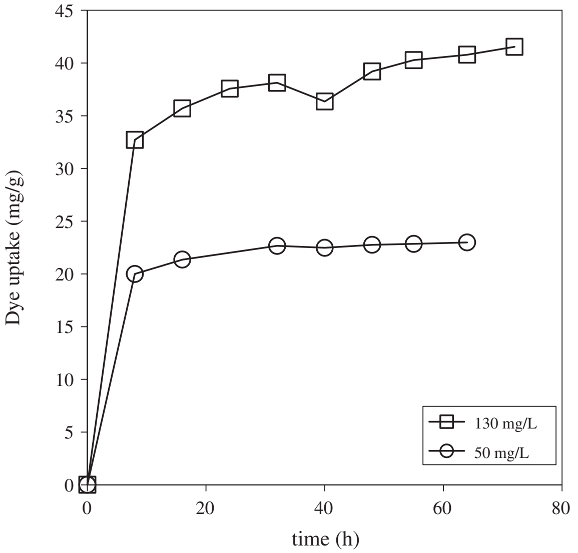

Fig. 5. Kinetic profiles of methylene blue dye removal onto AP2-H at two different initial concentrations.

Table 4
Constants of kinetic models

	Initial concentration A (mg/L)	
	50	130
$q_{e,\ \mathrm{Exp}}$ (mg/g)	23.1	42.5
Pseudo-first-order model		
k_1 (h^{-1})	0.057	0.032
$q_{e,\ \mathrm{Cal}}$ (mg/g)	4.35	13.0
R^2	0.944	0.894
Pseudo-second-order model		
k_2 (g/mg h)	0.009	0.021
h (g/mg h)	4.96	38.7
$q_{e,\ \mathrm{Cal}}$ (mg/g)	23.5	42.9
R^2	0.999	0.996

Notes: $q_{e,\ \mathrm{Exp}}$ – experimental equilibrium data; $q_{e,\ \mathrm{Cal}}$ – calculated equilibrium data.

From Fig. 5, the uptake of methylene blue dye was found to increase with increasing time. The equilibrium uptake over the studied period was reasonably tallied with that of adsorption isotherms. Rapid increase in adsorption was observed at the first 6 h, after which the uptake started to increase gradually. For initial concentration of 50 mg/L, a plateau obtained indicates the attainment of equilibrium was achieved as early as 30 h, while a longer period was required for higher concentration of 130 mg/L.

Table 4 obviously shows that the adsorption of methylene blue dye did not follow the pseudo-first-order kinetics. The R^2 values for the pseudo-second-order model were sufficiently closer to unity, and there is a good agreement between $q_{e,\ \mathrm{Cal}}$ and $q_{e,\ \mathrm{Exp}}$. Thus, the kinetic data could be well described by the pseudo-second-order model. The pseudo-second-order rate constant, k_2 increased more than twice when the initial concentration increases to 130 mg/L. In the same manner, the initial rate adsorption, h also increased to 38.7 g/mg h, that is, 7.8 times greater than that at 50 mg/L. These results are tied-up with the fact that higher concentration could promote greater driving force for rapid adsorption from the bulk solution to the liquid film interface, although the attainment of equilibrium would be much slower compared to at lower concentration. It is suggested that the rate limiting step was chemisorption process involving the formation of complexes with the inorganic constituents or oxides on the ash surface [34,42,43].

Table 5 represents some studies on methylene blue dye removal onto various adsorbents. In general, these adsorbents displayed different removal performance of methylene blue dye depending on their physical and chemical characteristics. Among the main factors that driven the adsorption are surface area and initial solution pH.

Methylene blue dye is a cationic dye that theoretically favors removal at high initial pH because of the deprotonation of surface site. However, it has been

Table 5
Removal of methylene blue by various adsorbents

Adsorbent	Adsorption capacity (mg/g)	pH	Surface area (m^2/g)	References
Fly ash	6.05	–	–	[35]
Thermal-treated rice husk	690	7.91	101	[36]
Baggase fly ash	6.46	–	–	[37]
Baggase bottom ash	143	–	–	[38]
Coal fly ash	7	6.16	21.1	[39]
Rice husk	8.07	6.8	–	[44]
Multi-walled carbon nanotubes	119	–	280	[45]
Gypsum	36	7.5	5.67	[40]
Natural Jordanian Tripoli	16.6	8.0	46.5	[46]
MgO nanoparticle	4.5	7.0	–	[47]
Sugar extracted spent rice biomass	8.13	5.2	0.407	[48]
$ZnCl_2$-activated rice husk carbon	9.73	–	181	[49]
HCl-treated fly ash	7.99	5.2	28.3	[50]
NaOH-treated fly ash	12.8	12	–	[51]
NaOH-treated waste activated sludge	53.7	7	–	[52]
$ZnCl_2$-treated sewage sludge	102	–	–	[53]
H_2SO_4-treated sewage sludge	194	5.0	390	[54]
HCl-treated biopolishing sludge ash	50.7	5.8	163	This study
HCl-treated anaerobic sludge ash	38.4	5.8	218	This study

reported that there is no significant change in the removal efficiency of methylene blue dye at pH greater than 4.0 [45].

Different types of ash-adsorbent derived from fly ash for methylene blue dye removal have been reported in literature [35–39,50,51]. And to the best of our knowledge, there is no reference to work so far regarding the evaluation of sludge ash in methylene blue dye removal. It is obvious that the ash-adsorbents prepared from this work possessed comparatively higher surface area and adsorption capacity at normal pH (non-adjusted) when compared to other ash-adsorbents reported in the literature (Table 5).

4. Conclusion

Adsorbents were prepared from the ash of palm oil mill effluent sludge. The surface area of ash-adsorbents increased after the treatment with 5 M HCl. Methylene blue dye showed a greater affinity to ash-adsorbents with a higher surface area. Adsorption of methylene blue dye could be well described as monolayer adsorption onto a homogeneous surface. From the mechanism and kinetic point of view, rapid transport of methylene blue dye molecules is expected to occur from the bulk solution to the liquid film interface, and the rate determining step was chemisorption involving the formation of complexes with the inorganic constituents or oxides on the surface of ash-adsorbents. Ash-adsorbents showed a comparable performance of methylene blue dye removal as compared to the other synthetic adsorbents. With simple treatment method, ash-adsorbent could become a suitable candidate for the removal of methylene blue dye from aqueous solution.

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