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Removal of Methylene Blue and Copper (II) by Oil Palm Empty Fruit Bunch Sorbents

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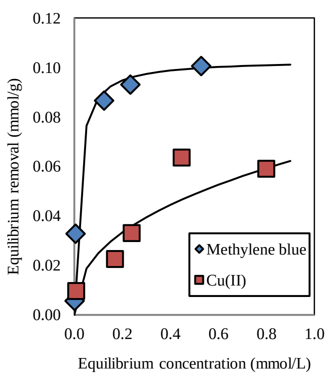
Graphical abstract



Abstract

This study aims to evaluate the adsorptive properties of oil palm empty fruit bunch for the removal of cationic pollutants in water. The untreated and hydrochloric acid-treated empty fruit bunches were characterized based on pH of adsorbent, specific surface area and surface functional groups. The adsorbents were then used to challenge varying concentrations of methylene blue dye and copper (II) in aqueous solution. Results show that the specific surface area of empty fruit bunch decreased upon the treatment with hydrochloric acid. The untreated adsorbent displays a higher equilibrium removal of the target pollutants due to its higher specific surface area of 28.4 m^2/g. The maximum removal were recorded as 0.103 and 0.075 mmol/g for methylene blue and copper (II), respectively. Oil palm empty fruit bunch is a promising candidate for the removal of cationic pollutants in aqueous solution.

Keywords: Adsorption; chemical treatment; copper (II); methylene blue; oil palm empty fruit bunch

1.0 INTRODUCTION

Industrial activities are important in developing the nation. Undeniably, however they usually cause pollution to the environment. The untreated discharged effluent, for example causes the contamination to the water bodies. The wastewater contains toxic substances such as heavy metals, organic chemicals and dyestuffs exceeding the maximum permissible limit set by the local authorities [1]. There are many associated risks and possible toxic effects from the exposure to these pollutants as they can easily be accumulated in soft tissues through food chain, and are not completely metabolized by human body. Heavy metals like copper (II), for example can lead to kidney and liver failure, and affect the skin, bones and teeth [1].

Treatment of industrial effluent could be achieved through a number of methods such as chemical precipitation, solvent extraction, electrodialysis, reverse osmosis, ion exchange, evaporation and adsorption [2-3]. However, the costs of these methods are too expensive. Amongst these methods, adsorption is acknowledged as a preferable treatment strategy because of its ability to remove contaminants at low concentration. Activated carbon is a commonly used adsorbent in adsorption, and it is efficient for the treatment of water because of its large surface area and pore volume, and high degree of surface reactivity [4-6]. Yet, producing activated carbon is rather costly, and to some extent may result in secondary pollution due to the use of excessive chemicals.

Malaysia is among the largest palm oil producer in the world. Currently, about 90 million tons of waste biomass such as empty fruit bunches, palm kernel shells and trunks are produced every year. Of which, 12.4 million tons are empty fruit bunches [5]. Empty fruit bunch (EFB) is a solid residue left after the fruit bunches are pressed to extract oil. This implies that

EFB is a renewable source of adsorbent in the removal of pollutants from water [4]. In addition, the use of EFB as adsorbent also helps in solving the present environmental problems related to the disposal and burning of the biomass.

The present work was aimed at evaluating the possibility of using the untreated oil palm empty fruit bunch as adsorbent to remove methylene blue and copper (II) from water. EFB was also treated with hydrochloric acid as it was reported that the chemical treatment could enhance the specific surface area of the material [7]. The treated EFB was employed for comparison. The removal performance by sorbents was compared and analysed using the Langmuir and Freundlich isotherm models. The possible removal mechanisms were also discussed.

2.0 MATERIALS AND METHODS

2.1 Preparation of Adsorbent

Empty fruit bunch was obtained from Sungei Kahang Palm Oil Sdn Bhd located at Kluang, Johor state of Malaysia. Methylene blue ($(CH_3)_2NC_6H_3(SN)C_6H_3N(CH_3)_2Cl$, molecular weight 319.85 g/mol) was purchased from HmbG Chemicals. Copper (II) chloride dehydrate ($CuCl_2{\cdot}2H_2O$, molecular weight 170.48 g/mol) and hydrochloric acid (HCl, molecular weight 36.5 g/mol, 37%) were purchased from R&M Chemicals, United Kingdom. All chemicals are of analytical-grade reagents, and were used without further purification.

Empty fruit bunch (EFB) was washed several times using tap water to remove dirt and mud, and finally was rinsed with distilled water. The sample was dried in an oven at 90°C for 24 hours. Then, the dried sample was cut to a size of approximately 5 cm. Twenty-five grams of EFB was soaked in 0.1 M HCl overnight, and then washed with distilled water to a pH 3 to 4. The untreated and HCl-treated sorbents were designated as EFB-A and EFB-B, respectively. The adsorbents were stored at room temperature for further use.

2.2 Characterization of Adsorbent

The specific surface area of adsorbents was determined using surface area analyser (Pulse ChemiSorb 2705, Micrometrics) at liquid N_2 temperature of 77 K. The presence of surface functional groups was determined via potassium bromide disc method using FTIR spectrometer (Spectrum One, Perkin Elmer).

2.3 Removal of Methylene Blue and Copper(II)

Desired weight of copper (II) and methylene blue were separately dissolved in distilled water to prepare the stock solutions (e.g., 269 mg of $CuCl_2{\cdot}2H_2O$ was dissolved in 500 mL distilled water for making 100 mg/L solution). Thereafter, dilutions were made to obtain solutions at different initial concentrations. A series of conical flasks containing 50 mL solution of varying concentrations was prepared. Then, 0.1g of adsorbent was added to each conical flask, and the mixture was allowed to equilibrate on an orbital shaker with the speed of 120 rpm at room temperature for 72 hours. Control solution was also prepared to represent the initial concentration.

The supernatant was separated by gravity filtration. The concentration of Cu (II) was measured using atomic absorption spectroscopy (AAnalyst 400, Perkin Elmer), while that of methylene blue was measured using vis-spectrophotometer (Halo vis-10, Dynamica) at a wavelength of 508 nm (a.u.=0.0813 × concentration (mg/L), R^2=0.986).

The removal capacity q_e was calculated by material balance from the difference between the initial concentration and the equilibrium concentration,

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

where q_e is the adsorption capacity (mg/g), C_o and C_e are the initial and equilibrium concentrations (mg/L), respectively, m is the adsorbent dosage (g) and V is the volume of solution (L).

3.0 RESULTS AND DISCUSSION

3.1 Characteristics of Adsorbent

Table 1 shows the characteristics and elemental composition of empty fruit bunch.

Table 1 Characteristics and elemental composition of empty fruit bunch

BET	28.4 m^2/g
pH	7.80
Ash	9.58
Elemental composition, dry-ash-free (%) [25]	
C	68.3
H	3.12
N	2.12
O	26.4

The specific surface area of the untreated empty fruit bunch (EFB-A) is 28.4 m^2/g, and the value decreased to 8.0 m^2/g upon the treatment with HCl. The decrease in specific surface area could be due to the collapse of pore channels. The result is somewhat opposite with what would be expected by the chemical treatment [7]. The pH of the adsorbents was recorded as 7.8 and 3.2 for EFB-A and EFB-B, respectively. The yield of EFB-B was calculated as 88.2%, and the weight loss is likely due to the partial de-mineralization of ash by hydrochloric acid. Figure 1 shows the spectra of the two adsorbents studied.

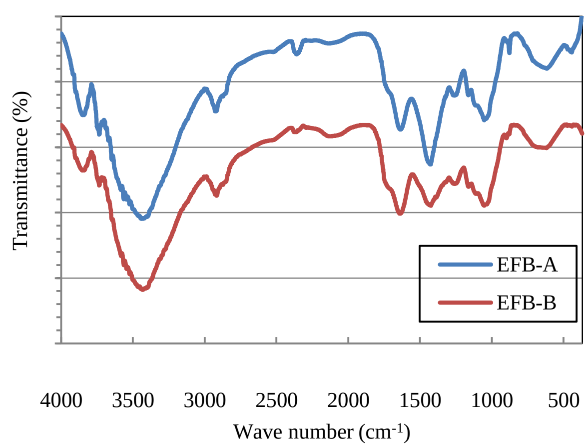


Figure 1 FTIR spectra of oil palm empty fruit bunch sorbents

In general, the FTIR spectra for both adsorbents are identical which indicate that they possess similar surface functional groups. However, the intensity of EFB-B spectra is somewhat lower than that of EFB-A. This is probably due to the diminishing of some functional groups as a result of HCl treatment.

The vibration at 1725-1700 cm^{-1} shows the presence of carboxylic groups, while the broadest peak at 3200-3600 cm^{-1} indicates the presence of O–H bond of hydroxyl group. Strong stretching vibration adsorption bands around 1740-3370 cm^{-1} represent the carbonyl and carboxylic groups on EFB sorbents. The peaks centred around 2930, 2357 and 569 cm^{-1} could be assigned to C-H (alkanes and alkyls), esters, phenol and benzene groups, respectively [8]. Alkene group (lignocelluloses) also presents as there is a broad peak between 1680-1600 cm^{-1}. For basic adsorbent (EFB-A, pH 7.8), the presence of negatively charged surface could also be attributed to the carboxylic and phenolic groups.

3.2 Removal of Methylene Blue and Copper(II)

Figures 2 and 3 show the removal of methylene blue and copper (II) by empty fruit bunch sorbents.

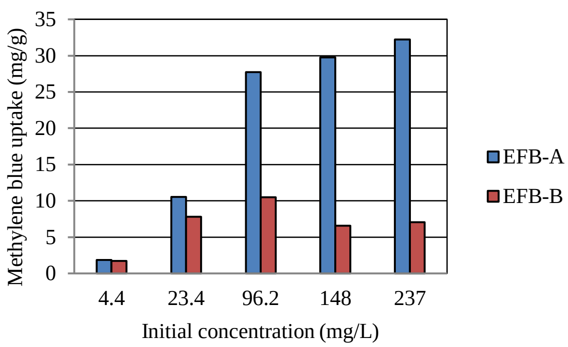


Figure 2 Removal of methylene blue by EFB-sorbents

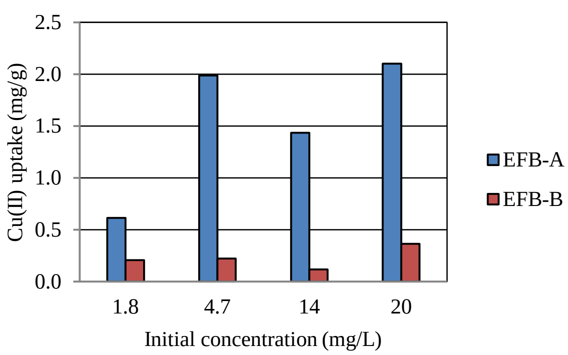


Figure 3 Removal of copper(II) by EFB-sorbents

At initial concentration of 4.4 mg/L, both EFB sorbents exhibit similar uptake of 1.9mg/g. The uptake of methylene blue was found to increase with increasing initial concentration, and EFB-A displays a greater removal of methylene blue than EFB-B at higher methylene blue concentration. On mass basis, the maximum removal was recorded as 32.3 and 10.5 mg/g for EFB-A and EFB-B, respectively. Similar trend was also observed for copper (II) removal (Figure 3). The untreated EFB sorbent shows a superior copper (II) removal of 2.1 mg/g that is 5.8 times higher compared to that of HCl-treated sorbent.

EFB-A possesses a specific surface area that is nearly three times greater than EFB-B. It gives EFB-A more sites and pore channels to accommodate the target pollutants, thus increasing the interaction probabilities between the sorbent sites and the adsorbates [7-8]. Moreover, EFB-A is a basic sorbent, while methylene blue and copper (II) are positively charged pollutants in water (Cu^{2+}, MB^{+}). Hence, the opposite charges enable the pollutants to be attracted towards the surface of EFB-A, and then become lodge on the available active sites.

3.3 Isotherm Studies

The adsorption data of methylene blue and copper (II) by EFB-A were further analysed using the two commonly used models, namely Langmuir and Freundlich models to ascertain the favourability of the adsorbent. The Langmuir model is used for describing the sorption isotherm in liquid phase, and is given as,

$$q_e = \frac{QbC_e}{1+bC_e} \qquad (2)$$

where Q (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 sites. The constants were determined by plotting C_e/q_e against C_e.

The Freundlich isotherm is applied to a non-ideal, multilayer sorption on heterogeneous surface. It is expressed as,

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (3)$$

where K_F and $1/n$ are the Freundlich constants which are indicators of the maximum adsorption capacity and intensity, respectively. The $1/n$ value ranging from 0 to 1 is considered to represent surface heterogeneity. The Freundlich constants were obtained by plotting log q_e against log C_e.

Figure 4 shows the equilibrium removal (on molar basis) of methylene blue and copper (II) onto EFB-A, and the respective isotherm constants are tabulated in Table 2.

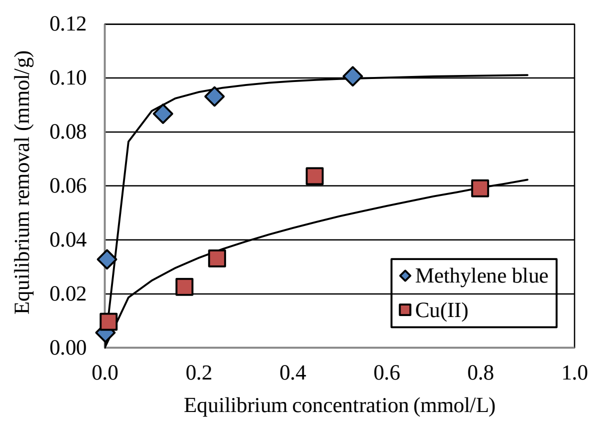


Figure 4 Equilibrium removal of methylene blue and Cu(II) by EFB-A (lines were predicted from isotherm models)

In general, the removal of the two target pollutants increased with increasing equilibrium concentration. The equilibrium removal of methylene blue demonstrates a more convex upward curve which indicates favourable adsorption because high solid loading could be obtained at lower equilibrium concentration. On molar basis, it is obvious that EFB-A exhibits higher affinity towards methylene blue, thus greater adsorption of methylene blue compared to that of copper(II).

Table 2 Constants of isotherm models

	Methylene blue	Cu (II)
Langmuir model		
Q (mmol/g)	0.103	0.075
b (L/mmol)	57.5	4.74
R^2	0.999	0.817
Freundlich model		
K_F	0.174	0.065
1/*n*	0.422	0.416
R^2	0.880	0.910

From the isotherm point of view, the adsorption of methylene blue onto EFB-A adequately fitted to the Langmuir model with R^2=0.999. It suggests that the adsorption is monolayer in nature and occurs on the homogeneous surface. On the other hand, the adsorption of copper (II) onto EFB-A could be fairly described by the Freundlich model. The maximum uptake as predicted by the Langmuir model are 0.103 and 0.075 mmol/g for methylene blue and copper (II), respectively. The results are comparable with the performance of chemically treated adsorbents found in the literature [7, 9-11]. In addition, it is also estimated that methylene blue possesses a twelve times greater adsorption intensity than copper (II).

The difference in the removal performance between methylene blue and copper (II) could be revolved around the ionic size. The hydrated ionic size (diameter) of copper (II) in water is 8.2 Å, while that of methylene blue is 15 Å. A smaller ionic size of copper (II) could be the reason for the lower removal performance on the macroporous (pore width > 50 nm) EFB. It is postulated that copper (II) is less likely to lodge on the surface with such texture. In an earlier work, we reported the increased affinity of copper (II) adsorption (0.052 mmol/g) onto mesoporous (2 nm < pore width < 50 nm, 66%) activated carbon with specific surface area of 1182 m^2/g [9]. On the other hand, we also reported that the macroporous texture of sludge adsorbent is suitable for reasonably good affinity of methylene blue removal (0.073 mmol/g) [10]. Nevertheless, this study has proven that the untreated empty fruit bunch could be a promising candidate for the removal of cationic pollutants from water.

■4.0 CONCLUSION

Empty fruit bunch sorbents were used to adsorb methylene blue and copper (II) from water. The untreated empty fruit bunch demonstrates a greater removal of methylene blue and copper(II) than the HCl-treated one. On molar basis, the adsorption of methylene blue onto the untreated sorbent is higher compared to that of copper(II). In addition, the sorbent exhibits superior affinity towards methylene blue. Empty fruit bunch is a promising adsorbent candidate for the removal of cationic pollutants from water.

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