Transactions on Science and Technology Vol. **6**, No. 1, 9 - 26, 2019

Application of Oil Palm Empty Fruit Bunch as Adsorbent: A Review

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ABSTRACT The abundance of oil palm wastes specifically oil palm empty fruit bunch (EFB) has possessed disposal issues that need to be tackled. Consequently, the utilisation of EFB as adsorbent for adsorbing pollutants from wastewater is a way forward. The unmodified EFB can be applied naturally but showed low adsorption capacity. The adsorption performance of EFB can be significantly improved upon modifications. This review covers the modification methods adopted to transform EFB into value-added adsorbent. Physical modifications discussed are heat pyrolysis, microwave irradiation and hydrothermal carbonisation. The output of heat pyrolysis followed by activation through oxidising gaseous and chemicals produced EFB activated carbon with high BET surface area and microporous which promotes high adsorption capacity. Besides, chemical modifications utilising acid, alkali, polymer grafting, organic and inorganic solvents provide high specificity on designing EFB adsorbent in the removal of targeted pollutants. Generally, this review serves as a guidance for researchers to move forward in searching for a simple, economic and environmental friendly technique to produce EFB based adsorbent with excellent properties and adsorption performance.

KEYWORDS: Empty fruit bunch fibre; Adsorbent; Adsorption; Modification

I **Received** 15 January 2019 II **Accepted** 21 January 2019 II **In press** 30 January 2019 II **Online** 9 February 2019 II © **Transactions on Science and Technology** I

INTRODUCTION

The Food and Agricultural Organisation of United Nations (FAO, 2018) had compiled the statistics on the world cultivated oil palm and the production of palm oil since year 1961. In year 2017, more than 21.09 million ha of land were cultivated with mature oil palm tree in 44 countries. The highest oil palm planting countries were Indonesia, Malaysia, Nigeria and Thailand, with the area of 9.28, 5.11, 3.04 and 0.76 million ha, respectively. The production of fresh fruit bunch (FFB) exceeded 317.57 million ton, where Indonesia (49.86%), Malaysia (32.04%), Thailand (4.59%) and Nigeria (2.44%) were the top four producing countries.

The oil palm empty fruit bunch (EFB) is generated once the oil palm fruitlets are stripped off. As much as 22% of FFB comprised of EFB (Yusoff, 2006) where 69.87 million ton of EFB was generated worldwide in year 2017. The EFB was initially applied as boiler fuel but was banned later as it gives off soot that caused air pollution to the surroundings. Since then, landfilling became the main disposal method for EFB. However, dumping EFB is also means nutrient loss which could be recycled in a gradual manner into the soil. A study by Abu Bakar et al. (2011) found that throughout the ten-year application of EFB on oil palm plantation had increased the carbon and nitrogen content in soil resulting higher FFB yield. This finding encourages the application of EFB in the plantation estates although it is time consuming for the actual outcomes to be seen. However, limitations such as labour shortage, logistical issues and oil palm pests are inevitable concerns for the management.

Another challenge for the utilisation of EFB is the high processing cost to transform EFB into value added products instead of direct utilisation. The application of EFB as a raw material for biofuel, paper production, briquette and activated carbon requires a few stages of treatment where heat, chemical, water and time is consumed at a large scale. In addition, secondary wastes maybe generated along the process of modification which eventually possesses secondary pollution if released into the environment prior to any treatment.

Oil palm EFB is a carbon rich material which is gaining new research interests in adsorption studies mainly due to its properties and abundance. In the past, the utilisation of natural EFB adsorbents has been focused on dye and heavy metal removal from wastewater. The increasing number of studies in the modifications of EFB also increased the adsorption of various pollutants from waterways. The objectives of this paper are to review (i) the methods conducted in the preparation of EFB adsorbents and (ii) the efficacy of EFB adsorbent in the removal of various pollutants from wastewater, in natural and modified forms. The published articles in various journals and proceedings from year 1997 to November 2018 are compiled and categorised based on the methods used to prepare EFB adsorbent. The literatures that utilised EFB adsorbents for the removal of various pollutants and their adsorption capacities are presented along. The efficiency of each modified adsorbent is discussed with respect to their preparation methods and the changes in physicochemical properties.

PROPERIES OF EMPTY FRUIT BUNCH

The basic information on the characteristics of EFB is shown in Table 1. The elemental content shows that carbon is the main composition of EFB followed by oxygen, hydrogen, nitrogen and sulphur. Just like any other agricultural products, EFB is made up of lignin, hemicellulose and cellulose components. The wide range of composition for each element may be affected by the sample origin including land fertility, local weather and the soil nutrients, different analytical instruments and sample preparation prior to analysis. The high carbon and cellulose content in EFB makes it a suitable candidate to be applied as adsorbent.

Table 1. Characteristics of natural EFB

Parameters	Range	References
C (%)	40.93-68.3	Idris *et* al. (2010), Yang *et al*. (2004), Nasir *et al*. (2015)
H (%)	2.88-7.33	Wahi *et al*. (2009),Mohammed *et al*. (2012), Yang *et al*. (2004)
N (%)	< 0.1-2.18	Shariff *et al*. (2014), Abdullah & Sulaiman (2013), Lee *et al*. (2014)
S (%)	0.04-0.92	Uemura *et al*. (2011), Parshetti *et al*. (2013), Abdullah & Sulaiman (2013)
O (%)	26.4-51.78	Nasir *et al*. (2015), Idris *et al*. (2010)
Lignin (%)	10-34.37	Umikalson *et al*. (1997), Ishola *et al*. (2014),
Hemicellulose (%)	19.5-38.8	Coral Medina *et al*. (2015); Saritpongteeraka *et al*. (2015)
Cellulose (%)	22.2-65	Mohammed *et al*. (2012), Mahjoub *et al*. (2012)
pH	7.20 – 7.80	Kavitha *et al*. (2013), Nasir *et al*. (2015)
Surface area (m^2/g)	1.48 – 28.4	Parshetti *et al*. (2012), Hidayu *et al*. (2013), Joseph *et al*. (2016); Khosravihafthany *et al*. (2013); Wirasnita *et* al. (2014), Nasir *et al*. (2015)

Besides, EFB exhibited neutral to slightly alkali character (pH 7.20 – 7.80) which is suitable for neutralising acidic soil (Kavitha *et al*., 2013) and favouring the adsorption of cationic pollutants due to electrostatic interaction (Arshadi *et al*., 2014). On the other hand, the Brunauer-Emmett-Teller (BET) surface area is one of the most measured characters of EFB in adsorption studies. The BET surface area of natural EFB measured ranged from 1.48 – 28.4 m^2/g. The modifications of EFB are usually expected to give rise to the BET surface area.

Fourier-transform infrared (FTIR) technique played an important role in determining the surface functional groups present and adsorption mechanism involved (Setiabudi *et al*., 2016). It is evident in Table 2 that the surface functional groups of EFB are multifunctional and varies upon modifications. The functional groups identified were hydroxyl, carboxylates, carbonyl, amides, phenol and alkyl groups among others at varied absorption wavenumbers that give rise to efficient reduction of pollutants in targeted wastewaters. Moreover, the wavelength detected at 1738 – 1717, 1264 – 1035, and 897 – 858 cm^{-1} were evident for the presence of lignin, hemicellulose and cellulose in EFB, respectively (Daneshfozoun *et al*., 2014a; Fatah *et al*., 2014; Wirasnita *et al*., 2015).

Table 2. The surface functional groups of natural EFB identified

Wavenumber (cm^{-1})	Inference	Compound	Reference
3600 –3200	O–H stretching vibration	Hydroxyl group of hemicellulose, cellulose, lignin and the adsorbed water constituents	Haron *et al*. (2009) Johari *et al*. (2013)
2930 – 2850	C–H stretching	CH$_3$ group stretching vibration	Nasir *et al*. (2015) Wirasnita *et al*. (2015)
2340 – 2283	C≡C C≡N	Alkynes Nitriles	Khosravihaftkhany *et al*. (2013)
1738 – 1717	C=O stretching	Carboxylic acid in ester group of hemicellulose or carbonyl ester of p-coumeric	Nasir *et al*. (2015) Daneshfozoun *et al*. (2014a) Wirasnita *et al*. (2015)
1680 – 1600	C=O stretching	Alkene group of lignocellulose	Nasir *et al*. (2015)
1648 – 1620	C=C C=O	Alkenes and carbonyls	Khosravihaftkhany *et al*. (2013)
1637 – 1635	N–H	Amide group	Wirasnita *et al*. (2015)
1507 – 1425	C=O vibration	Aromatic vibration in hemicellulose and lignin	Fatah *et al*. (2014)
1432 – 1319	C–H bending vibration	CH$_2$ bending vibrations in polysaccharides aromatic rings	Celino *et al*. (2014) Daneshfozoun *et al*. (2014a) Wirasnita *et al*. (2015)
1264 – 1035	C–O stretching Si–O stretching	Organic siloxane or silicone and anhydroglucose chains with a C–O stretch	Fatah *et al*. (2014) Wirasnita *et al*. (2015) Coates (2000)
897 – 858	C–H bending	β–glycodsidic bond, out of plane bending	Celino *et al*. (2014) Fatah *et al*. (2014) Daneshfozoun *et al*. (2014a)

EMPTY FRUIT BUNCH AS ADSORBENT

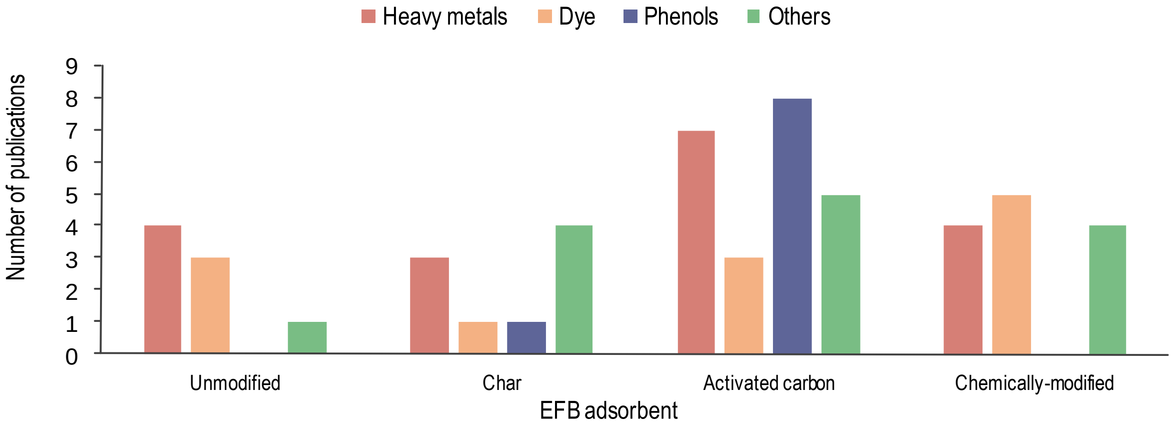

Figure 1. The types of EFB adsorbents

The utilisation of EFB as adsorbent is categorised based on modifications as shown in Figure 1. The most common adsorbates studied were heavy metals, dyes, phenols and other adsorbates include urea, oil, nutrient and pesticide and the measure of changes in colour, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in wastewater. Up to November 2018, there were 23 published articles related to EFB based activated carbon while 13 articles related to chemically modified EFB adsorbents. Publication related to the adsorption of phenolic compounds by unmodified and chemically modified EFB was not found, indicating data gap.

UNMODIFIED EMPTY FRUIT BUNCH AS ADSORBENT

Previous studies had shown natural EFB was capable of adsorbing dyes and heavy metals from aqueous solution (Table 3) (Nassar & Magdy, 1997; Rebitanim *et al*., 2012; Joseph *et al*., 2015; Nassar *et al*., 2004; Salamatinia *et al*., 2006; Khosravihaftkhany *et al*., 2013; Daneshfozoun *et al*., 2014a). The oxygen containing surface functional groups such as hydroxyls and carboxylic acids were claimed to be the reasons for adsorption of dyes and metal ions (Khosravihaftkhany *et al*., 2013).

Table 3. The adsorption studies using unmodified EFB

Adsorbate	Particle size (mm)	Isotherm	Kinetic model	Q_m (mg/g)	Reference
Reactive black 5	2 – 3	Langmuir	Pseudo-second order	7.34	Joseph *et al*. (2015)
Methylene blue	0.5	Langmuir	Pseudo-second order	50.76	Rebitanim *et al*. (2012)
Basic blue	0.3	Freundlich	-	91.33	Nassar & Magdy (1997)
Basic red	0.3	Freundlich	-	180.3	Nassar & Magdy (1997)
Basic yellow	0.3	Freundlich	-	327.57	Nassar & Magdy (1997)
Cu	-	Freundlich	-	3.5945	Salamatinia *et al*. (2006)
Fe	0.215 – 0.3	Langmuir	-	1.98	Nassar *et al*. (2004)
Fe	0.2 – 1.4	Langmuir	Pseudo-second order	8.887	Khosravihaftkhany *et al*. (2013)
Mn	0.215 – 0.3	Langmuir	-	2.21	Nassar *et al*. (2004)
Pb	0.2 – 1.4	Langmuir	Pseudo-second order	0.191	Khosravihaftkhany *et al*. (2013)
Pb	0.1 – 0.2	-	-	-	Daneshfozoun *et al*. (2014a)
Zn	-	Freundlich	-	2.6021	Salamatinia *et al*. (2006)
Ammonia	-	Freundlich	Pseudo-second order	8.435	Zahrim *et al*. (2014)

The natural EFB was able to adsorb of 7.34 mg/g of reactive black 5 (Joseph *et al*., 2015) and 50.76 mg/g methylene blue (Rebitanim *et al*., 2012). Both studies found that the adsorption best fitted the Langmuir isotherm model and pseudo-second-order kinetic model where chemisorption was proposed as the rate determining step. Nassar and Magdy (1997) found that the adsorption of basic dyes best fitted the Freundlich isotherm where the adsorption was heterogeneous. Nassar and Magdy (1997) also suggested the utilisation of cheaper EFB as an alternative for AC and the spent EFB can be used as solid fuel.

Metal ions such iron (Fe), manganese (Mn) and lead (Pb) experienced homogeneous adsorption (Khosravihaftkhany *et al*., 2013; Nassar *et al*., 2004) while copper (Cu) and zinc (Zn) experienced heterogeneous adsorption (Salamatinia *et al*., 2006) by unmodified EFB. The variation in adsorption isotherm was most probably due to the degree of leaching of water soluble organics and fatty acids from EFB which caused chemical oxygen demand (COD) introduction into wastewater during adsorption. The issue of COD can be resolved upon modifications of EFB.

PHYSICAL MODIFICATION

The physical modifications discussed in this section focused on heat pyrolysis, microwave and hydrothermal carbonisation. Sole pyrolysis step at high temperature and inert nitrogen or argon gas atmosphere produced EFB char. The continuum activation process that oxidised the EFB char is termed EFB activated carbon (AC).

Heat pyrolysis

Heat pyrolysis is the thermal conversion process under the absence of oxygen to remove volatile organic compounds yielding carbon-rich materials known as char. The varying parameters studied were temperature, heating rate, inert gas flow rate and heating time. The experimental parameters and the characteristics of EFB char are shown in Table 4.

Table 4. The conditions of pyrolysis and the characteristics of EFB char

Pyrolysis				BET surface area (m^2/g)	Average pore diameter (nm)	Adsorbate	Q_m (mg/g)	Reference
Temp. (°C)	Heating rate (°C/min)	N_2 flow rate (L/min)	Time (h)					
-	-	-	-	255.77	2.232	Methylene blue	-	Foo & Hameed (2011)
-	-	-	-	290.35	-	Phenol	-	Yap *et al*. (2005)
-	-	-	-	1.89	2.4818	Cu	49.4	Samsuri *et al*. (2014)
-	-	-	-	1.89	2.4818	Pb	58.8	Samsuri *et al*. (2014)
-	-	-	-	1.89	2.4818	Zn	45.7	Samsuri *et al*. (2014)
300	30	-	0.33	4.54	-	-	-	Sukiran *et al*. (2011)
300	3	0.1	1	1.46	-	Imazapyr	-	Yavari *et al*. (2017)
300	-	-	-	44.38	2.884	Zn	-	Zamani *et al*. (2017)
300-350	-	-	-	46.32	3.85	As	0.42	Sari *et al*. (2014)
300-350	-	-	-	46.32	3.85	Cd	15.15	Sari *et al*. (2014)
400	30	-	0.33	5.76	-	-	-	Sukiran *et al*. (2011)
500	30	-	0.33	4.85	-	-	-	Sukiran *et al*. (2011)
500	-	-	1	9.09	-	-	-	Wirasnita *et al*. (2015)
550	5	-	1	11.12	-	-	-	Shariff *et al*. (2014)
600	30	-	0.33	3.95	-	-	-	Sukiran *et al*. (2011)
615	8	0.15	2.13	421.26	1.441	Zn	-	Zamani *et al*. (2017)
700	30	-	0.33	3.34	-	-	-	Sukiran *et al*. (2011)

According to Table 4, the EFB char produced at temperature 300 – 700°C resulted in low BET surface area (3.34 – 5.76 m^2/g) showed not much significance when compared to natural EFB (Sukiran *et al*., 2011). The high heating rate of 30°C/min was the reason where the decomposition was not able to occur uniformly resulted in low BET surface area measured. The BET surface area can be improved where the pyrolysis conducted at low heating rate of 3 – 8°C/min with prolonged reaction time could eventually achieved BET surface area of 421.26 m^2/g (Zamani *et al*., 2017). Despite of the low BET surface area of EFB char, the average pore diameter indicated the development of mesopores and micropores. Hence, activation of EFB char was conducted by researchers to improve the BET surface area, development of mesopores and micropores to achieve high adsorption capacity.

Char Activation

The activation process in developing EFB AC is crucial. Activation process can be conducted through gaseous activation or by chemical means. The changes in BET surface area and the adsorption performance is discussed.

Gaseous activation

The EFB char was produced when heat pyrolysis reached the targeted temperature. Activation step was initiated when the oxidising gas such as air, carbon dioxide (CO_2) or steam were allowed to flow in replacing nitrogen gas, held for a period of time at temperature 700 – 1000°C to further encouraged surface area and micropores development (Table 5).

Table 5. The EFB AC prepared through gaseous activation

Pyrolysis		Activation		BET surface area (m^2/g)	Average pore diameter (nm)	Adsorbate	Q_m (mg/g)	Reference
Temp. (°C)	Heating rate (°C/min)	Agent	Temp (°C)					
-	-	Air	800	-	-	2,4-$C_6H_4Cl_2O$	27.25	Alam *et al.* (2007)
-	-	Air	1000	-	-	Zn	-	Alam *et al.* (2008)
700	8	CO_2	900	-	-	Phenol	66.67	Arshad *et al.* (2012)
900	23	CO_2	900	345.10	-	Phenol	-	Alam *et al.* (2009)
500	-	Steam	765	720	1.889	-	-	Hidayu *et al.* (2013)
900	20	Steam	900	635.16	4	Cd	-	Ma'an *et al.* (2011)
900	20	Steam	900	886.2	3.54	Mn	0.0315	Amosa (2015)
900	20	Steam	900	886.2	3.54	H_2S	0.0083	Amosa (2015)
950	20	Steam	900	886.2	3.54	COD	15.87	Amosa *et al.* (2016)
900	23	Steam	900	-	-	Hg	0.00088	Kabbashi *et al.* (2011)

Steam activation is a better activating agent in preparing EFB AC. The high BET surface area (635.16 – 886.2 m^2/g), mesopore and micropore development after steam activation is due to the smaller particles that are able to diffuse and react within the carbon matrix at higher reaction rate compared to air and CO_2 (Hashemipour *et al*., 2009). In addition, the surface functional groups were found to disappear after steam activation (Hidayu *et al*., 2013). The disappearance of surface functional groups during steam activation resulted in low adsorption capacity of metal ions due to the absence of electrostatic attraction. However, steam activation under high activating temperature at 765 – 900°C required high energy consumption and less cost effective for large scale production.

On the other hand, the activation process can be optimised using two-level full factorial design. Alam *et al*. (2009) and Ma'an *et al*. (2011) adopted full factorial design in the optimisation of the activation temperature, time and gaseous flow rate in producing EFB AC. The steam activated EFB AC after the optimised activation at 900C, at 2.0 mL/min steam flow rate for 15 min were able to develop EFB AC with BET surface area of 635.16 m^2/g (Alam *et al*., 2009). Moreover, Kadir *et al*. (2014) conducted steam activation on EFB AC using response surface methodology after the study by Hidayu *et al*. (2013) discovered that experimental value of BET surface area, 720 m^2/g was agreed to the predicted value 717.6 m^2/g through the optimised conditions of the statistical analysis. The optimisation of EFB AC using full factorial experimental design is not a favourable approach due to increasing number of experimental runs especially when the number of parameters studied exceeded four (Rashidi & Yusup, 2017).

Chemical activation

The chemical activation can occur before and after the pyrolysis of EFB. Table 6 summarises the chemical activation of EFB after pyrolysis. Chemical activation is capable of increasing the surface area and pore volume by removing tar and volatile matter that clogged the internal pores (Wahi *et al*., 2009; Wirasnita *et al*., 2015). The potassium hydroxide (KOH) and sodium hydroxide (NaOH) are strong oxidising agents that increased the BET surface area and promoted mesopores and micropores development (Wahi *et* al., 2009; Yap *et al*., 2005).

Chemical activation can be conducted through dry and wet impregnation. Dry impregnation refers to the mixing of dry KOH pellets with EFB char at fixed impregnation ratio followed by pyrolysis or carbonisation. Strong oxidising KOH coupled with CO_2 gas activation produced high BET surface area of 1141 m^2/g EFB AC (Hameed *et al*., 2009; Tan & Hameed, 2010; Tan *et al*., 2009). The role of KOH as catalyst accelerated the rate of decomposition through dehydration and the formation of potassium carbonate (Guo & Lua, 2002).

Table 6. The chemical activated EFB AC

Pyrolysis		Activation			BET surface area (m^2/g)	Adsorbate	Q_m (mg/g)	Reference
Temp (°C)	Heating rate (°C/min)	Agent	Temp (°C)	Time (h)				
700	10	CO_2 74% w/w KOH	814	1.9	-	$2,4,6\text{-}C_6H_2Cl_3OH$	500	Tan *et al*. (2009)
700	10	CO_2 74% w/w KOH	700	1.9	1141	$2,4,6\text{-}C_6H_2Cl_3OH$	-	Hameed *et al*. (2009)
700	10	CO_2 74% w/w KOH	844	1.8	-	Methylene blue	416.07	Tan & Hameed (2010)
800	5	71% w/w KOH	-	2.33	820	Acid Red 1	-	Auta *et al*. (2012)
400	-	20% w/v NaOH N_2	60 700	2 1	379.37	Hg	52.67	Wahi *et al*. (2009)
400	-	20% w/v NaOH N_2	60 700	2 1	379.37	Pb	48.96	Wahi *et al*. (2009)
400	-	20% w/v NaOH N_2	60 700	2 1	379.37	Cu	0.84	Wahi *et al*. (2009)
-	-	1000 mg/L $FeCl_3$	-	24	-	As(III)	31.4	Samsuri *et al*. (2013)
-	-	1000 mg/L $FeCl_3$	-	24	-	As(V)	15.2	Samsuri *et al*. (2013)

Wet impregnation is the immersion of EFB char in dissolved oxidising chemical prepared at desired concentration. Wahi *et al*. (2009) soaked the EFB char in 20% (w/v) of NaOH solution (equivalent to 5 M NaOH) for 2 h as the activation step followed by second carbonisation at higher temperature at 700°C under inert atmosphere. The experimental results showed that dry mixing produced EFB AC with BET surface area measuring 378.55 – 1141 m^2/g while wet mixing produced EFB AC with 379.37 m^2/g. The advantage of dry impregnation is cross contamination can be prevented while wet impregnation utilised water as medium is easily exposed to the diffusion of CO_2 from the atmosphere, causing interruptions through the chemical reactions shown (Lillo-Rodenas *et al*., 2003):

$$4NaOH + 2CO_2 \leftrightarrow 2Na_2CO_3 + 2H_2O$$

$$4KOH + 2CO_2 \quad \leftrightarrow 2K_2CO_3 + 2H_2O$$

Besides, the impregnation of transition metal compounds, iron chloride ($FeCl_3$) onto EFB char increased the adsorption capacity of As(III) and As(V) by coordination and surface complexation of the ferric compounds coated into the EFB char (Samsuri *et al*., 2013). The grafting of metal compounds onto EFB AC is more economically feasible as second carbonisation step can be skipped. However, the residual chemicals in the EFB AC caused secondary pollution and possessed toxicity towards the living organisms as it is more difficult to remove the residual chemicals within micropores. This problem can be overcome by rinsing with diluted acid which aimed to neutralise and remove the residual chemicals. For example, Wahi *et al*. (2009) utilised 5 M HCl to neutralise the excess NaOH at the end of modification to lower down the pH value in order to achieve more accurate adsorption results, especially the adsorption of metal ions is highly pH dependent.

On the other hand, the EFB treated with chemicals followed by heat pyrolysis is summarised in Table 7. Chemicals such as sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), KOH and zinc chloride ($ZnCl_2$) were used to treat natural EFB prior heat pyrolysis and activation. Lee *et al*. (2014) and Ooi *et al*. (2017) treated EFB with dehydrating H_2SO_4 followed by pyrolysis and activation produced high BET surface area and micropores EFB. The removal of acid-soluble compounds within EFB allowed to the pyrolysis and activation to take place at higher degradation rate during pyrolysis where the volatilisation of organic compounds was facilitated thus forming more pores within the EFB AC.

Moreover, the application of concentrated phosphoric acid (H_3PO_4) followed by pyrolysis produced 1031.5 m^2/g BET surface area EFB AC (Shaarani *et al*., 2010). This indicated pyrolysis after chemical treatment was sufficient to develop EFB AC and further activation became unnecessary. Similar study was further enhanced with 10% (w/w) ammonia which then increased the maximum adsorption capacity of 2,4-$C_6H_3Cl_2OH$ from 232.56 mg/g to 285.71 mg/g due to the increase in basic functional groups of ammonia (Shaarani *et al*., 2011). The surface functional groups analysis indicated the presence cyclic amides and amine group where the positively charged new nitrogen surface complexes improved the 2,4-$C_6H_3Cl_2OH$ uptake.

Additionally, the EFB mixed with KOH pellets followed by pyrolysis had BET surface area of 663 m^2/g where the external surface appeared to be porous and irregular (Abdul Khalil *et al*., 2013). The adsorption of Rhodamine B dye was studied through fixed bed column conducted by Auta (2012) utilising KOH treated EFB AC. The maximum adsorption capacity 69.86 mg/g of Rhodamine B dye was obtained at 200 mg/L of influent dye concentration, 10 cm bed depth and 15 mL/min of solution flow rate. The results obtained were found to fit the Thomas model adequately in describing the breakthrough behaviour of the adsorption process.

Table 7. Chemical activation followed by heat pyrolysis

Activation			Pyrolysis + Activation			BET surface area (m^2/g)	Adsorbate	Q_m (mg/g)	Reference
Agent	Temp (°C)	Time (h)	Agent	Temp (°C)	Flow rate (L/min)				
60% w/w H_2SO_4	-	-	N_2 CO_2	400 900	0.1 0.1	-	Urea	-	Ooi *et al*. (2017)
43% w/w H_2SO_4	-	-	N_2 CO_2	400 900	0.1 0.1	990	-	-	Lee *et al*. (2014)
conc. H_3PO_4	120	24	-	800	-	850.11	Cu	333.33	Nwabanne & Igbokwe (2012)
20% w/w H_3PO_4	RT	Overnight	N_2	450	0.15	1031.5	2,4-$C_6H_3Cl_2OH$	232.56	Shaarani & Hameed (2010)
20% w/w H_3PO_4 10% w/w NH_3	RT	48	N_2	450	0.15	-	2,4-$C_6H_3Cl_2OH$	285.71	Shaarani & Hameed (2011)
67% w/w KOH	-	-	N_2	-	0.15	-	Rhodamine B	69.86	Auta (2012)
0% w/w KOH	-	-	N_2	375 700	1	290.35	Phenols	-	Yap *et al*. (2005)
10% w/w KOH	RT	24	N_2	375 700	1	378.55	Phenols	-	Yap *et al*. (2005)
30% w/w KOH	RT	24	N_2	375 700	1	417.70	Phenols	90.09	Yap *et al*. (2005)
50% w/w KOH	RT	24	N_2	375 700	1	415.84	Phenols	91.74	Yap *et al*. (2005)
70% w/w KOH	RT	24	N_2	375 700	1	431.52	Phenols	89.29	Yap *et al*. (2005)
75% w/w KOH	85–90	24	-	800	-	663	-	-	Abdul Khalil *et al*. (2013)
10% w/v $ZnCl_2$	-	24	N_2	500	2.5	86.62	Bisphenol A	41.98	Wirasnita *et al*. (2014)

Strong dehydrating agent $ZnCl_2$ is known to promote charring and eliminate organic compounds prior to pyrolysis was able to increase the BET surface area from 9.09 m^2/g to 86.62 m^2/g (Wirasnita *et al*., 2015). The maximum monolayer adsorption capacity of bisphenol A was 41.98 mg/g which represented by Langmuir isotherm. Despite the lower BET surface area was accounted, the proposed adsorption process of bisphenol A was chemisorption where the carbon-carbon double bonds, hydrogen bonding between carboxyl and/or hydroxyl groups and the electron donor-acceptor complexes were involved (Wirasnita *et al*., 2014).

Microwave irradiation

Microwave provides energy to entire samples via a dielectric heating, whereby heat is transferred from the central part towards the outer surface producing more uniformly modified EFB

AC (Ahmad *et al*., 2018). Microwave irradiation also serves as an alternative for pyrolysis which saves time and energy meanwhile providing instant control and accelerate the rate of reaction (Omar *et al*., 2011; Puligundla *et al*., 2016).

Mubarak *et al*. (2014) utilised microwave in heating EFB in ferric chloride hexahydrate instead of pyrolysis. The modifications were optimised by using response surface methodology. The optimised conditions identified were irradiation of EFB in $FeCl_3$ with impregnation ratio 0.5 under 900 W microwave power for 20 min. The $FeCl_3$ impregnated EFB have high BET surface area of 890 m^2/g where the highest adsorption capacity of 265 mg/g methylene blue was adsorbed. The advantages of microwave technique is simple, safe to operate and time saving in the modifications step while yielding quality EFB adsorbent.

Foo and Hameed (2011) studied EFB AC impregnated with KOH followed by microwave irradiation at 2.45 GHz. Microwave irradiation improved the BET surface area from 255.77 m^2/g to 807.54 m^2/g. The adsorption of methylene blue had achieved 344.83 mg/g of maximum monolayer adsorption capacity. However, the improvement in terms of maximum monolayer adsorption capacity was not significant as the KOH treated EFB AC without microwave irradiation was able to remove 357.14 mg/g of methylene blue (Tan & Hameed, 2010).

Hydrothermal carbonisation

Hydrothermal carbonisation is a process that converts lignocellulosic materials into solid carbon with low oxygen to carbon ratio (Jamari & Howse, 2012). This process is gaining attention in the recent years due to its low operating temperature, where low energy also implies reduction in operating costs. Moreover, hydrothermal carbonisation is an exothermic process that is more environmental friendly as no gases is evolved throughout the process. The output of hydrothermal carbonisation is carbon-rich materials and wastewater which could be described as follow (Jamari & Howse, 2012).

$$C_6H_{10}O_5(s) \rightarrow C_6H_2O(s) + 5H_2O(l);\ \Delta H = -2.52\ \text{MJ/Kg}$$

The EFB was suspended in water under pressure controlled environment and temperature lower than pyrolysis (150 – 350°C) for a period of time (Parshetti *et al*., 2013). The mechanisms involved including dehydration, decarboxylation, hydrolysis, aromatisation and condensation polymerisation that converted EFB into high carbon content adsorbent while maintaining the carbohydrate structure of EFB (Funke & Ziegler, 2010; Jamari & Howse, 2012). The end product was often termed EFB hydro-char. However, the production of EFB hydrochar was modified to harness energy. Hence, data gap is identified where the hydrothermally treated EFB is yet to explore its adsorption performance.

CHEMICAL MODIFICATIONS

Chemical modifications on EFB adsorbents increase the adsorption efficiency of various pollutants. The chemicals used in modifying EFB including acids, alkalis, polymers, organic and inorganic solvents. The studies EFB are discussed in this section.

Acid and alkali

The acid and alkali modified EFB adsorbents and the adsorption studies are summarised in Table 8. Acids are widely utilised as the modifying agent in developing EFB adsorbents. The acidic reactions involved hydrolysis which partially cleaves off the lignin and hemicellulose content in EFB and to remove the acid soluble impurities on the surface of EFB (Lenihan *et al*., 2010).

Nasir *et al*. (2015) treated EFB with 0.1 M hydrochloric acid (HCl) discovered a decreased in BET surface area from 28.4 m^2/g to 8 m^2/g which can be explained by the collapse of the EFB pore channels. However, the reduction in BET surface area did not affect the removal performance of methylene blue and Cu ions. The adsorption of methylene blue by HCl modified EFB was homogeneous while Cu ions was heterogeneous, each represented by Langmuir and Freundlich isotherm model, respectively. The removal was attributed to the presence of carbonyl, hydroxyl, carboxylic, alkanes, alkyls, and esters in the HCl modified EFB instead of the surface area (Nasir *et al*., 2015).

Table 8. The acid and alkali modified EFB adsorbent

Modification			Adsorption studies				Reference
Chemical	Tem (°C)	Time (h)	Adsorbate	Isotherm	Kinetic	Q_m (mg/g)	
conc H_2SO_4	150	24	Methylene blue	-	-	-	Saad *et al*. (2007)
64% (w/w) H_2SO_4	45	45	Methylene blue	Langmuir	P2 IPD	144.93	Shanmugarajah *et al*. (2019)
0.1 M HCl	-	Overnight	Methylene blue	Langmuir	-	32.944	Nasir *et al*. (2015)
0.1 M HCl	-	Overnight	Cu	Freundlich	-	4.766	Nasir *et al*. (2015)
0.6 M Citric acid	RT	0.5	Methylene blue	Langmuir	P2 IPD	103.1	Sajab *et al*. (2013)
0.6 M Citric acid	RT	0.5	Cu Ni	Langmuir		126.85 7.864	Sajab *et al*. (2017)
10% (w/w) Acetic acid	100	2	Mn Ni Cu	Dubinin-Radushkevich	P2	0.003 0.003 0.005	Daneshfozoun *et al*. (2014b)
1.25 M NaOH	RT	1 12 72	Ammonia	-	-	-	Zahrim *et al*., 2014

RT: Room temperature
P2: Pseudo-second-order
IPD: Intraparticle diffusion

Shanmugarajah *et al*. (2019) isolated nanocrystalline cellulose from EFB through 4% (w/w) NaOH treatment, bleaching with acetate buffer and sodium chlorite, followed by hydrolysis using 64% (w/w) sulphuric acid to study its methylene blue adsorption behaviour. The modification was successful where 144.93 mg/g of maximum monolayer adsorption capacity was determined through the fitting into Langmuir isotherm. The adsorption was described to be homogenous with chemisorption as the rate limiting step through the fitting of pseudo-second-order kinetics.

Alkalis NaOH and KOH are the common chemical used in the industries in treating lignocellulosic materials. Alkali is capable of breaking the intramolecular and intermolecular hydrogen bonds between hydroxyl groups (–OH) of cellulose, hemicellulose and lignin moieties, leading to the defibrillation of fibres (Chowdhury *et al*., 2013). This process also known as mercerisation in the industrial process. Ibrahim *et al*. (2009) and Ibrahim *et al*. (2010) precipitated lignin from EFB using 20% (w/v) NaOH at 170°C which were able to remove 7.94 mg/g and 46.72 mg/g of Cu(II) and Pb(II) ions, respectively.

On the other hand, 0.10 – 5.0 M NaOH was first applied to initiate modifications and to enable the grafting of polyethyleneimine (Sajab *et al*., 2013) and surfactant cetyltrimethylammonium bromide (CTAB) (Danish *et al*., 2015) onto EFB to adsorb phenol red and methyl orange, respectively. The reason for NaOH application was to partially removed lignin and hemicellulose in EFB, altered the fibre structure enabling the penetration of chemicals and reduce the reaction time.

Polymer grafting

Polymer grafting on EFB aimed to increase the variety of pollutants to be adsorbed and to enhance adsorption capacity of pollutants (Table 9). The removal mechanisms by polymer grafted EFB adsorbents removed pollutants by chelation and coordination instead of ion exchange and surface adsorption by functional groups.

The grafting technique was complex where a few chemicals were needed and involved multiple steps. First, Haron *et al.* (2009) initiated the modifications using hydrogen peroxide followed by the addition methyl acrylate monomer for polymerisation yielding poly(methyl acrylate) on EFB. The intermediate was then treated with hydroxylamine in methanolic solution at pH 13 producing poly(hydroxamic acid) grafted EFB. The grafted EFB followed the Langmuir isotherm and pseudo-second-order model where the maximum monolayer adsorption capacity of Cu(II) ions achieved was 74.1 mg/g. The proposed adsorption mechanism was chemisorption, spontaneous and exothermic.

Table 9. Polymer grafting onto EFB adsorbent

Modification			Adsorption studies				
Agent	Temp. (°C)	Time (h)	Adsorbate	Isotherm	Kinetic	Q_m (mg/g)	Reference
5% (w/v) Polyethyleneimine	65	6	Phenol red	Freundlich	P2 IPD	156.7	Sajab *et al.* (2013)
5% (w/v) Polyethyleneimine	65	6	BOD TOC Color	-	P2 IPD	-	Sajab *et al.* (2014)
5% (w/v) Polyethyleneimine	65	6	Mo(VII) As(V)	Freundlich Langmuir	IPD	187.77 73.42	Sajab *et al.* (2017)
Poly(Hydroxamic acid)	75	2	Cu	Langmuir	P2	74.1	Haron *et al.* (2009)
Poly(ethyl Hydrazine)	Reflux	4	Ni	Langmuir	P2	42.19	Johari *et al.* (2013)

P2: Pseudo-second-order
IPD: Intraparticle diffusion

Besides, similar study by Johari *et al.* (2013) which also engrafted poly(methyl acrylate) onto EFB as the intermediate followed by reflux in hydrazine hydrate solution with 15% (v/v) ethanol for 4 h yielding final product poly(ethyl hydrazine) grafted EFB. The chelation of Ni ions by poly(ethyl hydrazine) was proposed to be adsorption mechanism where stable complex metal ion was formed. The adsorption isotherm fitted well with Langmuir isotherm and followed the pseudo-second-order kinetics. The adsorption occurred was endothermic, spontaneous and random at the solid-solution interface. Despite of the promising adsorption capacity of the polymer grafter EFB adsorbent, high capital investment and energy consumption for large scale production are a step-back for the industries. Furthermore, the remaining reagents and solutions after modifications turned into wastewater that requires treatment before disposal.

Organic solvent and inorganic solvent

Organic and inorganic solvents are utilised as modifying agents (Table 10). Modifying agents such as acetic anhydride (Asadpour *et al.*, 2016) and trimethylchlorosilane (Rattanawong *et al.*, 2007) increased the hydrophobicity of EFB which increased the adsorption capacity of oil adsorption. Both studies have a common step of utilising NaOH to eliminate lignin and hemicellulose in EFB allowing acetylation and silylation to take place. The substitution of acetyl group and silyl groups increased the esters groups while eliminated the hydroxyl groups which benefited the oil adsorption. The oil adsorption followed the homogenous adsorption evident by the best fitting of Langmuir isotherm.

Table 10. Organic and inorganic solvents as modifying agent

Modification			Adsorption studies				Reference
Agent	Temp (°C)	Time (h)	Adsorbate	Isotherm	Kinetic	Q_m (mg/g)	
1% (v/v) trimethylchlorosilane	RT	3	Oil	Langmuir	-	0.7594	Rattanawong *et al.* (2007)
Acetic anhydride	120	4	Tapis crude oil Arabian crude oil	Langmuir	P1 P2	10000 10000	Asadpour *et al.* (2016)
1% (w/v) Formaldehyde	150	24	Methylene blue	-	-	-	Saad *et al.* (2007)
1% (v/v) Cetyltrimethylammonium bromide	-	Overnight	Methyl orange	Langmuir	P1 P2 IPD	18.1	Danish *et al.* (2015)
10% (w/w) EDTA	100	2	Mn Ni Cu	Dubinin-Radushkevich	P1 P2	0.004 0.003 0.007	Daneshfozoun *et al.* (2014b)

RT: Room temperature
P1: Pseudo-first order
P2: Pseudo-second order

The adsorption methylene blue by 1% (w/v) formaldehyde modified EFB was reported to achieve 96.4% of removal performance at initial concentration of 50 mg/L (Saad *et al*., 2007). However, the adsorption isotherm and kinetic were not discussed in this article. Besides, the adsorption of methyl orange was conducted by EFB modified using 1% (v/v) cetyltrimethylammonium bromide (Danish *et al*., 2015). The adsorption followed the Langmuir isotherm where maximum monolayer adsorption was 18.1 mg/g. The methyl orange adsorption was exothermic and spontaneous which indicated no energy barrier to initiate the adsorption process.

Daneshfozoun *et al*. (2014b) compared the adsorption performance of Mn, Ni and Cu by EFB treated with 10% (v/v) ethylenediaminetetraacetic acid (EDTA) and 10% (w/w) acetic acid. The EDTA contains four carboxylic acid groups while acetic acid contains one carboxylic acid group. The EDTA-modified EFB showed better adsorption performance due to the excess carboxylic acid groups. The adsorption systems were well fitted in Dubinin-Radishkevich isotherm where the apparent energy suggested physisorption mechanism.

The organic and inorganic solvents removed and/or added surface functional groups improving the surface tension between liquids making EFB more susceptible for adsorption of pollutants, specifically the adsorption of oil. The utilisation of organic and inorganic solvents can be applied to modified adsorbents in treating the targeted pollutants.

FUTURE PROSPECTS

Converting EFB into value-added adsorbents is a way to solve the disposal issue and substituting the conventional adsorbents. The utilisation of EFB as an adsorbent has gained recognitions owing to its abundance, relatively low cost and rich in lignin, cellulose and hemicellulose. Physical and chemical modifications on EFB are able to transformed EFB into value-added adsorbents with high adsorption capacity. The target application of adsorbents should be determined first prior to conduct the modifications. Thus, EFB should be explored further in terms of high BET surface area, porosity and adsorption rate. The production costs can be overcome if chemical such as acids and alkalis are coupled with physical modification in developing EFB adsorbents. Nonetheless, modifications that are more environmental friendly, able to produce adsorbents with excellent physicochemical properties and adsorption performance is yet to be explored and developed, especially for pilot scale to industrial applications.

AKNOWLEDGEMENT

The authors would like to express their gratitude to the Malaysian Ministry of Higher Education under the Universiti Malaysia Sabah Research Priority Area Scheme (Project SBK0415-018), Postgraduate Research Grant Scheme (Project GUG0070-SG-2/2016) for the technical and financial support and the MyBrain15 scholarship for the first author.

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