INVESTIGATION OF PALM FIBRE-DERIVED ACTIVATED CARBON IN WASTEWATER TREATMENT

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Abstract

Untreated industrial wastewater has high concentration of hazardous pollutants, which will affect human health as these pollutants infiltrate into human basic necessities. Adsorption using activated carbon (AC) is commonly used technique in wastewater treatment for removal of organic and inorganic pollutants. Current AC production from biomass usually use strong acid or alkali as pretreatment agent. This research aims to stud the AC production by using a lower concentration of sulphuric acid (H_2SO_4) and potassium hydroxide (KOH). Deep eutectic solvent (DES), the reported environmental friendly pretreatment agent for biomass also investigated. The AC produced were characterised by using Brunauer, Emmett and Teller (BET) and Fourier Transform Infrared (FTIR). Adsorption process on the effect of initial concentration of lead and nitrate were investigated. The maximum micropore percentage of 91% was achieved by DES pretreated AC. All AC samples has similar functional groups as commercial activated carbon (CAC) based on FTIR results. AC undergo DES pretreatment showed the highest removal of NO_3 and Pb(II). It removed NO_3 and Pb(II) up to 19.85% and 95.29% respectively. The usage of DES as pretreatment agent is not only effective in AC production but also reduce environmental issue, as DES is a less hazardous chemical and reusable.

Keywords: Activated carbon, Adsorption, Deep eutectic solvent, Empty fruit bunch, Pretreatment.

1. Introduction

In 2014, there are 70% of industrial wastewater that is discharged without treatment as reported by United Nation Water [1]. Untreated industrial wastewater has high concentration of hazardous pollutants which will bring adverse effect when these pollutants infiltrate into human basic necessities such as water and food. Therefore, wastewater treatment processes are important to ensure the pollutants are discharged at an acceptable level. Adsorption process has been widely employed by industries as part of the treatment due to its simple design, ease of operation and convenience [2]. With adsorption process in wastewater treatment, the pollutants in wastewater will be adsorbed onto the surface of activated carbon (adsorbent) and removed from the wastewater before discharging into water bodies.

Commercial activated carbon is usually made from coal which is a non-renewable resource [3]. With the increasing demand of activated carbon (AC), it is crucial to explore renewable carbon sources in AC production. Lignocellulosic biomass especially the inexpensive agricultural residues have been explored to produce AC due to its carbonaceous characteristic. Empty fruit bunch (EFB) is used in this research to produce AC as it is available in abundance in Malaysia with low commercial value. Based on Hidayu and co-workers [4], it is concluded that EFB can be converted into activated carbon and proven to have comparable characteristic with commercial activated carbon based on FTIR examination.

AC is produced by going through two main processes; namely carbonisation and activation [2]. In carbonisation, the process decomposes the non-carbon components to produce char. After carbonisation, the char is activated by using activating agent to give the desirable characteristics such as pore structure and surface functional group to an AC [2, 5]. There are three types of activation process which are physical, chemical and physio-chemical activation. Physical activation is done after carbonisation; however for chemical activation, the raw material is impregnated with chemical activating agent prior to carbonisation. Physiochemical activation is the combination of both physical and chemical activation. A research reported on the pore structure of raw EFB and EFB-derived AC has shown that carbonisation and activation processes are important to produce AC with porous structure [6].

The performance and effectiveness of an AC are greatly affected by carbonisation and activation process. There are many researches investigating the effects of carbonisation and activation conditions on the AC produced from biomass [7, 8]. As reported by Abdullah et al. [9], the yield of AC increases as the concentration of $ZnCl_2$ increases until the concentration of $ZnCl_2$ reaches 15%. It has also reported that the concentration of $ZnCl_2$ affects the surface area of AC produced. Apart from that, the comparison of combustion, pyrolysis and the acid treatment sequence has only been done by Lee et al. [5] on the quality and properties of AC. Thus far, research on how the concentration of alkali and acid pretreatment affects the production of AC from EFB fibre is limited. Besides using acid and alkali as agent, another type of chemical agent called deep eutectic solvent (DES) is yet to be explored. Recently, a research uses DES in the production of porous carbon monolith [10] resulted in DES to be potentially applied in activation process.

In wastewater, pollutants are generally categorised as inorganic and organic compounds. Inorganic compounds are cations (copper, lead, mercury) and anions (nitrate, phosphate, sulphate). Whereas phenolic compounds, dyes and pesticides

fall into the organic compound category. Surface functional groups on activated carbon play a major role in wastewater treatment. Certain functional groups must exist on AC in order to remove the pollutants effectively. For instance, oxygen functional groups with proton donor must exist in order to remove heavy metal effectively as metal ions have the ability to form complex with the charged acid group [11]. The coconut based AC is widely used in wastewater treatment and gives promising results; however the investigation of EFB-derived AC in wastewater treatment is not well established yet. Thus far, only few researches have been using EFB-derived AC in wastewater treatment and the removal of pollutants have only been limited to dye [12], phenol [13] and heavy metals [14].

In this study, EFB has been chosen as the precursor for AC production. To date, the application of EFB- derived AC in wastewater treatment is not well established and the removal of anionic pollutants has not been done using EFB-derived AC. Hence, the removal of lead and nitrate will be studied using EFB-derived AC. To the best of our knowledge, no research has been carried out on comparing different concentration of pretreatment agent in the production of AC from EFB. Furthermore, DES as pretreatment agent has not been investigated in production of AC. Hence, the objective of the study is to investigate the application of DES as well as acid and alkali in reduced concentration in AC production. The characteristics of AC produced, in terms of porosity, structural functional groups and adsorption capacity on nitrate and lead will be evaluated.

2. Methodology

2.1. Material

Empty fruit bunch (EFB) fibre obtained from Furniu Fibre Sdn. Bhd, Ipoh, Perak was used as the raw material. The EFB fibre was washed and cleaned using distilled water to remove impurities. Based on ASTM D2867-99, the cleaned EFB fibre was dried in an oven at a temperature of 110°C overnight to reduce the moisture content of the fibre [15]. Sulphuric acid (H_2SO_4) and potassium hydroxide (KOH) and Deep eutectic solvent (DES) were used as pretreatment agents. For adsorption study, lead (Pb(II)) and nitrate (NO_3) stock solutions were prepared from lead nitrate and potassium nitrate, which were purchased from Merck. The lead and nitrate cell test were also purchased from Merck.

2.2. AC sample preparation

2.2.1. Pretreatment of EFB fibre

15g of cleaned EFB fibre were pretreated with 85% H_2SO_4, 50% H_2SO_4, 50% KOH, 25% KOH with ratio of solid to liquid ratio of 4:3 separately [5]. For H_2SO_4 and KOH pretreatment, the fibre was placed to the split tube furnace immediately after mixing the chemical reagents with fibres for pyrolysis. An inert condition for carbonisation was created by flowing nitrogen (N_2) gas with flow rate of 1 L/min. The sample was pyrolysed at 400 °C for 1 hour with heating rate ramping at 10 °C/min [5]. After carbonisation, the char was cooled down and rinsed with distilled water and dried in oven at 110°C overnight. The dried char was then proceeded to activation process with carbon dioxide (CO_2) gas.

The DES is prepared from choline chloride and urea with a molar ratio of 1:2. For DES pretreatment, solid to liquid ratio of 1:5 is employed [10]. The fibre was

pretreated for 4 hours at 110°C, washed and dried before pyrolysis process [10]. The same conditions for carbonisation and pyrolysis were adopted.

2.2.2. Control sample without pretreatment

Control sample was synthesised to provide a baseline comparison for the chemical pretreated samples. The preparation methods of control sample were similar but without chemical pretreatment. No rinsing and drying steps were required to remove the chemical reagents on the surface.

2.2.3. Activation process

For activation process, the furnace was heated up to 900°C with heating rate ramping at 10 °C/min and N_2 gas flowing at 1 L/min. When the furnace reached 900°C, the supply of N_2 gas was stopped and changed to CO_2 gas for 1 hour with flow rate 1 L/min. After 1 hour, the furnace was cooled down to room temperature by flowing N_2 gas at 1 L/min. After activation, the sample was rinsed with distilled water and dried. The list of samples with the sample codes were as tabulated in Table 1.

Table 1. List of samples.

Condition	Code
Pretreatment with 85% H_2SO_4	P85SA-AC
Pretreatment with 50% H_2SO_4	P50SA-AC
Pretreatment with 50% KOH	P50PH-AC
Pretreatment with 25% KOH	P25PH-AC
Pretreatment with DES	PDES-AC
Without pretreatment (Control sample)	WP-AC

2.3. Characterisation of activated carbon (AC)

EFB-derived AC samples were characterised using Brunauer, Emmett and Teller (BET) and Fourier Transform Infrared (FTIR) spectroscopy. Nitrogen adsorption isotherm was carried out using Micromeritics Instrument system at 77 K. Prior to analysis, the sample was degassed at 300 °C for 5 hours. BET model was used to determine the pore characteristics such as surface area, pore volume and pore size from the nitrogen adsorption isotherms. The nitrogen adsorption was carried out from relative pressure (P/P$_o$) of 0.01 to 0.99 [16].

FTIR spectroscopy (Perkin Elmer Spectrum 100) was used to study the surface chemistry of the activated carbon. For this analysis, approximately 1 g of powdered AC produced was required. FTIR spectra was measured with transmittance range from 4000 to 650 cm^{-1} with 16 attenuated total reflectance (ATR) unit scans with 4 cm^{-1} resolution. All sample spectra were baseline corrected and the transmittance value was normalized with the range from 0 to 100% [16].

2.4. Lead and nitrate adsorption process

The adsorption study was carried out with different concentration of Pb(II) and NO_3 solution. The Pb(II) concentration used for adsorption process were range from 3 ppm to 0.5 ppm. The lead stock solutions were prepared from lead nitrate, Pb(NO_3). As for NO_3, the concentration used were range 80 ppm to 30 ppm. The nitrate stock solutions were prepared from potassium nitrate, KNO_3.

0.1 g of AC sample with 50 ml of the stock solution was placed in a conical flask. The mixture was regulated at pH 7 by adding HCl or NaOH. The conical flask was placed in an incubating shaker with rotating speed of 150 rpm for 24 hours [17]. After 24 hours, the mixture was withdrawn and filtered. The concentration of the solution after adsorption was determined with test kit and was measured using Spectroquant ®. The amount of Pb(II) and NO_3 uptake were calculated using Eq. (1):

$$q_e = \frac{V\,(C_0 - C_e)}{W} \qquad (1)$$

where C_e is mass (mg) of adsorbed component per g of AC, C_0 is the initial concentration (mg/l), q_e is the equilibrium concentration of the component (mg/l), W is the weight of AC used (g) and V is the volume of solution (L).
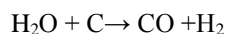
3. Results and Discussion

3.1. Pore development and structure of activated carbon

Nitrogen adsorption isotherm for each AC samples from different chemical reagent was conducted to study the pore characteristics. Pore characteristics such as surface area, pore size distribution, pore volume are obtained by using Branaeuer- Emmett-Teller (BET) model as recorded in Table 2.

Table 2. Pore characteristics of EFB-derived AC samples.

Sample	BET Surface Area (m2/g)	Micropore Suface Area (m2/g)	Average Pore Diameter (nm)	Micropore (%)
P85SA-AC	887.0664	734.4532	2.1054	82.80
P50SA-AC	739.9068	662.2668	2.4801	89.51
P50PH-AC	-	-	-	-
P25PH-AC	860.7611	590.5898	2.2838	68.61
PDES-AC	722.7199	660.7205	1.9133	91.42
WP-AC	800.0812	638.4178	1.9884	79.79

There was no data obtained for P50PH-AC as the structure collapsed and disintegrated due to high concentration of alkali was used. This is probably caused by excessive potassium hydroxide (KOH) molecules which decomposed into water during heat treatment. The water molecules brought in gasification process to the carbon at high temperature as shown below [19]:

$2KOH \rightarrow K_2O + H_2O$

$H_2O + C \rightarrow CO + H_2$

Therefore, the carbon became carbon monoxide (CO) and hydrogen gas (H_2). This explained why there was no carbon left after activation process. This phenomena was observed by Chai et al. [16] where no residue where left for 85% concentrated KOH sample. P25PH-AC has lower micropore surface area compared to other pretreated samples. This might be due to the phenomena explained above which cause widening of micropore to mesopore. Hence, micropore surface area

decreases. This can be correlate using the pore diameter as the average pore diameter are in mesopore range (2 nm- 50 nm) [20].

For acid pretreated AC, the BET surface area and micropore surface area are higher for P85SA-AC. It is suggested that the sulphuric acid (H_2SO_4) intercalated into the EFB fibre. During pyrolysis process, the H_2SO_4 decomposed to water and sulphur trioxide and these products intercalate and force the crystalline layers in carbon apart [21]. At higher concentration, more H_2SO_4 molecules intercalate into EFB fibre; hence, improve the development of porous structures in AC and increase the surface area. This is with good agreement with a report by Guo and Lua [22]. Table 2 shows that the BET surface area for P50SA-AC and PDES-AC are lower compared to WP-AC. Generally, chemically pretreated AC should have higher BET and micropore surface area than untreated AC [22, 23]. During pretreatment process, chemical reagent increase the surface area through creation of new micropores and increase the surface area [9]. However, the results obtained is not following the trend. This might be due to during the heat treatment, some of the inorganic oxide may redeposit back and block some of the pores [24]. Further analysis using SEM and XRD must be done to justify this. It can only be concluded that the pore characteristics are dependent on the heat treatment combination (pyrolysis temperature, nitrogen air flow rate, activation temperature) and type of chemical used.

For PDES-AC, it has comparable BET surface area as the other sample. Although it has the lowest BET surface area (722.72 m^2/g), but it has high micropore surface area (660.72 m^2/g) which is important for good adsorption. This implies that DES can be used as pretreatment agent in AC production to give porous structure. DES is usually used in pretreatment of biomass to improve sugar production by removing silica on biomass [10]. However, DES on AC production are still limited and the effect of DES on AC surface is not yet identified. Further analysis on surface morphology using SEM should be carried out. AC prepared from acid and DES pretreatment have shown to be different from WP-AC. Both of these treatment shows positive contribution to the development of porosity. From Table 2, it shows that the micropore percentage from these pretreatment are higher than WP-AC (80%). This concluded that acid and DES pretreatment were better than alkali pretreatment in term of producing microporous structure.

3.2. Surface chemistry of activated carbon

The FTIR spectra of raw empty fruit bunch (EFB) and all the EFB- activated carbon samples are as shown in Fig. 1. Based on Fig. 1, raw EFB shows the spectra with most peaks compared to others. The peak intensity of 3374 cm^{-1} for raw EFB spectra is high due to the moisture content in raw EFB. This peak is not intensify in all the AC samples as it has been removed during pyrolysis and activation process.

From Fig. 2, the spectra trend of all the EFB AC are similar to the commercial activation carbon (CAC) spectra. Hence, it shows each sample successfully been transformed into AC after pyrolysis and activation process, including the DES pretreated sample. This has further strengthen the potential of using DES in AC preparation.
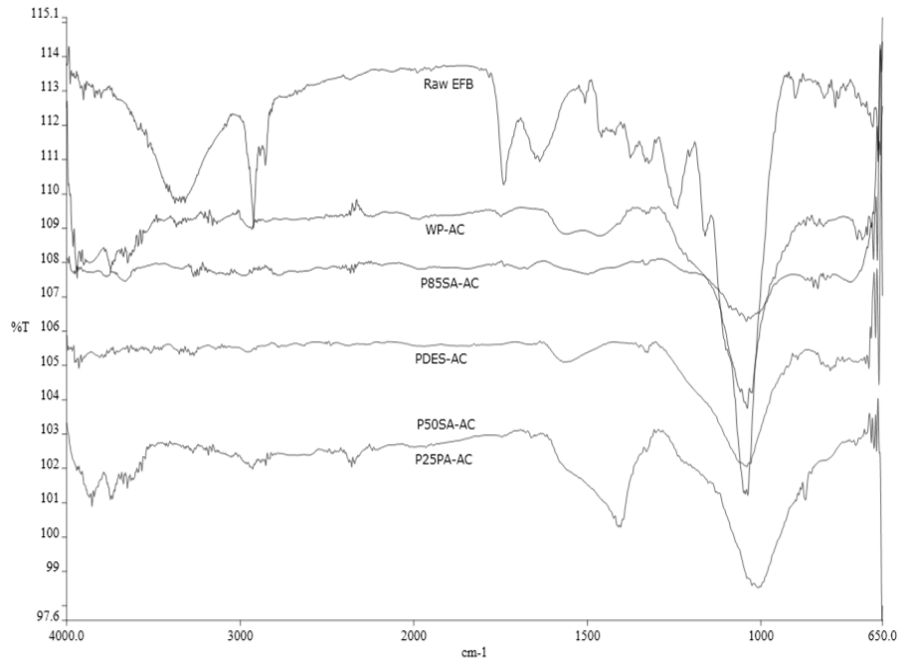
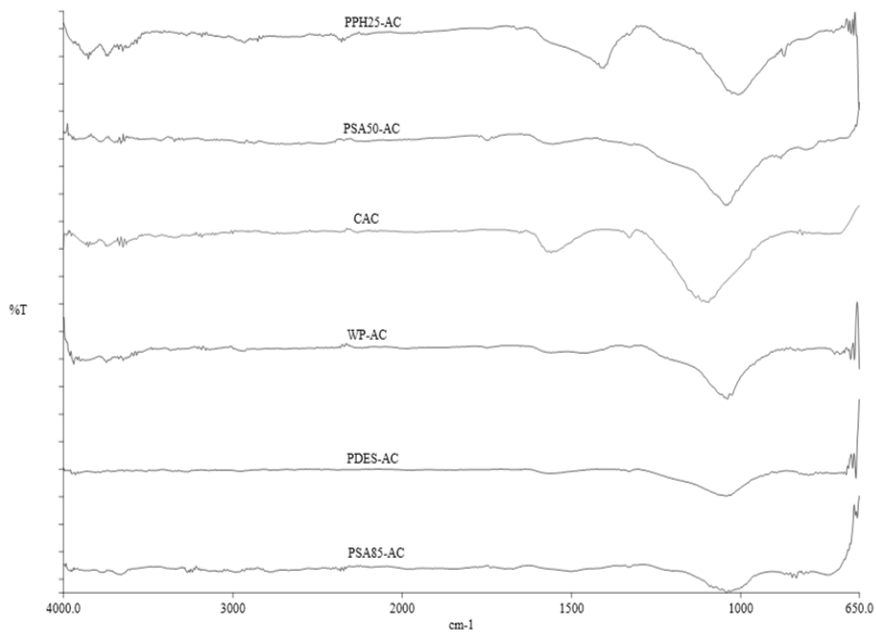**Fig. 1. FTIR spectra of raw EFB and AC samples.**

Fig. 2. FTIR spectra of CAC and AC samples.

Table 3 shows the detailed peak positions and assignments of raw EFB and EFB-AC samples. Based on Table 3, most of the adsorption peaks such as O-H at 3374 cm⁻¹, C-H at 2923 cm⁻¹ and C=O at 1641 cm⁻¹ in raw EFB are not visible in all the AC samples. The disappearance of these peaks as reported by Yacob et al. [28] where these functional groups vaporized as volatile materials when heat is applied. This is with good agreement with Hidayu et al. [4]. The C=O group of hemicellulose is visible in P50SA-AC but not in P85SA-AC. This might be due to at higher concentration of acid, it initiated more bond cleavage of C=O which depolymerized hemicellulose. As reported by Nasser et.al, acid breaks several bonds in aliphatic and aromatic groups which initially appear in raw EFB. This finding is consistent with the disappearance of C=O group [27].

Table 3. Detailed peak positions and assignments.

Wave Number (cm⁻¹)	Functional Group	1	2	3	4	5	6
3374	Stretching vibration of O-H hydroxyl group	•					
2923 & 2849	Stretching of C-H of lignocellulosic component	•					
1738	C=O stretching of hemicellulose (acetyl content) [25]	•	•		•	•	
1641	C=O stretching vibration in conjugated carbonyl of lignin [26]	•					
1515	C=C stretching vibration of aromatic rings of lignin [25, 26]	•	•	•	•		•
1400- 1480	Aromatic skeletal with C-H in plane deforming and stretching [26]	•	•			•	
1243	Syringyl ring breathing and C-O stretching in lignin and xylan [26]	•					
1158	C-O-C asymmetric stretching in cellulose I and cellulose II [26]	•					
1041	C-O stretching vibration (cellulose, hemicellulose & lignin) [26]	•	•	•	•	•	•
880, 870, 810	C-H aromatic out of plane [27]	•	•	•	•	•	•

*1: Raw EFB; 2: WP-AC; 3: P85SA-AC; 4: P50SA-AC; 5: P25PH-AC; 6: PDES-AC

Lignin structure which characterised by peak 1515 cm⁻¹ [25] on aromatic C=C stretching disappeared at P25PH-AC but visible in WP-AC, P85SA-AC, P50SA-AC and PDES-AC. This shows that lignin still intact even after acid and DES pretreatment which favorable in production of AC. As reported by Nor et al. [10], the DES made up of choline chloride and urea does not show much delignification on EFB; hence this explained the lignin peak around 1515 cm⁻¹ is still visible.

Another observation is on the intensity of C-O stretching vibration peak at 1041 cm⁻¹ based on Fig. 1. The intensity of this peak for P85SA-AC and P50SA-

AC are much lower than P25PH-AC. This might be due to the overall content of cellulose, hemicellulose and lignin. Pretreatment of biomass using acid breaks cellulose and hemicellulose structure effectively; whereas alkali breaks lignin [29]. P85SA-AC has lower intensity for peak 1041 cm^{-1} as compared to P50SA-AC. This might be due to high concentration acid that breaks cellulose and hemicellulose structure more effectively; hence resulting less cellulose and hemicellulose content. For P25PH-AC, the cellulose and hemicellulose structure still intact together; hence C-O stretching vibration peak at high intensity. As for aromatic skeleton with C-H in crystalline cellulose at peak around 1400 cm^{-1} to 1480 cm^{-1}, it was not found in P85SA-AC and P50SA-AC. This peak can only be found in WP-AC and P25PHAC, where it indicates the cellulose content still available.

3.3. Lead and nitrate adsorption study

Adsorption process carried out in two stages. The 1st stage is to identify the AC sample which results in highest adsorption for Pb (II) and NO$_3$. The 2nd stage is to study the effect of initial concentration of Pb (II) and NO$_3$ using the identified AC from 1st stage. Pb (II) adsorption by using EFB-derived AC has already been researched by Wahi and et al. [6]. However, the preparation of the AC in the article mentioned [6] was different with the preparation method in this paper. Besides that, there is no study done on NO$_3$ adsorption using EFB-derived AC till date.

3.3.1. 1st stage adsorption process

Pores act as active sites, which played a major role in adsorption process. Hence, pores development in AC is crucial [6]. After BET analysis, AC samples which have higher micropore surface area percentage than WP-AC are used for 1st stage adsorption process. These AC samples were P85SA-AC, P50SA-AC and PDES-AC. The outcome of Pb (II) and NO$_3$ removal by each AC sample are as shown in Fig. 3.
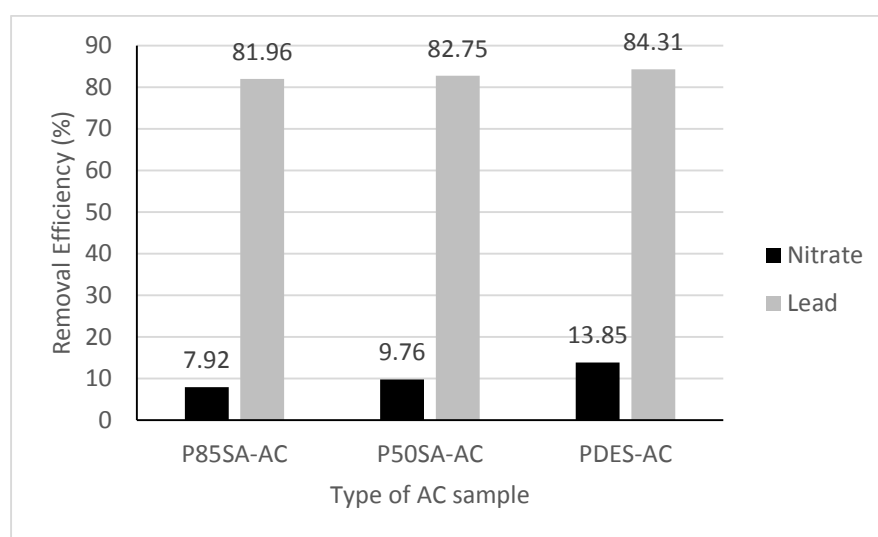

Fig. 3. Removal efficiency of each AC for lead and nitrate adsorption.

The result shows that acid and DES-pretreated AC sample are able to adsorb Pb (II) and NO_3. Due to the adsorption capacity, it is conclude that these AC acts like CAC and can relate it to the similar trend obtained from FTIR for these AC with CAC. Based on Fig. 3, Pb (II) and NO_3 removal are more effective using PDES-AC; hence it is used in 2nd stage adsorption process. PDES-AC is able to give the highest removal of Pb (II) and NO_3 despite having lowest BET surface area (722.72 m^2/g). However, PDES-AC has the highest micropore surface area percentage (91.4%) among all. Likewise, P50SA-AC has higher adsorption capacity for both Pb (II) and NO_3 compared to P85SA-AC. P50SA-AC has micropore surface area percentage of 89.5%, whereas P80SA-AC has micropore surface area percentage of 82.8%. This suggest that the amount of micropore produced is playing a more profound role compared to total surface area in pollutants adsorption. Furthermore, it is concluded that a lower concentration of sulphuric acid (50%) can be potentially used to pretreat EFB in AC production. This finding is significant as it suggests that a less hazardous pathway could be employed to produce AC with good adsorption capacity.

3.3.2. 2nd stage adsorption process- effect of initial concentration

The effect of initial Pb (II) and NO_3 concentration on removal percentage by PDES-AC is as shown in Fig. 4.
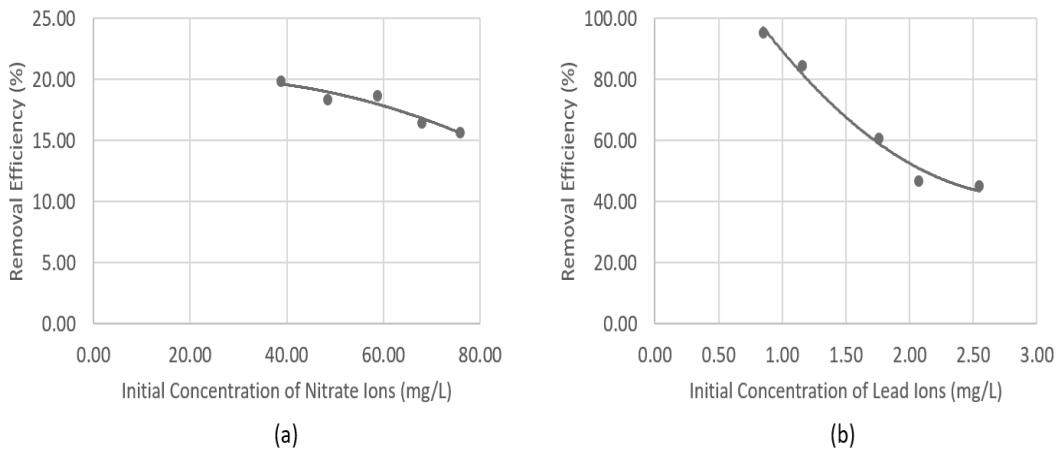

(a)   (b)

Fig. 4. (a) Nitrate removal using PDES-AC (b) Lead removal using PDES-AC.

Based on Fig. 4, the removal percentage of NO_3 and Pb (II) are found to reduce when the initial concentration increase. This can be explained that the active sites on AC for NO_3 and Pb (II) removal reduce as the initial concentration of NO_3 and Pb (II) increase. At lower initial concentration, there are more adsorption sites available on the AC [30] and facilitate almost 100% adsorption. At high initial concentration, most of the active sites are saturated as the amount of AC remain unchanged [6]. Thus, left most of the NO_3 and Pb (II) ions unabsorbed in the solution. The Pb (II) results are with good agreement with Wahi et.al where it used EFB to prepare AC [6].

Overall, it can be observed that NO_3 removal is not as effective as Pb (II). This might be due to the number of positively charged sites on AC. As reported

Demiral et al., it suggested that positively charged site favors the NO_3 adsorption due to electrostatic attraction [17]. In this paper, the PDES-AC might have lesser positively charged site compared to negatively charged site; hence resulting lesser NO_3 removal. The removal percentage of NO_3 was relatively low compared to NO_3 removal using zinc chloride ($ZnCl_2$) pretreated AC as reported by Demiral et al. [17] which has removal percentage of 41%. Hence, NO_3 adsorption is dependent on the types of chemical reagent used in preparation of AC. Acid pretreatment would protonate -OH group and give positive site which increase the electrostatic adsorption of anion [31]. Thus, it can be concluded that PDES-AC is able to remove NO_3 but at a lower efficiency compared to $ZnCl_2$ pretreated AC.

In order to compare the effect of pretreatment on AC production used for adsorption process, a control sample (WP-AC) is used. Table 4 shows the adsorption results and the removal efficiency of WP-AC and PDES-AC.

Table 4. Performance of WP-AC and
PDES-AC in adsorption of lead and nitrate ions

AC Sample	Pollutants	Initial Concentration (mg/L))	Final Concentration (mg/L)	Removal Efficiency (%)
WP-AC	Pb(II)	0.85	0.32	62.35
	NO_3	38.80	34.6	10.82
PDES-AC	Pb(II)	0.85	0.04	95.29
	NO_3	38.80	31.10	19.85

Based on Table 4, WP-AC has lower removal efficiency than PDES-AC. Hence, it is concluded that physiochemical activation able to produce AC with higher adsorption capacity compared to AC which has just undergone physical activation. This results might correlate with the micropore surface area as reported in Section 3.1, where PDES-AC has higher micropore surface area gives higher adsorption capability as compared to WP-AC. As reported by Nowicki and co-worker, it was found that chemically pretreated AC provides higher adsorption capability as compared to non-pretreated AC [32]. To conclude, DES pretreated improved the adsorption capacity of the AC and physiochemical activation is better than physical activation.

3.4. Comparison of AC produced from different lignocellulosic biomass

Table 5 shows the comparison of other research on Pb(II) and NO_3 adsorption by using biomass-derived adsorbents. It is not possible to have direct comparison on the removal efficiency as a different combination of parameters and conditions are employed in every work. Apart from the preparation conditions, the properties of each biomass used differ with biomass structure and lignin composition. However, qualitatively, it is proven that the Pb(II) uptake of EFB-derived AC has comparable removal efficiency of AC from other biomass. For NO_3, although it has lower removal efficiency compared to others, this can further investigated by using different type of DES. With this comparison made, it reinforced the practicality of employing EFB as precursor in AC production for Pb(II) and NO_3 removal.

**Table 5. Comparison of removal
efficiency on lead and nitrate ions by using AC.**

Type of Biomass Used	Activating Agent	Types of ion	Removal Efficiency (%)	Reference
Coconut Shell	Concentrated H_2SO_4	Pb (II)	92.50%	[33]
Empty Fruit Bunch	NaOH	Pb (II)	100.00%	[6]
Pecan Nutshell	-	Pb (II)	100.00%	[34]
Tamarind Wood	$ZnCl_2$	Pb(II)	97.74%	[35]
Carbon Residue	-	NO_3	21.00%	[31]
Lignite Granular Activated Carbon	$ZnCl_2$	NO_3	38.30%	[18]
Sugar Beet Bagasse	$ZnCl_2$	NO_3	41.20%	[11]
Empty Fruit Bunch	Deep Eutectic Solvent (Urea: CCl)	Pb (II)	95.30%	This Study
		NO_3	19.85%	

4. Conclusions

EFB- derived activated carbon produced through acid pretreatment (85% and 50% H_2SO_4), alkali pretreatment (25% KOH) and DES pretreatment have similar functional groups as CAC based on FTIR results. Acid and DES pretreated AC samples resulted higher micropore percentage than control sample. On the other hand, alkali pretreated AC resulted lower micropore percentage than control sample and hence, it is not suitable for adsorption. In terms of removing Pb(II) and NO_3, P50SA-AC has higher removal efficiency than P85SA-AC and this indicates that lower concentration of acid can be used for pretreatment in AC production. DES pretreated AC resulted to have highest adsorption of Pb(II) and NO_3 due to its high micropore percentage among all samples. The highest removal efficiency of NO_3 and Pb(II) using PDES-AC were 19.85% and 95.29% respectively. NO_3 can only be removed at lower percentage which might be due lack of positively charged surface on AC produced. From this study, DES which is a less hazardous chemical and reusable is proven to be a potential pretreatment agent in AC production. For future study, different type of DES can be investigated in AC production.

Acknowledgement

References

1. UN-Water (2014). Statistic Details. Retrieved September 29, 2016, from http://www.unwater.org/statistics/statistics-detail/en/c/211800/.

2. Bansal, R.C.; and Goyal, M. (2005). *Activated Carbon Adsorption.* Boca Raton, FL: CRC Press.

3. Anisuzzaman, S.M.; Joseph, C.G.; Taufiq-Yap, Y.H.; Krishnaiah, D.; and Tay, V.V. (2015). Modification of commercial activated carbon for the removal of

2,4-dichlorophenol from simulated wastewater. *Journal of King Saud University - Science*, 27(4), 318-330.

4. Hidayu, A.R.; Mohamad, N.F.; Matali, S.; and Sharifah, A.S.A.K. (2013) Characterization of activated carbon prepared from oil palm empty fruit bunch using BET and FT-IR techniques. *Procedia Engineering*, 68, 379-384.

5. Lee, T.; Zubir, A.; Jamil F.M.; Matsumoto, A.; and Yeoh, F.Y. (2014). Combustion and pyrolysis of activated carbon fibre from oil palm empty fruit bunch fibre assisted through chemical activation with acid treatment. *Journal of Analytical and Applied Pyrolysis*, 110 (1), 408-418.

6. Wahi, R.; Ngaini, Z.; and Jok, V. (2009). Removal of mercury, lead and copper from aqueous solution by activated carbon of palm oil empty fruit bunch. *World Applied Sciences Journal*, 5, 84-91.

7. El-Sayed, G.O.; Yehia, M.M.; and Asaad, A.A. (2014). Assessment of activated carbon prepared from corncob by chemical activation with phosphoric acid. *Water Resources and Industry*, 7-8, 66-75.

8. Bouchelta, C.; Medjram, M.S.; Bertrand, O.; and Bellat, J.P. (2008). Preparation and characterization of activated carbon from date stones by physical activation with steam. *Journal of Analytical and Applied Pyrolysis*, 82(1), 70-77.

9. Abdullah, A.H.; Kassim, A.; Zainal, Z.; Hussien, M.Z.; Kuang, D.; Ahmad F.; and Ong S.W. (2001). Preparation and Characterization of Activated Carbon from Gelam Wood Bark (*Melaleuca cajuputi*). *Malaysian Journal of Analytical Sciences*, 7(1), 65-68.

10. Nor, N.A.M.; Mustapha, W.A.W.; and Hassan, O. (2016). Deep Eutectic Solvent (DES) as a Pretreatment for Oil Palm Empty Fruit Bunch (OPEFB) in Sugar Production. *Procedia Chemistry*, 18, 147-154.

11. Bhatnagar, A.; Hogland, W.; Marques, M.; and Sillanpää, M. (2013). An overview of the modification methods of activated carbon for its water treatment applications. *Chemical Engineering Journal*, 219, 499-511.

12. Foo, K.Y.; and Hameed, B.H. (2011). Microwave-assisted preparation of oil palm fiber activated carbon for methylene blue adsorption. *Chemical Engineering Journal*, 166(2), 792-795.

13. Hameed, B.H.; Tan, I.A.W.; and Ahmad, A.L. (2009). Preparation of oil palm empty fruit bunch-based activated carbon for removal of 2,4,6-trichlorophenol: Optimization using response surface methodology. *Journal of Hazardous Materials*, 164(2-3), 1316-1324.

14. Daneshfozoun, S.; Bawadi, A.; and Abdullah, M.A. (2014). Heavy Metal Removal by Oil Palm Empty Fruit Bunches (OPEFB) Biosorbent. *Applied Mechanics and Materials*, 625, 889-892.

15. Hidayu, A.R.; Mohamad, N.F.; Matali, S.; and Sharifah, A.S.K. (2013). Preparation and characterization of activated carbon made from oil palm, *Procedia Engineering*, 68, 379-384.

16. Chai, I.; Lee, T.; and Lim, X.Y. (2016). Creatinine Adsorption by Activated Carbon Fibre derived from Empty Fruit Bunch. *Proceedings of 6th EURECA conference*. Taylor's University, Selangor, Malaysia, 145-156.

17. Demiral H.; and Gündüzoğlu, G. (2010). Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresource Technology*, 101(6), 1675-1680.

18. Ali Khan, M.; Ahn, Y.T.; Kumar, M.; Lee, W.; Min, B.; Kim, G.; Cho, D.W.; Park, W.B.; and Jeon, B.H. (2015). Adsorption Studies for the Removal of Nitrate Using Modified Lignite Granular Activated Carbon. *Separation Science and Technology*, 4616, 2575-2584.

19. Tan, I.A.W; Ahmad, A.L.; and Hameed, B.H. (2008). Preparation of activated carbon from coconut husk: Optimization study on removal of 2,4,6-trichlorophenol using response surface methodology. *Journal of Hazardous Materials*, 153(1-2), 709-717.

20. Williams, P.T.; and Reed, A.R. (2006). Development of activated carbon pore structure via physical and chemical activation of biomass fibre waste. *Biomass and Bioenergy*, 30(2), 144-152.

21. Tan, W.C.; Othman, R.; Matsumoto, A.; and Yeoh, F.Y. (2012). The effect of carbonisation temperatures on nanoporous characteristics of activated carbon fibre (ACF) derived from oil palm empty fruit bunch (EFB) fibre. *Journal of Thermal Analysis and Calorimetry*, 108(3), 1025-1031.

22. Guo J.; and Lua, A.C. (1999). Textural and chemical characterisations of activated carbon prepared from oil-palm stone with H_2SO_4 and KOH impregnation. *Microporous Mesoporous Material*, 32(1), 111-117.

23. Gundogdu, A.; Duran, C.; Senturk, H.B.; Soylak, M.; Imamoglu, M; and Onal, Y. (2013). Physicochemical characteristics of a novel activated carbon produced from tea industry waste. *Journal of Analytical and Applied Pyrolysis*, 104, 249-259.

24. Suzuki, R.M.; Andrade, A.D.; Sousa, J.C.; and Rollemberg, M.C. (2007). Preparation and characterization of activated carbon from rice bran. *Bioresource Technology*, 98, 1985-1991.

25. Yoon, L.W.; Ang, T.N.; Ngoh, G.C.; Chua, A.S.M. (2011). Regression analysis on ionic liquid pretreatment of sugarcane bagasse and assessment of structural changes. *Biomass and Bioenergy*, 36, 160-169.

26. Shi J.; and Li, J. (2012). Metabolites and chemical group changes in the wood-forming tissue of *Pinus Koraiensis* under inclined conditions. *BioResources*, 7(3), 3463-3475.

27. El-Hendawy, A.N.A. (2006). Variation in the FTIR spectra of a biomass under impregnation, carbonization and oxidation conditions. *Journal of Analytical and Applied Pyrolysis*, 75(2), 159-166.

28. Yacob, A.R.; Majid, Z.A.; Sari, R.; and Dasril, D. (2008). Comparison of various sources of high surface area carbon prepared by different types of activation. *Journal of Analytical Science and Technology*, 12(1), 264-271.

29. Kumar, P.; Barrett, D.M.; Delwiche, M.J.; and Stroeve, P. (2009). Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Industrial & Engineering Chemistry Research*, 48(8), 3713-3729.

30. Imamoglu, M.; and Tekir, O. (2008). Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks. *Desalination*, 228(1-3), 108-113.

31. Kilpimaa, S.; Runtti, H.; Kangas, T.; Lassi, U.; and Kuokkanen, T. (2014). Removal of phosphate and nitrate over a modified carbon residue from biomass gasification. *Chemical Engineering Research and Design*, 92(10), 1923-1933.

32. Nowicki, P.; Kazmierczak, J.; and Pietrzak, R. (2014). Comparison of physicochemical and sorption properties of activated carbons prepared by physical and chemical activation of cherry stones. *Powder Technology*, 269, 312-319.

33. Sekar, M.; Sakthi, V.; and Rengaraj, S. (2004). Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell. *Journal of Colloid and Interface Science*, 279(2), 307-313.

34. Vaghetti, J.C.P.; Lima, E.C.; Royer, B.; da Cunha, B.M.; Cardoso, N.F.; Brasil, J.L.; and Dias, S.L.P. (2009). Pecan nutshell as biosorbent to remove Cu(II), Mn(II) and Pb(II) from aqueous solutions. *Journal of Hazardous Materials*, 162(1), 270-280.

35. Acharya, J.; Sahu, J.N.; Mohanty, C.R.; and Meikap, B.C. (2009). Removal of lead(II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. *Chemical Engineering Journal*, 149(1-3), 249-262.