Optimization of Pb(II) Adsorption onto Australian Pine Cones-Based Activated Carbon by Pulsed Microwave Heating Activation

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ABSTRACT: *This study proposed a novel method for preparing activated carbon from Australian Pine cones (APCs) to optimize Pb(II) adsorption. Based on an analysis conducted, the APCs dried powder consisted of approximately 51.32 wt% of cellulose and 21.15 wt% of lignin on average. Experiments in batch mode at 100-rpm stirring speed, pH 4.7 (± 0.3) and 27 °C (± 2 °C) were conducted to obtain the maximum adsorption capacity of Australian Pine cones activated carbon (the APCs AC) over the independent variables of contact time, initial Pb(II) concentration in solution, the concentration of NaOH activator and Pulsed Microwave Heating (PMH). As the result, the maximum Pb(II) adsorption capacity was obtained when using the APCs AC with 1 M NaOH and the PMH activation. It follows Langmuir Isotherm Model (LIM) and the pseudo-second-order kinetics model (PSOKM) with the correlation coefficients (R^2) being 0.993 and 1, respectively. The LIM maximum Pb(II) adsorption capacity was 166.667 mg/g, the PSOKM maximum equilibrium Pb(II) adsorption capacity was 151.515 mg/g reached in 120-min contact time, and the PSOKM kinetics constant was 0.295 g/mg.min for 1571.89 mg/L of initial Pb(II) concentration. This optimum condition was reasonable because the PMH resulted from the dominant active site of the functional group of hydroxyl on the APCs AC for Pb(II) adsorption as shown by Fourier Transform Infrared Spectroscopy analysis, and more pores were shown in Scanning Electron Microscopy (SEM) analysis.*

KEYWORDS: *Australian pine cones; adsorption; isotherm; kinetics, pulsed microwave heating; optimization.*

INTRODUCTION

Heavy metals are non-biodegradable toxic pollutants, and it can be bio-accumulated in the food chain. It can be released uncontrollably to the environment from mining, agricultural and industrial activities [1-5]. Lead is one of the most hazardous among the heavy metals which can cause a very bad effect on all the system and organ of human body. It can damage the brain and kidneys leading to death, decrease the nervous system, and cause miscarriage in pregnant women. It also can cause blood and brain disorders and anemia [6-9]. Therefore, it is needed to treat lead from lead-contaminated wastewater before it is discharged to the environment.

Adsorption is one of the simpler and effective techniques to apply, among technologies proposed to remove heavy metal from the wastewater [10, 11], and the process can be economically friendly when using low-cost adsorbent material. Natural non-renewable adsorbents of zeolite, clay, phosphate, graphite oxide and cow bone had been applied to remove the lead contaminant from aqueous solutions [12-16]. Renewable natural adsorbents from biological wastes have been also chosen for the adsorption of lead using marine alga, ulva lactuca, oedogonium species, nostoc species and bacillus [17-19]. Modified agriculture wastes have been prepared for lead adsoprtion are maize cob and husk [20], rice husk [21], and guava seeds [22]. Activated carbon based on European Black Pine cone and Australian Pine cone was used for removal of lead(II) ions and copper (II) ions, respectively [23, 24].

Casuarina or *Casuarina equisetifolia L.* known as Australian Pine is fast-growing tree, and it has been planted to more than 60 countries in America, Europe, Africa, Ociania, and Asia [25]. This tree is broadly seeded for the production of wood timber, tannin, dye, and pulp, hold back of erosion, dan coastal restoration [26,27]. Activated carbon prepared from the leaves and needles has been used for the adsorption of chromium [28] and methyl violet 2B [29]. However, activated carbon prepared from Australian Pine Cones (APCs) for adsorption of lead ions has not been proposed in previous studies.

In all practice of microwave radiation methods, the starting material of activator and impregnated raw material was heated in the solid phases (char or powder), and the carbonation is taken place in a modified microwave oven with nitrogen gas injection [30-32]. To optimize Pb(II) adsorption capacity of activated carbon, a novel method is proposed in the present study whereas starting material of activator is in the aqueous phase, and pulsed microwave heating is applied without injection of nitrogen gas.

The main objective of this study is to propose a novel method in preparing activated carbon from Australian Pine cones (APCs) in optimizing Pb(II) adsorption by Australian Pine cones activated carbon (the APCs AC) at 27 °C (± 2 °C), pH 4.7 (± 0.3) and 1 atm over the independent variables of contact time, initial Pb(II) concentration in solution, the concentration of NaOH activator and Pulsed Microwave Heating (PMH).

The cellulose and lignin content of the APCs was quantified, and the chemical functional groups on the APCs dried powder and the APCs AC was analyzed using Fourier Transform Infrared Spectroscopy, and the surface morphology of were identified using a Scanning Electron Microscopy. The effect of contact time, initial Pb(II) concentration and the concentration of activator NaOH and the PMH during chemical activation were investigated at pH 4.7 (± 0.3) to obtain the maximum Pb(II) adsorption capacity onto the APCs AC.

EXPERIMENTAL SECTION
Materials

The APCs waste was picked from the floor of Australian pine plantation area for the coastal reclamation of Tsunami at Alue Naga in Banda Aceh, Indonesia. The APCs of 1 kg was rinsed entirely using tap water and dried at the temperature of 30 °C (± 2 °C) under the sun for 2 days and average relative humidity of 12%. The stock aqueous solution of 1600 mg/L Pb(II) was prepared from A.R. grade $Pb(NO_3)_2$ (99% pure from Aldrich) by dissolving 2.583 g (±0.001 g) $Pb(NO_3)_2$ in 1000 mL distilled water in the 1000-mL Erlenmeyer flask. The solution pH was obtained using pH indicator strips (pH 4.0 – 7.0, MERCK). The sample of 5 mL was taken from the stock solution and analyzed using Atomic Absorption Spectrophotometer (AAS) to obtain the Pb(II) concentration. The predetermined concentration of Pb(II) aqueous solution was prepared using a variable volume pipette for batch experiments of Pb(II) adsorption.

Methods
Activated Carbon Preparation

The dried APCs were ground to a powder using a rice mill. Contents of cellulose and lignin of the dried APCs powder were determined by the Chesson method [33]. For physical activation, the dried APCs powder of 1 kg was coated with at four layers of heavy duty aluminum foil. Carbonation of the dried APCs powder was taken place in a furnace (Nabertherm, More Than Heat 30-3000 °C, made in Germany) with the heating rate of 6.5 °C/ min for 2 h, physical activation was taken place at 800 °C (± 2 °C) for 1 h. It is an economically friendly method to apply heavy-duty aluminum foil coating instead of using nitrogen to limit the oxygen diffusion into the APCs carbon. The higher temperature of pyrolysis was applied

to get better performance of carbon as highlighted in the literature [34, 35]. Then, the APCs carbon of 0.05 kg was chemically activated using 250 mL of 0.5-1 M NaOH (1N, Gatt-Koller) in 500-mL beaker glass at 100-rpm stirring speed (HI 180-2 F Compact Magnetic Mini-Stirrer) for 3 h and at 27 °C (± 2 °C). Finally, the APCs AC was washed with distilled water many times and filtered using vacuum filter until the used distilled water reaching neutral pH of 7 (± 0.5).

To maximize adsorption capacity of activated carbon, a novel method in terms of microwave heating was applied where starting material of activator is in the aqueous phase and pulsed microwave heating is applied without injection of nitrogen gas. The APCs carbon of 0.05 kg was chemically activated using 250 mL of 1 M NaOH, and it was heated during activation using a modified microwave oven (220 V, 50 Hz Panasonic NN-ST342M TTE, made in China) with 100-rpm of magnetic stirring speed. Heidolph overhead stirrer (RZR-2000, Typ 501-12000, made in Germany) with the magnetic rod was installed from the bottom of the microwave. Microwave radiation of 15 min was pulsed at 0, 60 and 120-min during 3 h of chemical activation with the maximum temperature of 75 °C (± 2 °C). The maximum temperature was reached at 15-min radiation time. The APCs AC with the varying activation method was separately dried in an oven drier (Memmert, NN-ST342M, made in Western Germany) at 110 °C (± 2 °C) for 2 h to remove the excess water. Then, it was sieved (80-100 mesh) and stored separately in sealed bottles. It had been used within two weeks of adsorption experiments.

The APCs AC Characterization

Fourier Transform Infrared Spectroscopy (FT-IR) was used to investigate the chemical functional groups on the APCs AC at the spectra in the range of 400-4000 cm^{-1} using a Shimadzu IR Prestige 21 Spectrophotometer (Shimadzu Co. Kyoto, Japan). Transmission spectra of the samples were quantified using KBr pellets at 0.1% sample. Scanning Electron Microscopy (SEM) (HITACHI TM3000, Tokyo, Japan) with an accelerating voltage of 500VA 1 phase, 50/60Hz was used to investigate the physical morphology of the APCs AC.

Batch Study of Pb(II) Adsorption

All the experiments were carried out in batch mode. The APCs AC and Pb(II) aqueous solution (APCs AC-PbS)

system were taken place in 200-mL Erlenmeyer flask with 1 g of the APCs AC at 100-rpm stirring speed, 27 °C (± 2 °C), pH 4.7 (± 0.3) and 1 atm. The maximum Pb(II) adsorption capacity of the APCs AC was further obtained by varying the contact time (0–150 min), activator of NaOH concentration (0.5–1 mg/L) with and without the PMH, and predetermined initial Pb(II) concentration (75–1600 mg/L). The 1-mL samples of Pb(II) solution were taken using adjustable volume micropipette at 0, 10, 35, 65, 95 and 150 min of contact time whereas stirring was stopped for 1 min before sampling. Each sample was put into the 20-mL vial, and diluted 13 times with distilled water to minimize adsorbate lost when it was filtered using syringe filters. The 10-mL filtrate was taken for the AAS analysis, and the Pb(II) concentration in solution was calculated based on the AAS reading and dilution factor. The wide range of initial Pb(II) concentration (75–1600 mg/L) was applied to investigate the effect of initial Pb(II) concentration on the adsorption capacity of adsorbent in higher adsorbate initial concentration.

RESULTS AND DISCUSSION
Cellulose and lignin contents of the APCs

The lignocellulosic component of raw material plays an important role in forming the microporosity of activated carbon [36]. The contents of cellulose and lignin of the APCs powder were determined by the Chesson method [33], and the experiments and sample analysis were taken in duplicate to obtain the weight percent of cellulose and lignin in 1 g of the APCs dried powder as the raw APCs. As the result, it consisted of approximately 51.32 wt% of cellulose and 21.15 wt% of lignin on average. The lignocellulosic component is higher than the one in rice husk which is 38–45 wt% of cellulose and 12–20 wt% of lignin [37]. Meanwhile, the cellulose and lignin of European Black pine sapwood are 44.6 and 25.3 wt%, respectively [38] but the lignocellulosic component of the cones has been not obtained [23]. In addition, the lignocellulosic component of APCs dried powder is also higher than the one in maize cob which is 32.25 wt% of cellulose and 13.79 wt% [39].

Fourier transform infrared spectroscopy analysis

Fourier Transform InfraRed (FT-IR) spectroscopy ranging from 400 to 4000 cm^{-1} (see Fig. 1) was applied to investigate the chemically functional groups of the APCs
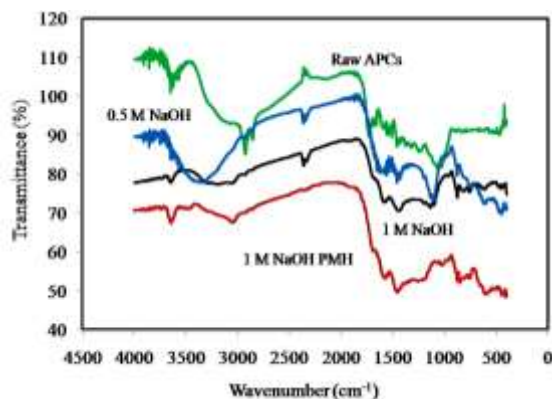
Fig. 1: The FT-IR spectra of APCs raw material, the APCs carbon activated using 0.5 M NaOH, 1 M NaOH and pulsed microwave heating (PMH).

raw material, the APCs AC without and with the PMH. As can be obtained in Fig. 1, the intense band of O–H stretching (at 3500-3700 cm^{-1} of wavenumber [40] with the intense band at approximately 3643.53 cm^{-1}) for the APCs activated using 0.5 M NaOH, 1 M NaOH and 1 M NaOH with the PMH is 3645.45 cm^{-1}. As expected, hydroxyl groups were released from the APCs raw material by physical (pyrolysis) and chemical activation, which showed by decreasing the peak transmittance of O–H stretching. Pyrolysis followed by 0.5 NaOH activation caused the peak transmittance decreased from 105.74 to 87.45%., 1 M NaOH activation decreased it to 77.83%, and the PMH lowered it to 67.39%. It means that increasing the NaOH concentration from 0.5 to 1 M for the APCs chemical activation and applying the PMH during 1 M NaOH activation can lower hydroxyl groups in the APCs AC.

As clearly shown in Fig. 1, the peak transmittance of aldehyde C–H stretching (at 2700-2980 cm^{-1} [41] with the peak at 2862.36 cm^{-1}) decreased from 91.39 to 80.98% when the NaOH concentration was raised from 0.5 to 1 M, respectively, and applying the PMH during 1 M NaOH activation dropped it to 70.97%. In addition, the aromatic C–H stretching with the band at 3000-3100 cm^{-1} [41] with the peak at 3051.38 cm^{-1} declined from 86.16 to 77.58% for the increase in NaOH concentration from 0.5 to 1 M. It then fell to 67.55% for the PMH during 1 M NaOH activation.

It is really clear to see in Fig. 1 that increasing NaOH concentration and applying the PMH can break the C=O stretching of esters at 1720-1740 cm^{-1} with the peak

at 1732.08 cm^{-1} [41] where the peak transmittance of C=O stretching dropped from 91.61 to 83.81% for the increasing NaOH concentration from 0.5 to 1 M, respectively, and it dropped to 66.62% as the result of the PMH during 1 M NaOH activation. This indicated that the PMH can diminish favorable compounds of esters in the APCs carbon by 20.51%. The same trend also occurred for the C=C stretching of aromatic rings at 1570-1580 cm^{-1} [41] with the peak at 1577.77 cm^{-1} where the intense band decreased from 92.68 to 81.39, 72.83 and 53.29% for the APCs with 0.5 M NaOH, 1 M NaOH and 1 M NaOH with the PMH, respectively. The C–H asymmetrical and symmetrical stretching (at 1317-1450 cm^{-1} [42] with multiple bands and the most intense band at 1454.32 cm^{-1}) also decreased due to increasing NaOH concentration and applying the PMH as shown in Fig. 1. The most intense band felt from 80.57 to 70.56% for the increasing NaOH concentration from 0.5 to 1 M, respectively. Then, it slightly decreased to 49.52% for 1 M NaOH with the PMH. This implied that the PMH can remove a significant amount of hydrogen in the APCs AC with 1 M NaOH. In addition, carboxyl acids (the C–O stretching at 1000-1260 cm^{-1} [42] with the most intense band at 1136.07 cm^{-1}) were removed by 21.37% implied by the decrease in the peak from 72.37 to 56.12% for 1 M NaOH activation and the PMH, respectively. Moreover, a significant decrease in the peak transmittance of C–C stretching (at 400-700 cm^{-1} [42] with the intense band at 601.79 cm^{-1}) occurred for 1 M NaOH, which is from 76.31 to 49.07% as the result of the PMH.

In general, the FT-IR analysis showed that NaOH activation and the PMH can remove hydrogen functional groups, esters, aldehyde, carboxyl acids, and aromatic rings. Chemical activation using more concentration of NaOH with the PMH produced the APCs AC with more hydroxyl groups indicated by the strong band presented on the FT-IR analysis. The presence of more hydroxyl functional group on the APCs AC might result in more potential active site for Pb(II) adsorption onto the APCs AC.

Scanning electron microscopy (SEM) analysis

The SEM micrographs (2000-2500X) of the surface morphology of the raw APCs, the APCs with 1 M NaOH activation, and the APCs with 1 M NaOH activation and the PMH are shown in Figs. 2, 3 and 4, respectively.
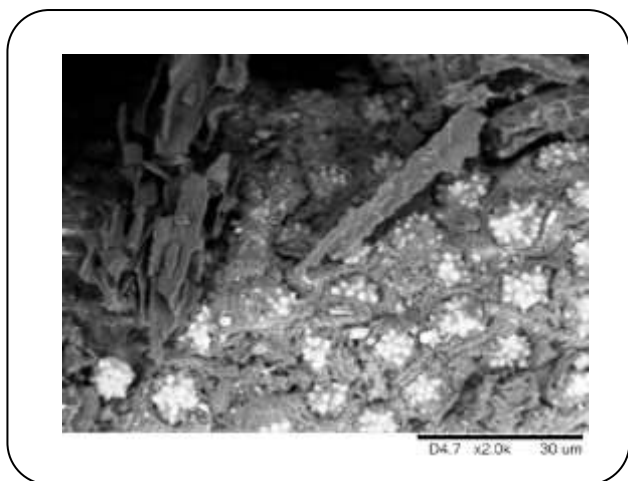
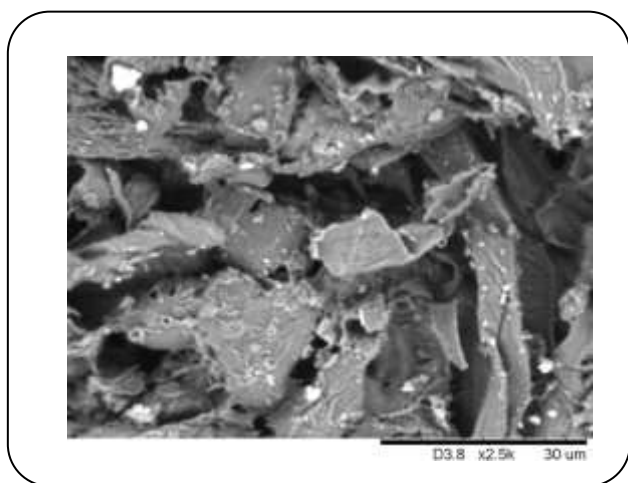*Fig. 2: The SEM micrographs of the raw APCs.*

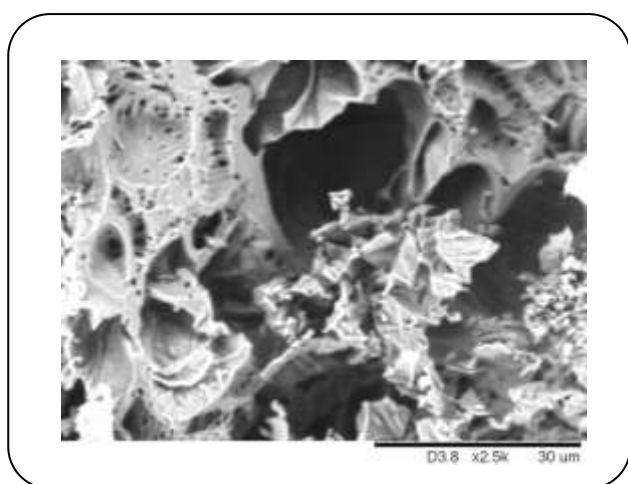*Fig. 3: The SEM micrographs of the raw APCs with 1 M NaOH activation.*

Fig. 4: The SEM micrographs of the APCs AC with 1 M NaOH activation and the PMH.

As can be observed in Figs. 2, there are irregular pores closed by round substances sticking one another on the pores of the raw APCs surface, and the raw APCs surface is not really dense and smooth. It seems that the substances could be the molecules of volatile compounds because the substances were removed from the pores as the result of pyrolysis followed by 1 M NaOH activation, as can be seen in Fig. 3. Interesting to note that applying the PMH during 1 M NaOH activation created larger pores and larger cavities on the APCs AC surface, as clearly shown in Fig. 4. Compared to the wall of the pore shown in Fig. 3, the wall of the pore of the APCs AC surface with the PMH is almost full with macropores as shown on the left part and right top part of Fig. 4. It is reasonable because simultaneous internal and volumetric heating of the PMH can lead NaOH penetrating in the pore wall, it broke all the stretchings in the APCs AC as discussed in the FT-IR analysis, and it created macropores at the wall of the pore, as also addressed in the previous study [43].

Effect of contact time on adsorption capacity

In general, contact time really affects adsorption capacity on activated carbon. The adsorption capacity of activated carbon can be increased exponentially over contact time [44, 45], and equilibrium adsorption can be reached at 24 h of contact time [44]. The adsorption capacity trend over contact can be varied for different adsorbate whereas it can be stable at the maximum adsorption capacity, and even it can be decreased after reaching equilibrium [20]. Therefore, it was necessary to determine the dependence of adsorption capacity on contact time in the APCs AC-PbS system with the condition shown by the legend of Fig. 5.

As shown in Fig. 5, Pb(II) adsorption capacity of the APCs AC increases exponentially over contact time which it is really clear shown by the APCs AC with 0.5 M of NaOH activator. It can be obtained from the bottom line in Fig. 5 that it increases sharply, in the beginning, 10-min contact time from 0 to 44.09 mg/L, it gradually increases to 83.28 mg/g at the 35-min contact time, and then it slowly increases to the maximum adsorption capacity of 92.90 mg/g at 65-min contact time. However, the adsorption capacity equilibrium for the APCs AC with 0.5 M NaOH is 5.08% lower than the maximum adsorption capacity as can be seen in Fig. 5. It is attained from 95-min contact time, which is 88.18 and 88.17 mg/g
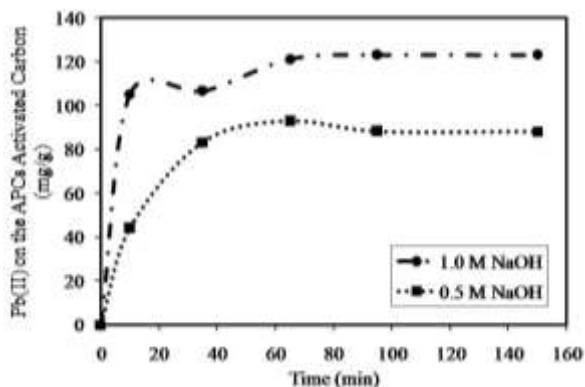
Fig. 5: Effect of contact time on Pb(II) adsorption capacity in the APCs AC in the APCs AC-PbS system consisting of 1 g of the APCs AC activated using 0.5 and 1 M NaOH, 100 mL of Pb(II) aqueous solution with 1571.89 mg/L of predetermined initial concentration, 75 rpm of magnetic stirring at 27 °C (± 2 °C), pH 4.7 (± 0.3) and 1 atm.
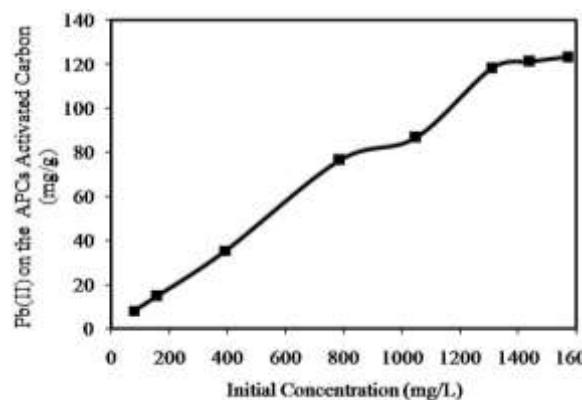

Fig. 6: Effect of initial Pb(II) concentration in solution on the adsorption capacity in the APCs AC-PbS system consisting of 1 g of the APCs AC activated using 1 M NaOH, 100 mL aqueous solution of initial Pb(II) concentrations ranging from 78.61 to 1571.89 mg/L, magnetic stirring at 75 rpm, 27 °C (± 2 °C), pH 4.7 (± 0.3) and 1 atm.

at the contact time 95 and 150 min, respectively. Meanwhile, it increases dramatically over contact time for the APCs AC with 1 M of NaOH, and the trend is in two phases as shown by the top line in Fig. 5. The first phase is the extremely rapid increase in the adsorption capacity from 0 to 105.24 mg/g during 10-min contact time. The second phase is slow phase with very small increase in the adsorption capacity to 106.55 mg/g at 35-min contact time, and gradual increase to 120.99 and 123.00 mg/g at 65 and 95-min contact time, respectively. The equilibrium adsorption capacity for the APCs AC with 1 M of NaOH is 122.99 mg/g at 130-min contact time.

Effect of concentration of NaOH activator on adsorption capacity

As expected, the adsorption capacity of the APCs AC depends on the concentration of NaOH activator, as can be seen in Fig. 5. The adsorption capacity of the APCs AC was slightly improved by 138,67% from 44.09 to 105.24 mg/g at 10-mins contact time when the concentration of NaOH was increased from 0.5 M to 1 M, respectively. The increase of 50% in the concentration of NaOH resulted in 39.47% increase in the equilibrium adsorption capacity from 88.18 to 122.99 mg/g at 130-min contact time. The effect trend of NaOH concentration on the adsorption capacity of the APCs AC is reasonable because the higher NaOH concentration was applied,

the lower the C=C stretching was formed in the APCs AC leading to the larger surface for Pb(II) adsorption onto the APCs AC. The presence of more hydroxyl functional group on the APCs AC increased with the increase of OH⁻ ions in the activating solution, and it produced more potential adsorption site on the APCs AC surface. This result is supported by the fact that greater surface area of activated carbon prepared from corncob and sawdust was obtained when the KOH and K_2CO_3 activator mass was increased [46, 47]. This trend is also supported by the result reported in the previous study that the mesopore volume of activated carbon increased with the increasing NaOH concentration [48]. Therefore, the concentration of NaOH being 1 M was taken into account for further investigation on the APCs AC adsorption capacity.

Effect of initial Pb(II) concentration

The effect of initial Pb(II) concentration on the adsorption capacity of the APCs AC was studied at the predetermined concentrations ranging from 75 to 1600 mg/L with the condition shown by the legend of Fig. 6. Wide range of initial Pb(II) concentration is also acceptable based on the previous study where the highest adsorbate initial concentration possibly applied was 3159 mg/L [49]. As can be observed from Fig. 6, the equilibrium Pb(II) adsorption capacity of the APCs AC based on the AAS reading is 7.82, 14.60, 35.19, 76.27, 86.59, 117.99, 121.10 and 123.00 mg/g for the initial
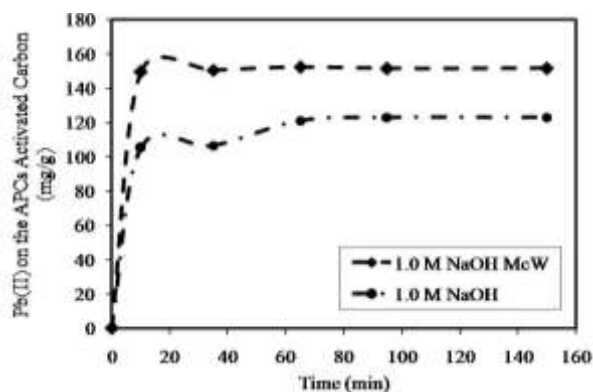
Fig. 7: Effect of pulsed microwave heating during chemical activation on Pb(II) adsorption capacity of the APCs AC in the APCs AC-PbS system consisting of 1 g of the APCs AC activated using 1 M NaOH with and without the PMH, 100 mL of Pb(II) aqueous solution with 1571.89 mg/L of predetermined initial concentration, magnetic stirring at 75 rpm, 27 ºC (± 2 ºC), pH 4.7 (± 0.3) and 1 atm.

Pb(II) concentration in solution being 78.61, 157.20, 392.91, 786.11, 1048.10, 1309.89, 1441.03 and 1571.89 mg/g, respectively with the equilibrium Pb(II) concentration in solution being 0.31, 11.19, 40.94, 23.45, 182.11, 129.99, 230.01 and 341.88 mg/g, respectively.

As viewed in Fig. 6, the Pb(II) adsorption capacity linearly increases from 78.61 to 786.11 mg/g with the increase in the initial Pb(II) concentration from 7.82 to 76.27 mg/L, and following the last point, it increases a bit to 86.59 mg/g at 1048.10 mg/g of the initial Pb(II) concentration. The trend typically occurs for the adsorption capacity over the rest initial concentration ranged. Overall, Pb(II) adsorption capacity of the APCs AC seems to follow an exponential growth over initial Pb(II) concentration in solution. It is reasonable because the available active site on the ACS AC was very limited leading to the saturation of active sites on the ACS AC. The maximum adsorption capacity of 123.00 mg/g for 1571.89 mg/L of the initial Pb(II) concentration. Hence, the initial Pb(II) concentration of 1571.89 mg/L was taken into account for the further studies.

Effect of pulsed microwave heating during chemical activation

Pulsed microwave heating has been applied as a promising method for preparing activated carbon. In all practice of the microwave radiation method, the starting material of activator and impregnated raw material was heated in the solid phases (char or powder), and the carbonation is taken place in a modified microwave oven with nitrogen gas injection to clean the air in the microwave [32]. In contrast to the previous method, the starting materials in the current study is in the form of NaOH solution-the APCs carbon, and it was taken place in a modified microwave oven without nitrogen gas injection with microwave heating pulsed for 15-min radiation time at 0, 60 and 120-min during 360-min activation time, as mentioned in the materials and method section.

Fig. 7 shows the effect of the PMH during chemical activation on Pb(II) adsorption capacity of the APCs AC. As clearly shown in Fig. 7, Pb(II) adsorption capacity on the APCs AC sharply steps up from 105.23 to 149.42 mg/g at 10-min contact time when applying the PMH. This rapid increase is acceptable because the PMH could reduce the activation time. This trend is supported by the fact that microwave heating can increase the chemical reactivity rate of activator [30]. In addition, microwave heating results in simultaneous internal and volumetric heating [31]. It can lead Na_2O, Na, Na_2CO_3, CO, and CO_2 as the reaction products of NaOH and C. These reaction products can diffuse into the internal structure of the APCs AC matrix to form wider and new pores and even micropores at the wall of the pore, as discussed previously in the SEM analysis regarding to Figs. 3 and 4. This phenomenon is the same as the activation of carbon using KOH [50].

The increase of 41.99% in the adsorption capacity at the 10-min contact, time doesn't change too much at 35-min contact time which is 41.22%. The equilibrium adsorption capacity for the one with the PMH also increases from 122.97 to 151.56 mg/g at the 130-min contact time, as can be obtained in Figs. 7. Overall, the equilibrium adsorption capacity of the APCs AC can be increased by 23.25% when the APCs AC was treated with the PMH during chemical activation.

Pb (II) adsorption isotherm in the APCs-Pb system

The Langmuir and Freundlich adsorption isotherm models were used to investigate the effect of the PMH during activation of the APCs carbon on Pb(II) adsorption isotherm. The maximum Pb(II) adsorption capacity of the APCsAC was worked out using the Langmuir model [51, 52] is linearized to Eq. (1) [42]:
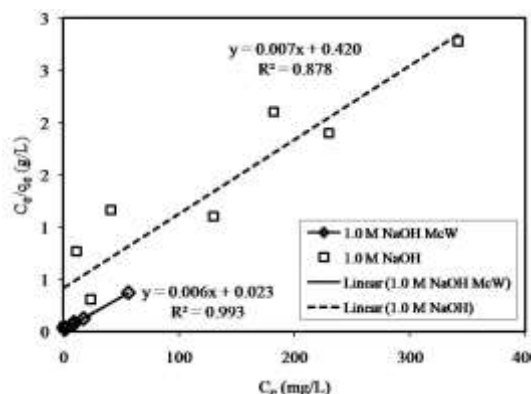
Fig. 8: Langmuir isotherm for Pb(II) adsorption in the APCs AC-PbS system consisting of 1 g of the APCs AC activated using 1 M NaOH with and without the PMH (McW), 100 mL aqueous solution of initial Pb(II) concentrations ranging from 78.61 to 1571.89 mg/L, magnetic stirring at 75 rpm, 27 ºC (± 2 ºC), pH 4.7 (± 0.3) and 1 atm.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \qquad (1)$$

Where C_e (mg/L) represents the equilibrium Pb(II) concentration in solution, q_e (mg/g) is the equilibrium adsorption capacity, q_m (mg/g) denotes the monolayer adsorption capacity, and K_L (L/mg) is the Langmuir equilibrium constant. The values of q_m and K_L can be obtained using the slope, $1/q_m$ and the intercept, $1/(q_m K_L)$ of a regression line made in Excel, C_e/q_e versus C_e shown in Fig. 8. Meanwhile, the Freundlich model [52] is linearized to Eq. (2) [53, 54]:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \qquad (2)$$

Where K_F (L/g) represents the Freundlich equilibrium constant presenting adsorption capacity and $1/n$ is the adsorption intensity. The values of $1/n$ and K_F can be obtained using the slope, $1/n$ and the intercept, $\log K_F$ of a regression line made in Excel, $\log q_e$ against $\log C_e$ shown in Fig. 9.

In Fig. 8, data for the square plots presenting the result based on the APCs AC without the PMH was taken from the previous discussion presented in Fig. 6. Meanwhile, for the APCs AC with the PMH, the equilibrium Pb(II) adsorption was 7.83, 15.67, 39.16, 78.47, 103.92, 130.15, 142.36 and 151.56 mg/g for the initial Pb(II) concentration in solution being 78.61,
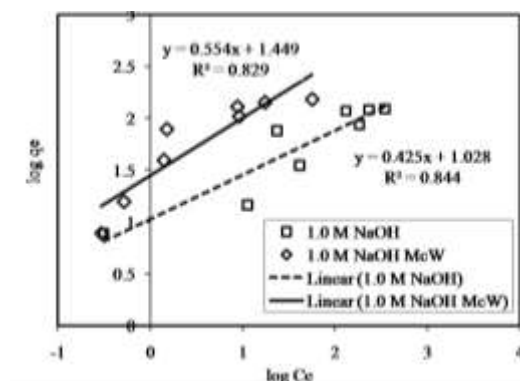

Fig. 9: Freundlich isotherm for Pb(II) adsorption in the APCs AC-PbS system consisting of 1 g of the APCs AC activated using 1 M NaOH with and without the PMH (McW), 100 mL aqueous solution of initial Pb(II) concentrations ranging from 78.61 to 1571.89 mg/L, magnetic stirring at 75 rpm, 27 ºC (± 2 ºC), pH 4.7 (± 0.3) and 1 atm.

157.20, 392.91, 786.11, 1048.10, 1309.89, 1441.03 and 1571.89 mg/L, respectively with the equilibrium Pb(II) concentration in solution being 0.29, 0.52, 1.39, 1.51, 9.19, 8.76, 17.52 and 56.29 mg/L , respectively, and the data is presented by the diamond plots in Fig. 8.

As can be calculated from the slope and intercept of the straight lines in Fig. 8, the Langmuir mono-layer adsorption capacity (q_m) and equilibrium constant (K_L) for the APCs AC activated using 1 M NaOH with the PMH is 166.667 mg/g and 0.261 L/mg, respectively with the correlation coefficients (R^2) being 0.993. It is 142.857 mg/g and 0.017 L/mg, respectively with the correlation coefficients (R^2) being 0.878 for the APCs AC activated using 1 M NaOH without the PMH. Hence, the PMH during NaOH activation can increase the Langmuir-based adsorption capacity of the APCs AC to adsorb Pb(II) by 16.67%, and the Langmuir equilibrium constant being less than 1 indicates favorable adsorption of Pb(II). Meanwhile, the Freundlich equilibrium constant (K_F) and adsorption intensity ($1/n$) for the one without the PMH is 10.666 L/g and 0.425, respectively ($R^2 = 0.844$), as can be seen in Fig. 9. It is 28.119 L/g and 0.554, respectively ($R^2 = 0.829$) for the one with the PMH. This also confirms that the PMH during NaOH activation can increase the adsorption capacity. Overall, Langmuir isotherm is better than Freundlich isotherm to present the Pb(II) adsorption in the APCs AC-PbS system. This result also shows that each active site of the ACS AC should adsorb only
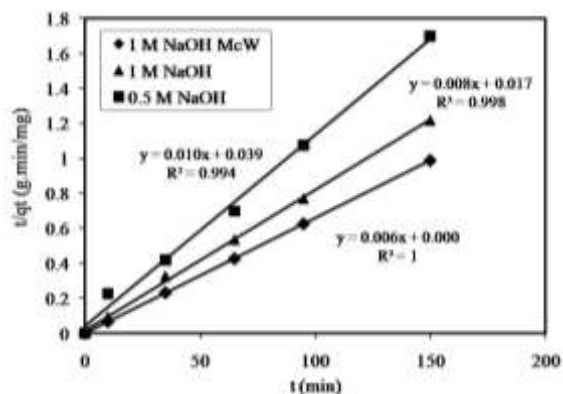
Fig. 10: Pseudo second-order kinetics model of Pb(II) adsorption in the APCs AC-Pb system with 1 g the APCs AC (separately activated using 0.5 and 1 M NaOH, 1 M NaOH with the PMH), 100 mL aqueous solution with the best initial Pb(II) concentration of 1571.89 mg/L, magnetic stirring at 75 rpm, 27 °C (± 2 °C), pH 4.7 (± 0.3) and 1 atm.
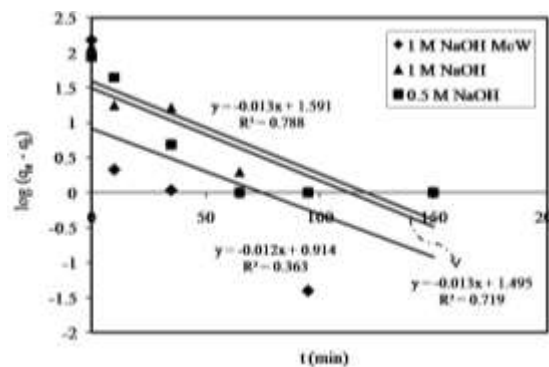
Fig. 11: Pseudo first-order kinetics model of Pb(II) adsorption in the APCs AC-Pb system with 1 g the APCs AC (separately activated using 0.5 and 1 M NaOH, 1 M NaOH with the PMH), 100 mL aqueous solution with the best initial Pb(II) concentration of 1571.89 mg/L, magnetic stirring at 75 rpm, 27 °C (± 2 °C), pH 4.7 (± 0.3) and 1 atm.

one molecule of Pb(II) ion to form a monolayer on the ACS AC surface, and it should be chemical adsorption taken place in the system [55].

Pb (II) adsorption kinetics in the APCs AC-Pb system

A kinetics studies of Pb (II) adsorption on the APCs AC was done to investigate the effect of independent variables of activator concentration and the PMH on the adsorption rate and equilibrium adsorption capacity of the APCs AC. The linear form of pseudo-first-order kinetics model (PFOKM) [56], and the linear form of Pseudo Second-Order Kinetics Model (PSOKM) [57] presented by Eq. (3) and (4), respectively were used to obtain the constants of adsorption rate and equilibrium adsorption capacity:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_L t}{2.303}\right) \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_H q_e^2} + \frac{t}{q_e} \qquad (4)$$

Were q_t (mg/g) is the adsorption capacity of APCs AC at the time of t (min), q_e (mg/g) is the equilibrium adsorption capacity, k_L (/min) represents the adsorption rate constant of pseudo first-order, and k_H (g/mg.min) denotes the PSOKM rate constant.

The k_H and k_L values of the APCs AC with different independent variable were obtained using the slope of linear trendlines in Figs. 10 and 11, respectively, and the q_e values were worked out using the intercepts of linear trendlines in Figs. 10 and 11, respectively.

As clearly highlighted in Figs. 10 and 11, the PSOKM R^2 values being 0.994, 0.998 and 1, are much higher than the PFOKM R^2 values being 0.788, 0.719 and 0.363 for the APCs AC with 0.5 NaOH, 1 M NaOH, and 1 M NaOH with the PMH, respectively. The R^2 values indicate that Pb(II) adsorption kinetics in the APCs AC-Pb system follows the pseudo-second-order kinetics. It is important to note that increasing the NaOH concentration from 0.5 to 1 M for the APCs chemical activation can increase the equilibrium adsorption capacity of the APCs AC by 25% from 100 to 125 mg/g. Meanwhile, applying the PMH during chemical activation can lift it up by 21.21% from 125 to 151.515 mg/g. These results are reasonable because increasing the activator concentration and applying the PMH produce more pores and the dominant functional group of hydroxyl as active site for Pb(II) adsorption onto the APCs AC, as addressed in the previous discussion of FT-IR analysis. This condition can also result in faster adsorption of Pb(II) adsorption onto the APCs AC. As expected, the PSOKM rate constant of Pb(II) adsorption increased by 19.61% from 0.051 to 0.061 g/mg.min as a result of increasing the NaOH concentration from 0.5 to 1 M, respectively. Interestingly to note that Pb(II) adsorption onto the APCs AC is faster when applying the PMH, and the k_H value being 0.298 g/mg.min.

Table 1: Adsorption of Pb(II) by activated carbons.

Adsorbent	T (°C)	pH	q_m (mg/g)	Ref.
The APCs AC PHM	27	4.7	166.67	PS
The APCs AC	27	4.7	142.86	PS
The AS AC	25	6.5	22.85	[58]
The CS AC	25	5.6	76.66	[59]
The DP AC	25	6	30.7	[60]
The EBPC AC	25	5.2	27.53	[23]
The PH AC	20	6	113.96	[61]
The PS AC	27	3	95.2	[62]

A comparison of adsorption capacity by adsorbent prepared from agricultural wastes is listed in Table 1.

The AC and PS stand for activated carbon and this study, respectively; and the AS, CS, DP, EBPC, PH, and PS stands for apricot stone, coconut shell, date pits, European black pine cones, peanut husks and palm shell, respectively. As listed in Table 1, the Pb(II) adsorption capacity by the APCs AC PMH (1 M NaOH with the PMH) is higher than the ones by the AS, CS, DP, EBPC, PS and the PH AC.

CONCLUSIONS

The cone of fast-growing Australian Pine is promoting agriculture wastes to be prepared as the adsorbent for adsorption of Pb(II) in aqueous solutions because Australian Pine Cones (APCs) consisted of 51.32 wt% of cellulose and 21.15 wt% of lignin on average. A novel method for preparing activated carbon from Australian Pine Cones (APCs) was applied optimize Pb(II) adsorption on the APCs activated carbon (APCs AC). It was prepared by physical and chemical activation and a Pulsed Microwave Heating (PMH) during the chemical activation. Experimental results showed that the APCs AC adsorption capacity increased exponentially with contact time and the initial Pb(II) concentration in solution.Pb(II) adsorption onto the APCs AC follows Langmuir isotherm model (LIM) and the pseudo-second-order kinetics model (PSOKM) with the correlation coefficients (R^2) being 0.993 and 1, respectively. The PMH increased Pb(II) adsorption capacity of the APCs AC with the maximum adsorption capacity being 166.667 mg/g (1 NaOH with the PMH) with Langmuir equilibrium constant being 0.261 L/mg. The PMH also increased the PSOKM equilibrium adsorption capacity from 125 to 151.515 mg/g with *the PSOKM kinetics constant* being 0.061 and 0.295 g/mg.min, respectively. These increases were supported FT-IR and SEM analyses that the can produce more pores and the functional group of hydroxyl in the APCs AC.

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