Activated Carbons from Palm Kernels Shells Prepared by Physical and Chemical Activation for Copper Removal from Aqueous Solution

T M Asnawi¹, H Husin*¹, A Adisalamun², W Rinaldi¹, M Zaki¹, F Hasfita³
¹Chemical Engineering Department, Faculty of Engineering, Syiah Kuala University, Darussalam-Banda Aceh, 23111, Indonesia
²Chemical Engineering Department, Faculty of Engineering, Malikus Saleh University, Lhokseumawe, 24300, Indonesia
*e-mail: husni_husin@che.unsyiah.ac.id

Abstract. Preparation and evaluation of activated carbon from the palm kernel shell (PKS), an abundant agricultural residue, by physical and chemical activation were carried out. The activation treatment of adsorbent with and without chemicals modification was evaluated. The physical activation using nitrogen gas and chemical treatment using 10 wt.% of sodium hydroxide and nitrogen gas as the activating agent. This study evaluated the activation temperature and nitrogen gas rate. The results showed that activated carbon treated with NaOH followed by heating under nitrogen gas had the highest iodine number of 1062.8 mg/g and methylene-blue number of 247.2 mg/g (heating at 750 °C, nitrogen gas flow rate of 100 mL/min). The equilibrium data obtained at various initial concentration reasonably fit well with the Langmuir adsorption isotherm. The adsorption of Cu(II) ions fit with the Langmuir isotherm pattern with adsorption capacity (Xm) of 8.9445 mg/g and kf value of 0.16802 L/mg for activated carbon without NaOH treatment. The adsorption capacity of activated carbon with NaOH and heating at 750 °C under nitrogen gas was obtained 12.0773 mg/g and kf value of 0.15076 L/mg. Those results suggested the prepared adsorbent could be considered as a promising candidate for Cu(II) ions for wastewater treatment.

1. Introduction
Recent development of industrial revolution generation 4.0 is appealing to focal concerns on environmental impacts. Waste derived from industries, hospitals, and mining can be chemicals such as pesticides, herbicides, chlorine, heavy metals and other organic wastes [1]. Some of it have the following hazardous and toxic heavy metals such as: Cu, Cr, Hg, Cd, etc. [2]. Metals can affect the ecosystem damaged or dead, illness, reduce speed, decrease the metabolism ability of biota, and cause various diseases of living organisms [3]. Heavy metals elements that enter the environment have an inherent nature and are readily absorbed by biota so that immersed into humans body and food chain [4]. Copper as heavy metal, Cu(II) is containing in water body in the form of ions and compounds. Cu(II) include essential heavy metals, even though it is toxic but small amount are needed in the human body. The certain amount of metal is required for human health, but if it exceeds the threshold of its presence in water will be toxic to humans [5]. Liquid wastes from refineries, tannery plants, electroplating and batteries, metal finishing and manufacturing are the main copper source that pollutes the ecosystems. Cu(II) naturally enters water through erosion, rock erosion, or in the
atmosphere brought down by rainwater. Heavy metal ions could not be decomposed but can be accumulated in living organisms [6]. Many technologies have been used to reduce heavy metal ions in industrial wastewater, such as: filtration, sedimentation, flocculation, adsorption, and others. These methods are less effective considering the nature of water in a dissolved state, not as suspension or sediment, and adsorption could be the more cost-effective [7]. The most widely used and effective adsorbent applied for heavy metals removal is activated carbon. This is due to the heavy metals are in a dissolved state in the water body so that it is not easily removed by other methods. The commercial activated carbon is the most widely used adsorbent recently in adsorption process but its price is still comparable expensive. The efforts to explore the potential for a comparable low-cost adsorbent from the low-cost raw material are of great concern among researchers. One of the agricultural residues that attract much attention in this research is Palm Kernel Shells (PKS). PKS are available in abundance as by-product generated from Palm Oil Mills with approximately 15 t/tonns per year in Indonesia [8]. This biomass by-product is classified as a potential low-cost adsorbents and are also environmentally friendly materials [9]. PKS is the shell fractions left after the nut has removed after crushing in the Palm Oil mill. Kernel shells are a fibrous material and could be handled in bulk directly from the product line to the end user. This study proposed the preparation of activated carbon from PKS. The adsorption of Cu(II) ions in aqueous solutions by Palm Kernel Shells activated carbon (PKS AC) was investigated over independent variables i.e. activating by chemical sodium hydroxide (NaOH) concentration, temperature of physical activation, initial adsorbate concentration, initial pH of adsorbate solution and adsorption temperature on the preparation method of PKS AC on its adsorption capacity in term of iodine and methylene blue number and adsorption capacity.

2. Materials and Methods

2.1 Materials
The PKS waste was collected from an Oil Palm Mill in Meulaboh, in the district of West Aceh, Aceh Province, Indonesia. The production of PKS as by-product of Palm Oil Mill approximately 6.6 ton/y. The 2.0 kg PKS was rinsed using tap water, and then it was dried in an oven (Memmert: NN-ST342M, Germany) at 110 °C for 24 h. The Cu(II) ions aqueous solution was made by dissolving 4 g (0.001) of CuSO4.5H2O (99% pure, from Aldrich) in 2000 mL of distilled water in the Erlenmeyer flask. The sample of 2 mL was taken, it was diluted with 10 mL distilled water in the vial for Atomic Absorption Spectrophotometer (AAS) analysis. The concentration of Cu(II) ions in the stock solution were calculated based on the dilution factor of 6. The predetermined Cu(II) ions concentration for all the adsorption experiments was prepared using the stock solution and general dilution formula. The equipment are a vertical reactor, tube furnace, shaker, spectrophotometer, vacuum filter, oven, scales, sieve, grinder, Erlenmeyer, burl 50 ml, 1 L flask, dropper, and pH meter. While the materials used are PKS, distilled water, methylene blue, NaOH 0.1 N, HCl 0.1 N, sodium thiosulfate, phenolphthalein indicator, starch, iodine solution, copper nitrate Cu (NO3)2.3H2O, HNO3, ethanol, and nitrogen gas.

2.2 Synthesis of activated carbon from palm kernel shells
The research consisted of three stages; PKS pyrolysis, physical activation, and chemical activation. The dried PKS was milled to the powder using a ball mill and then it was sieved to get the size in the range of 80-100 mesh. A tube furnace (TF-80/120/160, HumanLab Inc. 300-1500 °C, Korea) was used for pyrolysis of the dried PKS powder. The tube furnace (TF) heating rate was at 45 °C/min, and it took 12.75 min to get the TF final temperature of 600 °C for pyrolysis with nitrogen gas pumped at 5 mL/min with the initial TF temperature of 30 °C. The physical activation took place at 600 °C (1 °C) for 1 h. After the TF was turned off, the PKS carbon was left in the TF overnight to gradually decrease the PKS carbon temperature. Chemical activation of the PKS carbon was conducted for 6 h in 250-mL beaker glass consisting of 200 mL NaOH solution at 0.1 M (prepared using NaOH, Merk). It was stirred at 75-rpm using a hot plate stirrer (IKA, type C-MAG HS 7) at 30 °C. The PKS activated carbon (PKS AC) was washed using distilled water and filtered out using vacuum filter for many
times until the waste water reaching neutral pH of 7. The chemical activation was separately repeated to prepare the PKS AC with 0.3 M NaOH and the PKS AC with 0.5 M NaOH. The two types of PKS AC were separately dried in porcelain cups using an oven drier (Memmert, type NN-ST342M, Western Germany) at 110 °C for 2 h to remove the remaining water. The PKS AC were stored in different sealed bottles in a desiccator for adsorption experiments within 2 weeks. Cu(II) solution samples of 2 mL at the contact time of 0, 10, 20, 40, 60, 90 and 120 min (in time series) were analyzed using the AAS.

2.3 Experiments of Cu (II) adsorption
Adsorption experiments of Cu(II) ions as shown in Figure 1 were conducted in batch mode. The system of the PKS AC-solution consisted of 1.0 g of the PKS AC and 100 mL of Cu(II) ions solution (Cu (NO3)2.3H2O) in 200-mL beaker glass, and it was stirred at 75-rpm and 1 atm. The Cu(II) ions adsorption capacity of the PKS AC over independent variables was investigated by varying Cu(II) initial adsorbate concentrations (5, 10, 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mg/L, based on the AAS reading), the contact time (0–80 min), NaOH concentration for chemical activation (0.1–0.5 M), initial pH of Cu(II) ions solution (3–6) and adsorption temperature (30–60 °C).

![Figure 1. Experimental set up of batch mode adsorption](image)

The optimum condition with the highest Cu(II) ions adsorption capacity of the PKS AC was obtained. Cu(II) solution samples of 2-mL at the contact time 0, 10, 20, 40, 60, 90 and 120 min (in time series) were analyzed using the AAS based on the procedure in the previous study. The Cu(II) ions adsorption isotherm studies were using the experimental data.

3. Result and Discussion

3.1. Iodine and methylene blue number

Iodine number is the amount of iodine adsorbed by 1.0 g of PKS activated carbon. The iodine number represents a pore volume measure of size ranging from 10 to 28 Å [10]. This number gives an indication of the magnitude of the adsorption capacity of the activated carbon micropore. Activated carbon that has a large percentage of pore size in the range of 10 s/d 28 Å is particularly suitable for absorbing substances that have small molecular weights from its solution. The iodine number of physically activated carbon is greater when compared with the chemically activated one method the physically activated under the same activation conditions [11]. Experimental results showed that the iodine number of physically activated carbon ranging from 875.7 mg/g to 1019 mg/g, while for the chemically activated one ranging from 1098 mg/g to 1098 mg/g, as shown in Figure 2.a.
Iodine number is the amount of iodine adsorbed by 1.0 g of PKS activated carbon. The iodine number represents a pore volume measure of size ranging from 10 to 28 Å [10]. This number gives an indication of the magnitude of the adsorption capacity of the activated carbon micropore. Activated carbon that has a large percentage of pore size in the range of 10 s/d 28 Å is particularly suitable for absorbing substances that have small molecular weights from its solution. The iodine number of physically activated carbon is greater when compared with the chemically activated one method the physically activated under the same activation conditions [11]. Experimental results showed that the iodine number of physically activated carbon ranging from 875.7 mg/g to 1019 mg/g, while for the chemically activated one ranging from 1098 mg/g to 1098 mg/g, as shown in Figure 2.a. Iodine number was increased with the increase of temperature to 750 °C for physical activation treatment. As the activation temperature increasing to 800 °C, the iodine number slowly decreased and tended to stationary. In the chemical activation the iodine number appears to increase with the increasing temperature until the activation temperature reached 650 °C, at the same N₂ gas flow rate with the physical activation. As the activation temperature raised higher, the iodine number decreases after reaching the maximum value. This phenomenon is likely due to the absolute volume of macropores decreased with the increasing of burn-off. It was revealed that the weight loss was not lead to the formation of new micropores. The decrease in absolute micropore volume at higher burn-off may affect the burning of walls between adjacent pores. This process causes the micropores changing into larger pores. The maximum iodine number obtained from the study was 1019 mg/g for physical activation adsorbent pretreated at 750 °C under the nitrogen gas flow rate of 150 mL/min, meanwhile for chemical activation one was 1062.8 mg/g under nitrogen gas flow rate 100 mL/min. This result was in line with the evidence that the chemical activation requires lower temperature for activation as compared to the physical activation [12].

The methylene blue number indicated the molecular adsorption capacity of the activated carbon that has similar molecular sizes to the methylene blue and the mesoporous presence in the carbon active [13]. Both physical and chemical activation methods show the same tendency to increase the methylene blue number. The methylene blue number increased as the activation temperature increasing. Methylene blue number obtained for physical activation methods ranging from 146 mg/g to 208.5 mg/g and for chemical activation methods range from 195.0 mg/g to 247.2 mg/g. The increasing of methylene blue number is due to the burn-off process which continues to produce new mesopores resulting from the release of volatile components contained in carbon. The formation of new mesopores can also be produced by the breakdown of micropores [14]. The higher methylene
blue number in the chemical activation method is due to the more micropores in activated carbon being split into mesopores and macropores than that of physical activation. The iodine and methylene blue numbers obtained from this experiment obtained higher than the required standards for activated carbon.

3.2. The Cu(II) Ions Adsorption Equilibrium Study

The Cu(II) ions equilibrium study was carried out on activated carbon which gave maximum absorption capacity. The physically activated carbon pretreated at temperature 750 °C under the nitrogen gas flow rate of 100 mL/min, and chemically activated one the temperature was 650 °C under the nitrogen gas flow rate 100 mL/min.

![Figure 3. Langmuir's Isotherm and linearized curve of Cu(II) ions adsorption on physically activated PKS AC at 750 °C under 100 mL/ min of nitrogen gas](image)

The Cu(II) ions adsorption isotherm in the activated carbon is obtained by plotting a curve as the relationship between the equilibrium concentration in the liquid phase (Ce) with the equilibrium concentration in the solid phase (Qe). The plot of the Ce value against Qe shows the adsorption characteristics of Cu(II) ions by activated carbon fitting very well to the Langmuir isotherm, as shown in Figure 3 and 4.

![Figure 4. Langmuir's Isotherm and linearized curve of Cu(II) ions adsorption on physical + chemical activated with NaOH PKS AC at 650 °C under 100 mL/ min of nitrogen gas](image)
The adsorption isotherms for Cu(II) onto PKS AC and their Langmuir and Freundlich adsorption isotherm plots are shown in Figs. 2 and 3 it can be seen that the absorption of Cu(II) ions follows Langmuir’s isotherm with maximum adsorption capacity (X_m) and Langmuir (K) constant value and obtained by plotting Ce/Qe to Ce as follows:

a) Physical activation

\[ Y = 0.1118X + 0.6654 \]  

Where; \( X_m = 8.9445 \text{ mg/g} \) dan \( K_f = 0.16802 \text{ L/mg} \)

b) Chemical activation

\[ Y = 0.00828X + 0.5492 \]  

Where; \( X_m = 12.0773 \text{ mg/g} \) and \( K_f = 0.15076 \text{ L/mg} \)

The following comparison shows the graph of Freundlich Isotherm on the absorption of Cu(II) ions using chemically activated with NaOH PKS AC at 650 °C under 100 mL/min of nitrogen gas. From Figure 4 and 5, it can be seen that the corresponding values of the constants appearing in the Langmuir and the Freundlich equations. The correlation coefficients (R^2) obtained from the Langmuir and Freundlich model are 0.998 and 0.8647 for Cu(II) onto PKS AC, respectively. These results show that the Langmuir model gives a better fit of the experimental data than that of the Freundlich model for the adsorbent. It would be indicated that the surface of the physical activated PKS AC is energetically homogeneous, the adsorbed species are independent of each other (no associative adsorption) and they form a monolayer. The Langmuir monolayer adsorption capacity value toward Cu(II) adsorption onto PKS AC of chemical and physical activated obtained by the linear method of analysis was \( X_m = 12.0773 \text{ mg/g}; K_f = 0.1451 \text{ L/mg} \) and \( X_m = 8.9445 \text{ mg/g} \) and \( K_f = 0.16802 \text{ L/mg} \), respectively. The higher adsorption capacity of chemical activated PKS AC compared to the physical one can be explained by the enhancement in the specific surface area and metallic affinity due to the small size and chemical structure of surface enriched with hydroxyl functional groups during chemical activation with NaOH on the surface of the adsorbent. This functional groups expected to develop metallic affinity enhancement. It can be concluded that chemical activation with NaOH plays an important role in the enhancement of Cu(II) removal efficiency.

Figure 5. Freundlich Isotherm and linearized curve of Cu(II) ions adsorption on physically activated PKS AC at 750 °C under 100 mL/min nitrogen gas
4. Conclusion

The adsorption of Cu(II) ions onto activated carbon prepared from palm kernel shell (PKS AC) was investigated in batch mode over independent variables of activating chemicals (NaOH) concentration, the temperature of physical activation, initial adsorbate concentration, initial pH of adsorbate solution and adsorption temperature. Chemical activation treatment of PKS AC provided a better adsorption characteristics on Cu(II) ions in solution compared to physical activation. The PKS AC iodine numbers activated by the physical and chemical activation reached 1019.1 mg/g and 1062.8 mg/g, by activation conditions temperature 750 oC and 650 °C under nitrogen gas flow rate 100 mL/min, respectively. Methylene blue number of the PKS AC was obtained for physical and chemical activation was reached to 208.5 mg/g and 247.2 mg/g, respectively. Methylene blue number increased with the increasing activation temperature and nitrogen gas flow rate. The equilibrium model for the absorption of Cu(II) ions onto activated carbon prepared from palm kernel shell (PKS AC) obtained fitting with the Langmuir isotherm model. The Cu(II) adsorption capacity by physical activated and chemically activated of PKS AC obtained was Xm = 8.9445 mg/g with K = 0.1713 L/mg, and Xm = 12.0773 mg/g with K = 0.1451 L/mg, respectively. The high uptake capability of PKS AC adsorbent makes it potentially attractive for the removal of Cu(II) ions in wastewater treatment, especially for the treatment of toxic effluent from metal finishing process.

Acknowledgements

The authors would like to appreciate the Syiah Kuala University, Indonesia, for providing financial support under Universitas Syiah Kuala, Laboratories Research Grant year 2018.

References

[1] Nethaji S., Sivasamy A. and Mandal A.B., 2013, Preparation and characterization of corn cob activated carbon coated with nano-sized magnetite particles for the removal of Cr(VI), Biore. Tech., 134, 94-100.
[2] Zhang J., Fu H., Lv X., Jie T. and Xu X., 2011, Removal of Cu(II) from aqueous solution using the rice husk carbons prepared by the physical activation process, Biomass and Bioenergy, 35, 464-72.
[3] Sun Y., Yue Q., Gao B., Gao Y., Qian L. and Wang Y., 2013, Adsorption of hexavalent chromium on Arundo donax Linn activated carbon amine-crosslinked copolymer, Chem. Eng. J., 217, 240-47.
[4] Song J., Zou W., Bian Y., Su F. and Han R., 2011, Adsorption characteristics of methylene blue by peanut husk in batch and column modes, Desalination, 265, 119-29.
[5] Samarghandi M.R., Al-Musawi T.J., Mohseni-Bandpi A. and Zarrabi M., 2015, Adsorption of cephalixin from aqueous solution using natural zeolite and zeolite coated with manganese oxide nanoparticles, J. of Molec. Liquids, 211, 431-41.
[6] Olaniran A.O., Balgobind A. and Pillay B., 2017, Bioavailability of heavy metals in soil: impact on microbial biodegradation of organic compounds and possible improvement strategies, Int. J. of Molec. Sci., 2013, 14, 10197-28.
[7] Ohman N.H., Alias N.H., Shahruddin M.Z., Abu Bakar N.F., Nik Him N.R. and Lau W.J., 2018, Adsorption kinetics of methylene blue dyes onto magnetic graphene oxide, J. of Environ. Chem. Eng., 6, 2803-11.
[8] Hambali E and Rivai M., 2017, The Potential of Palm Oil Waste Biomass in Indonesia in 2020 and 2030, IOP Conf. Series: Earth and Environ. Sci., 65, 012050.
[9] El-Aziz A., Kamal M.E., Ali K.H., Abdel-Aziz K.A., and Kamel M.S., 2018, Biodegradable grafting cellulose/clay composites for metal ions removal, Int. J. of Biol. Macromol., Volume 118(Pt B), pp.2256-2264.
[10] Jow J.J., Guo Z.-S., Chen H.-R., Wu M.-S. and Ling T.-R., 2010, Determination of the iodine adsorption number of carbon black by using a direct cathodic reduction method, Electrochem.
Comm., 12, 1605-08.

[11] Kadirvelu K., Thamaraiselvi K. and Namasivayam C., 2001, Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Biore. Tech. 76, 63-65

[12] Gebru K.A. and Das C., 2017, Removal of Pb (II) and Cu (II) ions from wastewater using composite electrospun cellulose acetate/titanium oxide (TiO$_2$) adsorbent, J. of Wat. Proc., 16, 1-13.

[13] Narvekar A.A., Fernandes J.B. and Tilve S.G., 2018, Adsorption behavior of methylene blue on glycerol based carbon materials, J.of Environ. Chem. Eng., 6, 1714-25.

[14] Prauchner, M. J. and Rodriguez-Reinoso, F., 2012, Chemical versus physical activation of coconut shell: A comparative study, Microp. and Mesop. Mat., 152 163–71.