UTILIZATION OF ACTIVATED CARBON FROM PALM KERNEL SHELLS AS THE BIOADSORBENT OF LEAD WASTE

*Muhammad Faisal1, Asri Gani1 and Zahrul Fuadi2

1Department of Chemical Engineering, Universitas Syiah Kuala, Banda Aceh, Indonesia
2Department of Mechanical Engineering, Universitas Syiah Kuala, Banda Aceh, Indonesia

*Corresponding Author, Received: 01 May. 2020, Revised: 28 Dec. 2020, Accepted: 12 Jan. 2021

ABSTRACT: This research aimed to evaluate the use of palm kernel shells for activated carbon to adsorb lead (Pb) ions. The pyrolysis was performed on oil palm kernel shells at a temperature of 380 oC to obtain charcoal which was then chemically activated with liquid smoke. Before and after activation, the sample of charcoal was assessed with scanning electron microscopy (SEM). The activated carbon was then used to adsorb Pb (II) ions in concentrations of 30, 60, 90, 120, and 150 mg/L. The adsorption process was performed in a batch reactor with contact times of 30, 60, 90, 120, and 180 minutes at an agitation speed of 150 rpm. The initial concentration of Pb (II) ions and concentration after adsorption were determined with an atomic absorption spectrophotometer (AAS). Research has shown that initial concentrations and contact times affect the efficiency of Pb (II) removal. The highest adsorption efficiency (> 90%) was obtained at a contact time of 150 minutes and an initial concentration of 60 mg/L. Pb adsorption onto the activated carbon of palm kernel shells demonstrated best fit with both Langmuir and Freundlich isotherm models. Kinetics studies showed that the pseudo first-order reaction was more suitable (R² = 0.9359).

Keywords: Palm kernel shell charcoal, Pb (II), Activated carbon, Pyrolysis, Liquid smoke

1. INTRODUCTION

The continual expansion of industrialization has accelerated developments in the chemical industry, causing increased industrial waste-more and more is being discharged into the environment. Nature’s capacity to tolerate the burden of waste is very limited, and it is believed that its normal self-purification systems have been exceeded. Among the wastes that pollute the environment and cause disturbing water pollution today are heavy metals, such as lead ions (Pb), commonly found in the industrial waste of manufacturers of batteries, paper, metallurgy, explosives, paints, and other colouring materials [1-3]. Pb (II) is a soft, blackish-brown metal that is easily extracted from mining. It comes from the earth's crust in the form of pure, organic, and inorganic material. Industrial processes play an important role in increasing the levels of this heavy metal.

Lead belongs to the group of toxic metals that are harmful to living things accumulatively and not easily degraded [4,5]. Pb compounds can enter the human body through the respiratory and digestive tracts or through direct contact with the skin. According to the US Environmental Protection Agency (EPA), lead tolerance levels in drinking water and wastewater are 0.015 and 0.1 mg/L, respectively [6]. Levels of Pb higher than these limits are known to poison the human body both acutely and chronically. In addition, continuous Pb poisoning in childhood can cause neurotoxic disorders, cancer, and damage to the kidneys, pancreas, brain, and liver [7-9]. To avoid its harmful effects on living things, heavy metal concentration has to be reduced to a safe level by properly treating the waste before discharge into water systems.

There are several ways to remove heavy metals like Pb from wastewater, including precipitation and ion exchange, electrodialysis, evaporation, and absorption using activated carbon [10]. The most frequent problem in heavy metal waste treatment is its high cost, thus, effective and low-cost techniques are needed. One such technique is adsorption. The adsorption process occurs on the surface of the adsorbent material’s pores, and the metal in the liquid undergoes a process of transferring metal mass from the liquid to the adsorbent’s surface [11]. This is among the most frequently used methods for removing toxic metals from wastewater [12]. Adsorption is a physical-chemical process in which the adsorbates—in this case, the pollutants—accumulate on the surface of solids used as adsorbents. The process is suitable for wastewater with low metal concentrations, especially in industries with limited financial resources [13,14]. Many types of adsorbent have been developed to remove Pb from wastewater, including zeolites [14,15], Ethylene diamine tetra acetic acid (EDTA) magnetic graphene oxide [16], papaya seed [17], chlorapatite nanoparticles [18], montmorillonite [19], Areca catechu shell [20], palm tree leaves [21], chitosan [22], modified
bentonite and magnetic cellulose [23], charcoal from celery [24], rapeseed biomass [25], the bark of Cordia macleodii trees [26], and natural zeolite [27]. The challenge in adsorption technology is to select economical and efficient alternative adsorbents to minimize operating costs, especially in developing countries [28]. An alternate adsorbent that has been proposed is charcoal from oil palm shell pyrolysis. Before being used to adsorb heavy metals, the charcoal is activated chemically and physically. Several studies have shown that the activated carbon from the pyrolysis process is capable of removing heavy metals with fairly high removal efficiency [29]. This research aims to study the ability of activated carbon from pyrolysis of oil palm shells to remove Pb (II).

2. MATERIALS AND METHODS

2.1 Preparation of Activated Carbon from Oil Palm Shells

A pyrolysis reactor (stainless steel, homemade) with a height of 60 cm and an inner diameter of 40 cm was used to pyrolyze palm shells at 380°C. The temperature in the reactor was kept constant throughout the pyrolysis. The procedure for making charcoal and liquid smoke followed that in previous studies [30,31]. Five kg of palm shells were loaded into the reactor, and the reactor was tightly sealed. A steam channel in the lid connected to the condenser unit condensed the vapor into liquid smoke. After the pyrolysis process was complete, the reactor was opened and the resulting charcoal was ground in a ball mill for 24 hours to reach nano size particles. The charcoal was then activated using the liquid smoke, previously purified by distillation, by immersing it in the liquid smoke solution for 24 hours. Then the activated carbon was filtered and washed with distilled water to a neutral pH before being dried in an oven dryer at a temperature of 105°C until the weight became constant. The surface morphology of the activated carbon was analysed using scanning electron microscopy (SEM) (JEOL-JSM 6510 LA, Shimadzu, Japan).

2.2 Adsorption Test

Carbon nanoparticles activated by liquid smoke were then used to adsorb Pb metal prepared from a lead sulphate (PbSO₄) solution. The initial concentration of Pb (II) varied from 30, 60, 90, 120, to 150 mg/L. One hundred ml of PbSO₄ was put into an Erlenmeyer and one gram of adsorbent was added and stirred at 150 rpm speed. The contact times between Pb (II) and adsorbent solutions were 30, 60, 90, 120, 150, and 180 min at room temperature. After the adsorption process was complete, the filtrate was separated by centrifuging. Pb (II) analysis was carried out using AAS (AA-7000, Shimadzu, Japan).

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characteristics

Figs. 1a and 1b show the results of SEM analysis of the palm shell carbon before and after activation. Surface morphology showed a better surface after activation by liquid smoke than before. The figures also show that the size of the activated carbon particles reached nanometres, that was, below 500 nm. Particles of the liquid smoke-activated carbon have a smaller size than that of NaOH-activated carbon particles under the same conditions and activation methods [29], demonstrating that activation in an acidic atmosphere reduced the size of the active carbon particles. Liquid smoke as an activator contains various chemical compounds, such as acetic acid, phenolic compounds, and other compounds with varying concentrations [32,33], allowing the adsorbent’s surface to adsorb metal ions. In Fig. 1, it can also be seen that the shape of the activated carbon surface was uneven but that nanometre sizes of the activated carbon dominated.

![Fig. 1 SEM analysis of the palm shell carbon before and after activation](image-url)
3.2 Effect of Contact Time and Initial Concentration on the Adsorption Efficiency of Pb (II)

Fig. 2 shows the effect of contact time on the adsorption efficiency of Pb (II) at various initial concentrations. At 150 rpm agitation, an initial concentration of 30 mg/L and a contact time of 30 min, as shown in Fig. 2, the adsorption efficiency was 75%. At the beginning of the adsorption of Pb (II) metal ions, the adsorbent surface had not absorbed much, so the adsorption process was less effective. This due to at a contact time of 30 min, the adsorbent and adsorbate had not fully bonded, resulting in fewer adsorbed ions. The adsorption efficiency increased to 92% at min 150.

Fig. 2 The effect of contact time on the adsorption efficiency of Pb (II) at various initial concentrations

Fig. 3 shows the effect of initial concentration on the adsorption efficiency of Pb (II) at various contact times. At an initial concentration of 60 mg/L, the adsorption efficiency for contact times of 30, 60, 90, 120, and 180 mins were 70%, 72%, 73%, 73%, 77%, 93%, and 34%, respectively. The same trend was observed for all contact times (i.e., 30, 90, 120, and 150 min). The efficiency of adsorption decreased with increasing initial concentration. Low adsorption efficiency at 180 min was due to the saturation of the adsorbent's surface impeding further adsorption. At this point, the diffusion and adhesion of adsorbed solute molecules occurred more, thereby increasing the adsorption efficiency. The same trend has been reported in the literature for lead adsorption using zeolite-NaX [34]. The results of this study indicate that for all contact times, the greater the initial concentration, the smaller the absorption efficiency produced. Thus, in this study, the adsorption of Pb (II) was preferred at low initial concentrations.

3.3 Isotherm Studies

Changes in the adsorbate concentration by the adsorption process following the adsorption mechanism can be studied by determining the adsorption isotherm. Isotherm studies were carried out to determine the adsorption equilibrium, capacity, and mechanism. The Freundlich and Langmuir isotherm models are most commonly used to analyse equilibrium data. The Freundlich isotherm model is applied to multilayer adsorption with a heterogeneous distribution. The model provides a relationship between solid and liquid concentrations and is very helpful in connecting isotherm data collected in various concentrations.

Fig. 4 Isoterm Langmuir

\[ y = 0.1097x + 1.1323 \]
\[ R^2 = 0.9359 \]

Fig. 5 Isoterm Freundlich

\[ y = 0.3224x + 0.3222 \]
\[ R^2 = 0.9701 \]
The Langmuir isotherm model assumes monolayer adsorption with a homogenous distribution of energetic adsorption sites. The Langmuir and Freundlich adsorption isotherm models on Pb metal are shown in Figs. 4 and 5, respectively. Figs. 4 and 5 show that the $R^2$ values for Langmuir and Freundlich were 0.93 and 0.97, respectively. This indicates that the adsorption of Pb (II) metal using liquid smoke-activated charcoal from palm shells tended to follow the pattern of the two isotherms, namely the adsorption of monolayers on the adsorbent’s outer surface and multilayer adsorption on heterogeneous surface sites. Table 1 shows the parameters and constants of the Langmuir and Freundlich isotherms. As can be seen from the Table 1, the Freundlich constant ($K_F$) representing adsorption capacity was 2.099 mg/g with adsorption intensity ($n$) of 3.101. The $K_F$ obtained from this research was higher than the results of Lou et al. [23]. For the Langmuir isotherm, the adsorption ability ($q_m$) of the activated carbon to adsorb Pb ions was 9.11 g/mg. This value was lower than that of previous studies using zeolite-NaX adsorbents [34]. The strength of the interaction between Pb (II) ions and the activated carbon is indicated by the value of $K_L$, which was 0.096. Previous studies reported that Pb (II) adsorption using chitosan-g-maleic anhydride-g-methacrylic acid copolymer tended to follow the Freundlich isotherm [22], whereas the adsorption of Pb (II) using adsorbents from rapeseed biomass tended to follow the Langmuir isotherm [25].

Table 1. Constant values of both Langmuir and Freundlich isotherm models of Pb (II) adsorption

|           | Langmuir | Freundlich |
|-----------|----------|------------|
| $R^2$     | 0.935    | 0.970      |
| $q_m$ (mg/g) | 9.11    | 3.101      |
| $K_L$ (L/mg) | 0.096  | 2.099      |
| $n$       |          |            |
| $K_F$ (mg/g) |        |            |

In the Langmuir isotherm, to assess whether the adsorption process is favourable, irreversible, or unfavourable, the dimensionless separation factor ($R_L$) value can be used, which is calculated with the following equation:

$$R_L = \frac{1}{1 + K_L C_i}$$

where $K_L = $ Langmuir constant and $C_i = $ initial concentration.

A value of $R_L$ between 0 and 1 indicates that the adsorption process is favourable. Adsorption is linear if the value of $R_L = 1$, irreversible if $R_L = 0$, and unfavourable if $R_L > 1$ [35]. Fig. 6 shows the relationship between the initial concentration and separation factor values for Pb (II) adsorption.

As shown in Fig. 6, the value of $R_L$ at an initial concentration of 30 mg/L was 0.25, and it dropped to 0.05 at an initial concentration of 150 mg/L. The $R_L$ values were between 0 and 1 for all initial concentrations, demonstrating that the adsorption process was favourable.

4. CONCLUSIONS

This research investigated the ability of adsorbents from palm kernel shell charcoal activated by liquid smoke to adsorb Pb (II) metal ions. The SEM test results showed that the activated adsorbents had better pore size for adsorption. At contact times of 30–150 min and initial concentrations of 30–150 mg/L, the efficiency of Pb (II) adsorption ranged from 40%–93%. At a contact time of 180 min, efficiency dropped dramatically as a result of the adsorbent's saturation. The best condition was achieved at 150 min contact time and an initial concentration of 30 mg/L. The results of the isotherm equilibrium analysis showed that the adsorption process was suitable for the Langmuir and Freundlich isotherm models.

5. ACKNOWLEDGMENTS

The work was financially supported by Universitas Syiah Kuala (Grant No. 289/UN11/SP/PNBP). We wish to thanks Sandi Putra Kelana and Dodi Eko Nanda for conducting experiments and data analysis.

6. REFERENCES

[1] Hanafiah M.A.A.M., Ngah W.S.W., and Ibrahim S.C., Kinetics and Thermodynamic Study of Pb(II) Adsorption from Aqueous Solution onto Rubber (Hevea brasi- liensis) Leaf Powder. Journal of Applied Sciences, Vol. 6, Issue 13, 2006, pp. 2762–2765.
[2] Paulino A.T., Guilherme M.R., Reis A.V., Tambourgi, E.B., Nozaki, J., and Muniz, E.C., Capacity of Adsorption of Pb\textsuperscript{2+} and Ni\textsuperscript{2+} from Aqueous Solutions by Chitosan Produced from Silkworm Chrysalides in Different Degrees of Deacetylation. Journal of Hazardous Materials, Vol. 147, 2007, pp. 139–147.

[3] Saifuddin N., and Raziah A.Z., Removal of Heavy Metals from Industrial Effluent using Sacccharomyces Cerevisiae (Baker’s Yeast) Immobilized in Chitosan/Lignosulphonate Matrix. Journal of Applied Sciences Research, Vol. 3, Issue 12, 2007, pp. 2091–2099.

[4] Ince O. K., Ince M., Yonten V., and Gok A., A Food Waste Utilization Study for Removing Lead(II) from Drinks. Food Chemistry, Vol. 229, 2017, pp. 637–643.

[5] Begum A., Krishna S.H., Khan I., Ramaiah M., Veena K., and Vinuta K., Nutrients and Heavy Metal Profile of Madivala Lake, Bangalore South, Karnataka. Rasayan Journal of Chemistry, Vol. 1, Issue 3, 2008, pp. 572-582.

[6] Guidelines for Drinking Water, US Environmental Protection Agency (US EPA), 2001.

[7] Zhou Y., Zhang L., and Cheng Z., Removal of Organic Pollutants from Aqueous Solution using Agricultural Wastes: A Review. Journal of Modern Science, Vol. 2, Issue. 1, 2016, pp. 255-263.

[8] Dai Y., Zhang K., Li J., Jiang Y., Chen Y., and Tanaka S., Adsorption of Copper and Zinc onto Carbon Material in an Aqueous Solution Oxidized by Ammonium Peroxydisulphate. Separation and Purification Technology, Vol. 2, 2017, pp. 255-263.

[9] Sahu M.K., Mandal S., Dash S.S., Badhai P., and Patel R.K., Removal of Pb (II) from Aqueous Solution by Acid Activated Red Mud. Journal of Environmental Chemical Engineering, Vol. 1, 2013, pp. 1315-1324.

[10] Zhu Q., Zehuan W. L., Ye A.H., and Feng X., Hydrothermal Synthesis of Silico-Manganese Nanohybrid for Cu(II) Adsorption from Aqueous Solution. Journal of Water Resource, Vol. 12, Issue 1, 2016, pp. 332-342.

[11] Qaiser S., Saleemi A. R., and Ahmad M. M., Heavy Metal Uptake by Agro Based Waste Materials. Journal of Biotechnology, Vol. 10, Issue 3, 2007, pp. 411-419.

[12] Mahitti U.F., Preparation and Use of Chemically Modified MCM-41 and Silica Gel as Selective Adsorbent for Hg (II) Ions. Journal of Hazardous Material, Vol. 154, 2008, pp. 578-587.

[13] Gupta S.S. and Bhattacharyya K.G., Immobilization of Pb (II), Cd (II) and Ni (II) Ions on Kaolinite and Montmorillonite Surfaces from Aqueous Medium. Journal of Environmental Management, Vol. 87, 2008, pp. 46-58.

[14] Salem A., and Sene R.A., Removal of Lead from Solution by Combination of Natural Zeolite-Kaolinite-Bentonite as a New Low Cost Adsorbent. Chemical Engineering Journal, Vol. 174, 2011, pp. 619-628.

[15] Apiratikul R., and Pavasant P., Sorption of Cu \textsuperscript{2+}, Cd\textsuperscript{2+}, and Pb\textsuperscript{2+} Using Modified Zeolite from Coal Fly Ash. Chemical Engineering Journal, Vol. 144, Issue 2, 2008, pp. 245-258.

[16] Cui L., Wang Y., Gao L., Hu L., Yan L., Wei Q., and Du B., EDTA Functionalized Magnetic Graphene Oxide for Removal of Pb ( II ), Hg ( II ) and Cu ( II ) in Water Treatment: Adsorption Mechanism and Separation Property. Chemical Engineering Journal, Vol. 281, 2015, pp. 1–10.

[17] Garba Z.N., Bello I., Galadima A., and Lawal A.Y., Optimization of Adsorption Conditions using Central Composite Design for the Removal of Copper (II) and Lead (II) by Defatted Papaya Seed. Karbala International Journal of Modern Science, Vol. 2, Issue.1, 2016, pp. 20-28.

[18] Keochaiyom B., Wan J., Zeng G., Huang D., Xue W., Hu L., Huang C., Zhang C., and Cheng M., Synthesis and Application of Magnetic Chlorapatite Nanoparticles for Zinc (II), Cadmium (II) and Lead (II) Removal from Water Solutions. Journal of Colloid and Interface Science, Vol. 505, 2017, pp. 824-835.

[19] Sani H.A., Ahmad M.B., Hussein M.Z., Ibrahim N.A., Musa A., and Saleh T.A., Nanocomposite of ZnO with Montmorillonite for Removal of Lead and Copper Ions from Aqueous Solutions. Process Safety and Environmental Protection, Vol. 109, 2017, pp. 97-105.

[20] Muslim A., Aprilia S., Suha T.A., and Fitri Z., Adsorption of Pb (II) Ions from Aqueous Solution Using Activated Carbon Prepared from Areca Catechu Shell: Kinetic, Isotherm and Thermodynamic Studies. Journal of the Korean Chemical Society, Vol. 61, Issue 3, 2017, pp. 89-96.

[21] Soliman A.M., Hanan M ., Thiemann T., Majedi Y., Labata F.T., and Nathir Alrawashdeh A.F., Removal of Pb ( II ) Ions from Aqueous Solutions by Sulphuric Acid-Treated Palm Tree Leaves. Journal of the Taiwan Institute of Chemical Engineers. Vol. 58, 2016, pp. 264-73.

[22] Lavanya R., Gomathi T., Vijayalakshmi K., Saranya M., Sudha P.N., and Anil S., Adsorptive Removal of Copper (II) and lead (II) using Chitosan-g-maleic Anhydride-g-Methacrylic Acid Copolymer. International
[23] Luo X., Lei X., Xie X., Yu B., Cai N., and Yu F., Adsorptive Removal of Lead from Water by the Effective and Reusable Magnetic Cellulose Nanocomposite Beads Entrapping Activated Bentonite. Carbohydrate Polymers, Vol. 151, 2016, pp. 640-648.

[24] Zhang T., Zhu X., Shi L., Li J., Li S., Lü J., and Li Y., Efficient Removal of Lead from Solution by Celery-Derived Biochars Rich in Alkaline Minerals. Bioresource Technology, Vol. 235, 2017, pp. 185-192.

[25] Morosanu I., Teodosiu C., Paduraru C., Ibanescu D., and Tofan L., Biosorption of Lead Ions from Aqueous Effluents by Rapeseed Biomass. New Biotechnology, Vol. 39, 2017, pp. 110-124.

[26] Wanjari A.K., and Chaudhari U.E., Removal of Cr (VI), Pb (II), Mn (II) And Bi (III) From Aqueous Solutions Using Granular Activated Charcoal Prepared From Cordia Macleodii Tree Bark. Rasayan Journal of Chemistry, Vol. 10, Issue 1, 2017, pp. 82-85.

[27] Utami A.R., Sugiarti S., and Sugita P., Synthesis of NaP1 and Faujasite Zeolite from Natural Zeolite of Ende-NTT as Lead (Pb(II) Adsorbent. Rasayan Journal of Chemistry, Vol. 12, Issue 2, 2019, pp. 650 - 658.

[28] Yusoff S. N., Kamari A., Putra W.P., Ishak C.F., Mohamed A., Hashim N., and Isa M.I., Removal of Cu (II), Pb (II) and Zn (II) Ions from Aqueous Solutions Using Selected Agricultural Wastes: Adsorption and Characterisation Studies. Journal of Environmental Protection, Vol. 5, 2014, pp. 289-300.

[29] Faisal M., Gani A., and Abubakar, Removal of Copper Ions from Aqueous Solution using Palm Shell Charcoal Activated by NaOH. International Journal of GEOMATE, Vol.15, Issue 48, 2018, pp.143-147.

[30] Faisal M., and Gani A., The Effectiveness of Liquid Smoke Produced from Palm Kernel Shells Pyrolysis as a Natural Preservative in Fish Ball. International Journal of GEOMATE, Vol. 15 Issue 47, 2018, pp. 145-150.

[31] Faisal M., Gani A., Husni, Baihaqi A., and Daimon H., Pyrolysis of Oil Palm Kernel Shell into Liquid Smoke and Its Application to Control Anthracnose Disease on Chili (Capsicum annum L.). Journal of Engineering and Applied Sciences, Vol. 11, Issue 12, 2016, pp. 2583-2587.

[32] Faisal M., Chamzurni T., and Daimon H., A study on the Effectiveness of Liquid Smoke Produced from Palm Kernel Shells in Inhibiting Black Pod Disease in Cacao Fruit In Vitro. International Journal of GEOMATE, Vol. 14 Issue 43, 2018, pp. 36-41.

[33] Faisal M., Gani A., Husni and Daimon H., A Preliminary Study of the Utilization of Liquid Smoke from Palm Kernel Shells for Organic Mouthwash. International Journal of GEOMATE Vol. 13, Issue 37, 2017, pp. 116-120.

[34] Pankaj K. Pandey S.K. Sharma S.S. , and Sambi, Removal of lead(II) from Wastewater on Zeolite-NaX. Journal of Environmental Chemical Engineering, Vol. 3, Issue 4, 2015, pp. 2604-2610.

[35] Snoussi Y., Abderrabba M. , and Sayari A., Removal of Cadmium from Aqueous Solutions by Adsorption onto Polyethyleneimine-Functionalized Mesocellular Silica Foam: Equilibrium Properties. Journal of the Taiwan Institute of Chemical Engineers, Vol. 66, 2016, pp.372-378.