

Impact of Sodium Hydroxide Concentration and Reaction Time on the Modification of Empty Fruit Bunch for Heavy Metal Adsorption

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The extraction of palm oil from its fresh fruit bunch by-produced at least 89.63 million ton of empty fruit bunch annually and it often ended up in landfill. Thus, it is important to address this issue by finding alternative use for empty fruit bunch such as utilization as adsorbent. The objectives of this work were to identify the most appropriate (i) sodium hydroxide concentration and (ii) reaction time for the modification of empty fruit bunch fiber into low-cost heavy metal adsorbent. The empty fruit bunch fiber was obtained from a local mill, thoroughly cleaned, oven dried, cut into required size, reacted with sodium hydroxide of various concentration and reaction time, rinsed, oven dried and experimented as adsorbent. Results revealed that the most appropriate sodium hydroxide concentration and reaction time for the modification of empty fruit bunch fiber was 0.1 M and 12 h. The adsorbent produced under this optimized modification setting was codenamed as EFBFo.1M 12h and it has the adsorption capacity of 5.14 and 14.31 mg/g for copper(II) and lead(II), respectively.

Keywords: Sodium hydroxide, concentration, reaction time, empty fruit bunch fiber, adsorption

I. INTRODUCTION

Oil palm is the most planted vegetable oil crop in the world that produced more than 64.02 million ton/year of palm oil into global market (The Statistic Portal, 2017). The United States Department of Agriculture (USDA) reported that as in year 2016, the global accumulative harvested area was 20.29 million ha across 28 countries worldwide (USDA, 2010). Based on the fresh fruit bunch (FFB) productivity of 20.08 ton/ha/year (Yusoff,

2006), the global FFB production of 407.45 million ton/year can be expected and this figure is on the rise. As the oil was extracted from the FFB, it by-produced empty fruit bunch (EFB) at the rate of 89.63 million ton/year.

Traditionally EFB was used as mulch in oil palm estate; however, this practice is no longer popular because it is labor intensive and the transportation of the EFB from mill to estate incurred high cost (Chiew and Shimada, 2013). Thus, EFB is left lying in vicinity of mill and often caught fire (Kamaludin *et al.*, 2012). A large majority of EFB ended up in landfill which

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sacrificed its potential commercial usefulness and value. Therefore, there is an important urgency to address this issue by finding alternative use for the EFB such as utilization as adsorbent.

Previous studies had shown that EFB is able to adsorb heavy metals at its natural state (Khosravihaftkhany *et al.*, 2013; Salamatinia *et al.*, 2007; Nassar *et al.*, 2003). Furthermore, EFB biochar was proven to have higher adsorption capacity of heavy metals (Samsuri *et al.*, 2014), but the production of biochar and activated carbon requires high production cost and high energy consumption. The application of sodium hydroxide (NaOH) on plant-based fiber is a common delignification technique in textile, paper and pulp industry (M'hamdi *et al.*, 2017). However, the NaOH treated fibers has not yet been studied for its adsorption of heavy metals, indicating data gap.

The objectives of this work were to identify the most appropriate (i) sodium hydroxide concentration and (ii) reaction time for the modification of empty fruit bunch fiber into low-cost adsorbent for the adsorption of copper(II) and lead(II) ions from aqueous solution.

II. MATERIALS AND METHODS

A. Preparation of Empty Fruit Bunch Fiber

The EFB, which was in long fiber form, was obtained from a local palm oil mill. It was laid on clean canvas and exposed to sun from 0800 to 1400 hrs for three consecutive days in order to reduce its moisture content. Impurities such

as oil palm shell, mesocarp fiber and small stone were manually removed by hand.

In order to remove residual oil, the pre-cleaned EFB was then further cleaned. It was intensively washed with clean flowing tap water, rinsed and soaked overnight in distilled water. This second stage cleaning process took seven consecutive days and six nights to accomplish.

The impurities free EFB was dripped off its water content and loaded into clean aluminum tray and oven dried at 103 °C until constant weight was achieved. The oven dried EFB was allowed to cool to room temperature and manually cut into the length of 10 mm.

The cut EFB was sieved utilizing a sieve shaker and two sieving pans with the sieve opening of 250 and 500 μm respectively. The sieved EFB which has the dimension of 10 mm in length and $250 < \text{Ø} \leq 500 \mu\text{m}$ in geometrical mean diameter was kept in airtight container and known as EFBF hereafter.

B. Preparation of Modifying Agent

In order to prepare the modifying agent 2.0 M NaOH stock solution, a precise amount of 80.00 g NaOH pellet was dissolved in distilled water to 1 L. This stock solution was then diluted accordingly to produce NaOH solution of other concentrations (0.1 – 1.5 M).

C. Preparation of Adsorbent EFBF1

The EFBF1 series adsorbent was prepared by reacting 12.5 g of EFBF with 500 mL of NaOH,

as modifying agent, in a well stirred 1 L glass beaker at room temperature for 24 h. In each individual batch of modification, the NaOH concentration was varied from zero to 2.0 M while other parameters remained unchanged. Ultrapure water was used to represent 0 M NaOH.

At the end of the reaction time, the reacted EFBF was extensively rinsed with distilled water, in batches, until a constant pH of 7.40 was achieved. The thoroughly rinsed reacted EFBF was dripped off its water content and loaded into clean aluminum tray and oven dried at 103 °C until constant weight was achieved. The oven dried EFBF-based adsorbents were individually codenamed as EFBFXM (where X represents the modifying agent concentration used) and kept in airtight container until their utilization in the batch adsorption experiment.

D. Preparation of Adsorbent EFBF2

The EFBF2 series adsorbent was prepared after the adsorption performance of the EFBF1 adsorbents was evaluated where 0.1 M NaOH concentration was adopted as the preferred modifying agent concentration.

While the preparation method of the EFBF2 adsorbent series was similar to the preparation method of the EFBF1 adsorbent series, in each individual batch of modification, the NaOH reaction time was varied (1 – 36 h).

At the end of the designated reaction time, the treated EFBF was extensively rinsed with

distilled water, in batches, until a constant pH of 7.19 was achieved. The thoroughly rinsed reacted EFBF was then dripped off its water content and loaded into clean aluminum tray and oven dried at 103 °C until constant weight was achieved. The oven dried EFBF-based adsorbents were individually codenamed as EFBF0.1M Yh (where Y represents the reaction time) and placed in airtight container until their utilization in the batch adsorption experiment.

E. Batch Adsorption Experiment

In order to assess the adsorption performance of the prepared EFBF-based adsorbents, 0.20 g of each adsorbent was equilibrated with 100 mL of 50 mg/L Cu(II) and Pb(II) ions solution, respectively, for 180 min in triplicate. The experiment was conducted in the physical setting of pH 4.25, lab temperature of 25°C and agitation rate of 150 rpm. At the end of the contact time, the equilibrated mixture was filtered via Advantec 1 Ø 90 mm, diluted where necessary and analyzed utilizing ICP-OES.

III. RESULTS AND DISCUSSIONS

A. Effect of Modifying Agent Concentration

The adsorption of Cu(II) and Pb(II) ions from aqueous solution by EFBF1 series adsorbents were as shown in Figure 1(a). Among the EFBF1 series adsorbents, the EFBF0.1M adsorbent was the best performer. It has the adsorption

capacity of 5.17 ± 0.09 mg/g for Cu(II) and 14.06 ± 0.14 mg/g for Pb(II). The increase in adsorption performance was attributed to the partial solubilisation of lignin and soluble organic component in the EFBF parent material which in turn exposed more adsorption sites to the Cu(II) and Pb(II) ions for adsorption processes to occur (Wartelle and Marshall, 2000).

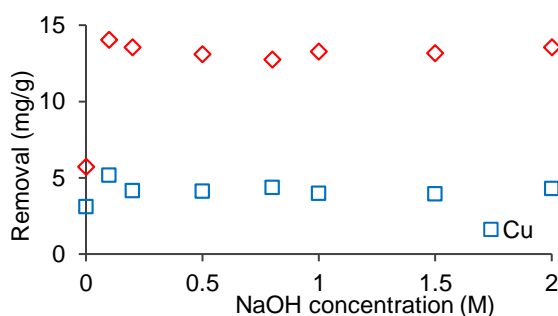


Figure 1(a). Effect of modifying agent concentration on the adsorption of Cu(II) and Pb(II) ions

Therefore, the most appropriate NaOH concentration to be applied in the modification of EFBF was 0.1 M. Possibly this is also the reason other researchers had used 0.1 M NaOH for the modification of *Eucalyptus sheathiana* bark (Afroze et al., 2016), *Melia azedarach* leaves (Khokhar et al., 2015), orange peel (Feng et al., 2010), reed shoot (Southichak et al., 2006) and silverleaf nightshade leaves (Baig et al., 1991) in their efforts in converting agricultural biomasses into adsorbents.

B. Effect of Modification Time

The adsorption of Cu(II) and Pb(II) ions from aqueous solution by EFBF2 series adsorbents were as shown in Figure 1(b). The EFBF0.1M

12h was the best performing adsorbent in the EFBF2 series adsorbent with the adsorption capacity of 5.14 and 14.31 for Cu(II) and Pb(II) ions, respectively. Thus, the appropriate 0.1 M NaOH reaction time to be applied in the modification of EFBF was 12 h.

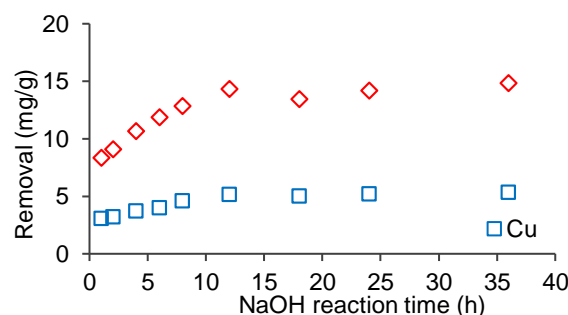


Figure 1(b). Effect of reaction time on the adsorption of Cu(II) and Pb(II) ions

Further increase in the 0.1 M NaOH reaction time beyond 12 h did not result in any increment which suggested that the hydrolysis in the internal particle pores of the EFBF had thoroughly completed at 12 h.

IV. SUMMARY

The present investigation revealed that the best NaOH concentration and NaOH reaction time to be employed in the modification of EFBF into heavy metal adsorbent were 0.1 M and 12 h, respectively. From the results of this study, we are able to reduce the NaOH consumption; thus, reducing environmental footprint and financial cost in the production of the EFBF0.1M 12h adsorbent. We also manage to identify the most appropriate reaction time to be employed and thus are able to reduce the production time as well.

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- [1] Afroze, S., Sen, T.K. & Ang, H.M. (2016). Adsorption removal of zinc (II) from aqueous phase by raw and based modified *Eucalyptus sheathiana* bark: Kinetics, mechanism and equilibrium study. *Process Safety and Environmental Protection*, vol. 102, pp. 336–352.
- [2] Baig, T.H., Garcia, A.E., Tiemann, K.J. & Gardea-Torresdey, J.L. (1999). Adsorption of heavy metal ions by the biomass of *Solanum elaeagnifolium* (silverleaf nightshade). *Proceedings of the 1999 Conference on Hazardous Waste Research*, pp. 131–142.
- [3] Chiew, Y.L. & Shimada, S. (2013). Current state and environmental impact assessment for utilizing oil palm empty fruit bunches for fuel, fiber and fertilizer – A case study of Malaysia. *Biomass and Bioenergy*, vol. 51, pp. 109–124.
- [4] Feng, N., Guo, X. & Liang, S. (2010). Enhanced Cu(II) adsorption by orange peel modified with sodium hydroxide. *Transactions of Nonferrous Metals Society of China*, vol. 20, pp. s146–s152.
- [5] Kamaludin, N.H., Ghazali, A. & Daud, W.W. (2012). Potential of fines as reinforcing fibers in alkaline peroxide pulp of oil palm empty fruit bunch. *Bioresources*, vol. 7, no. 3, pp. 3425–3438.
- [6] Khokhar, A., Siddique, Z. & Misbah (2015). Removal of heavy metal ions by chemically treated *Melia azedarach* L. leaves. *Journal of Environmental Chemical Engineering*, vol. 3, pp. 944–952.
- [7] Khosravihaftkhany, S., Morad, N., Teng, T.T., Abdullah, A.Z. & Norli, I. (2013). Biosorption of Pb(II) and Fe(II) from aqueous solutions using oil palm biomasses as adsorbents. *Water, Air & Soil Pollution*, vol. 224, pp. 1455.
- [8] M'hamdi, A.I., Kandri, N.I., Zerouale, A., Blumberga, D. & Gusca, J. (2017). Life cycle assessment of paper production from treated wood, *Energy Procedia*, vol. 128, pp. 461–468.
- [9] Nassar, M.M., Ewida, K.T., Ebrahiem, E.E., Magdy, Y.H. & Mheaedi, M. H. (2004). Adsorption of iron and manganese using low cost materials as adsorbents. *Adsorption Science & Technology*, vol. 22, no. 1, pp. 25–37.
- [10] Salamatina, B., Kamaruddin, A.H. & Abdullah, A.Z. (2007). Removal of Zn and Cu from wastewater by sorption on oil palm tree-derived biomasses. *Journal of Applied Sciences*, vol. 7, no. 15, pp. 2020–2027.
- [11] Samsuri, A.W., Sadegh-Zadeh, F. & She-Bardan, B.J. (2014). Characterization of biochars produced from oil palm and rice husks and their adsorption capacities for heavy metals. *International Journal of Environmental Science and Technology*, vol. 11, pp. 967–976.
- [12] Southichak, B., Nakano, K., Nomura, M., Chiba, N. & Nishimura, O. (2006). *Phragmites australis*: A novel biosorbent for the removal of heavy metals from aqueous solution. *Water Research*, vol.

40, pp. 2295–2302.

- [13] The Statistic Portal (2017). Consumption of vegetable oils worldwide from 1995/1996 to 2015/2016, by oil type (in million metric tons). Viewed 8th September 2017. Retrieved from <https://www.statista.com/statistics/263937/vegetable-oils-global-consumption/>
- [14] United States Department of Agricultural (USDA) (2010). Foreign Agricultural Service: Production, supply and distribution. Viewed 4th September 2017. Retrieved from <https://apps.fas.usda.gov/psdonline/app/index.html#/app/advQuery>
- [15] Wartelle, L. and Marshall, W. (2000). Citric acid modified agricultural by-products as copper ion adsorbents. *Advances in Environmental Research*, vol. 4, pp. 1–7.
- [16] Yusoff, S. (2006). Renewable energy from palm oil – innovation on effective utilization of waste. *Journal of Cleaner Production*, vol. 14, pp. 87–93.