Study of Adsorption Capacity of Cobalt Nitrate Hexahydrate onto Shredded Palm Oil Empty Fruit Bunches

Nur Ain Athirah binti Othman, Dr. Rusmi Alias

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*—** Three different concentration of cobalt nitrate hexahydrate were prepared to be impregnated onto Shredded Palm Oil Empty Fruit Bunches (SPOEFB); 1%, 3% and 5%. This process was performed in order to study the adsorption capacity of cobalt nitrate hexahydrate. The adsorption capacity increased as the cobalt nitrate hexahydrate solution increased however, a little slow down when at highest concentration (5%). The SPOEFB were treated by two ways; washed by water taps and unwashed to examine their effect on the adsorption capacity. Between that two ways, the washed SPOEFB shows the better adsorption capacity which are 0.252, 2.807 and 3.169 for 1%, 3% and 5% respectively compared to the adsorption capacity of unwashed SPOEFB which are 0.168, 2.781 and 3.144 for 1%, 3% and 5% respectively. The washed SPOEFB shows the a bit higher presence of the cobalt nitrate on it compared to the unwashed SPOEFB since the washed SPOEFB had more surface area for the cobalt to be attached as the impurities on them before were more likely had been removed during the washing process.

***Keywords*—** *Cobalt nitrate, empty fruit bunches, adsorption capacity, impregnation, washed*

I. INTRODUCTION

Due to the depletion of natural resources like fossil fuels and the environmental issues nowadays lead to the invention of renewable energy which is more clean and environmental-friendly. The rapid growth of human population and urbanization also contributes to the invention of renewable energy resources in order to support the increasing demand of energy needs. Since the sources of the pollution comes from the gas emission resulted from combustion of fossil fuels, it is recommended to substitute the fossil fuels with the clean renewable energy resources. Most of the renewable energy resources come from the natural sources which are constantly replenished never run out. For example, biomass energy, solar energy, wind power and geothermal energy.

Among the natural energy resources, biomass energy is the most promising technology as the clean renewable energy resources because of the easily and readily availability of the biomass. Moreover, biomass is abundant waste that largely generated every day which approximately 220 billion tons per year (H. Hassan, 2016). In addition, the use of biomass as the replacement for fossil fuels contributes to low environmental impacts where the biomass emits low carbon dioxide (CO_2) which helps in reducing the global warming where the growing biomass traps the released CO_2 from combustion of biomass through photosynthesis (H. Hassan, 2016).

This non-edible biomass can be converted into valuable products like fuels and useful chemicals through the thermal conversion process. The thermal conversion is a process that using the heat and with or without the presence of oxygen in order to convert the biomass into the product which in energy forms (Agricultural Ecosystems Research Group). For example, gasification, combustion and pyrolysis. Among all the thermal conversion processes, the pyrolysis had been recommended as the technology that will be used to convert the biomass into the valuable products. This is because the high yield of liquid oil from the pyrolysis which the liquid oil or known as bio-oils can be substitute the fossil fuels and promising the clean environment in future.

However, the poor quality of bio-oils produced like low caloric value, corrosion problem and instability (Daud, 2014). Other than that, the high viscosity and unstable oxygenated compounds prohibit the direct use of bio-oil as a fuel source (Nor Aishah Saidina Amin, 2012). Thus, leads to another method called as catalytic pyrolysis which enhancing the quality of bio-oils. The catalytic pyrolysis method is performed by the help of the metal catalyst-impregnated biomass of oil palm empty fruit bunches (Simon Eibner, 2015). With the addition of the catalyst, the quality of the pyrolysis product can be upgraded. For example, the cracking of tar can be performed more efficiently to produce lighter and less complex tar molecules and the bio oils become less corrosive by reducing the formation of carboxylic acid (Whyte, Loubar, Awad, & Tazerout, 2015).

There are many ways in using the catalyst in a pyrolysis process such as catalyst can be added during the pyrolysis in the reactor or catalyst also can be used as the bed material in fluidized bed reactor or catalyst can be placed at the outlet of reactor (Simon Eibner, 2015). Among all the ways suggested, the insertion of catalyst onto the biomass before pyrolysis process is the best technique. This is because the metal catalyst impregnation method will generate in situ catalyst where the catalyst is located more closely to the lignocelullosic structure of biomass thus give the impacts on the pyrolysis products (Simon Eibner, 2015).

Moreover, some researches on the catalytic activity of alkali metal, alkaline earth metal and transition earth metal on production of bio-oils, for example, the impregnation of the metal catalyst had showed the remarkable impacts on product yield and bio-oils composition. This is due to the uniform dispersion of metal in the biomass matrix and closer contact position with the lignocellulosic structure (Xiaoyien Lim, 2014). Therefore, this type of catalyst treatment has gained the great attention from the researchers nowadays. Nitrate salts are the most preferable solution to be used as the medium for the metal impregnation because of theirs low pH value which contributes to the impregnation efficiency (Simon Eibner, 2015).

In this research study, the SPOEFB had been treated with two ways which are unwashed and washed by the tap water. This reasearch had been conducted to study the adsorption capacity of cobalt nitrate hexahydrate onto SPOEFB and also the effect resulted from different early treatment for SPOEFB.

II. METHODOLOGY

A. Materials

Shredded Palm Oil Empty Fruit Bunches (SPOEFB) which taken from a palm oil mill at Pahang were divided into two categories where some empty fruit bunches were prepared as unwashed while another were washed and being dried overnight at 105°C in a laboratory oven.

B. Impregnation

The stock solution which is cobalt nitrate hexahydrate was prepared with three different concentrations 1% w/w, 3% w/w and 5% w/w. The SPOEFB then were directly soaked into the prepared stock solutions for 24 hours. After that, that SPOEFB along with cobalt nitrate hexahydrate solution were filtered and dried overnight at 80°C. The solutions were being sent to Atomic Absorption Spectroscopy (AAS) for analyzing the concentration of the solution left. Meanwhile, the filtered SPOEFB were being dried overnight at 80°C. Then, the cobalt-impregnated SOPEFB were burned in a furnace at 550°C. The analysis by using X-ray Diffraction laser on ash was performed in order to verify the presence of cobalt nitrate on the SPOEFB.

III. RESULTS

A. Analysis from Atomic Absorption Spectroscopy (AAS)

The Atomic Absorption Spectroscopy analysis was performed in order to determine the changes in the concentration of cobalt nitrate solution during the impregnation process. Table 1 and Table 2 show the changes on concentration of cobalt nitrate solution before and after 24 hours.

Table 1: Initial and final concentration of cobalt nitrate solution for unwashed SPOEFB

	Initial concentration (ppm)	Final concentration after 24 hours (ppm)
1%	14.6	11.24
2%	96.64	41.02
3%	113.48	50.6

Table 2: Initial and final concentration of cobalt nitrate solution for washed SPOEFB

	Initial concentration (ppm)	Final concentration after 24 hours (ppm)
1%	14.6	9.56
2%	96.64	40.5
3%	113.48	50.1

All the data obtained from the AAS analysis were displayed in Figure 1 and Figure 2 for further understanding.

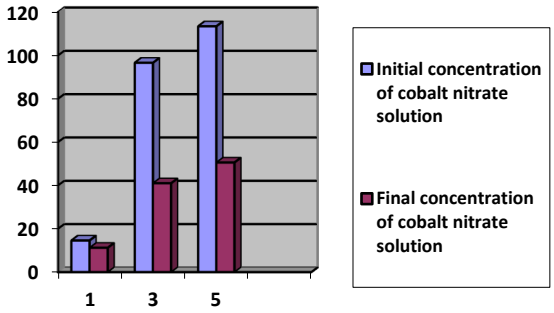

Fig. 1: The chart on the changes in the concentration of cobalt nitrate solution for unwashed SPOEFB

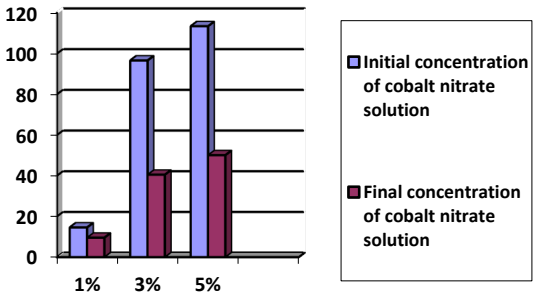

Fig. 2: The chart on the changes in the concentration of cobalt nitrate solution for washed SPOEFB

Based on data from Table 1 and Table 2, the percentage of cobalt nitrate had been removed were determined by using the formula as below.

$$q = \frac{C_0 - C_f}{C_i} \times 100$$

The graph of percentage of the removed cobalt nitrate from the solution versus the initial concentration of cobalt nitrate hexahydrate solution for unwashed SPOEFB and washed SPOEFB had been displayed in Figure 3 and 4 respectively.

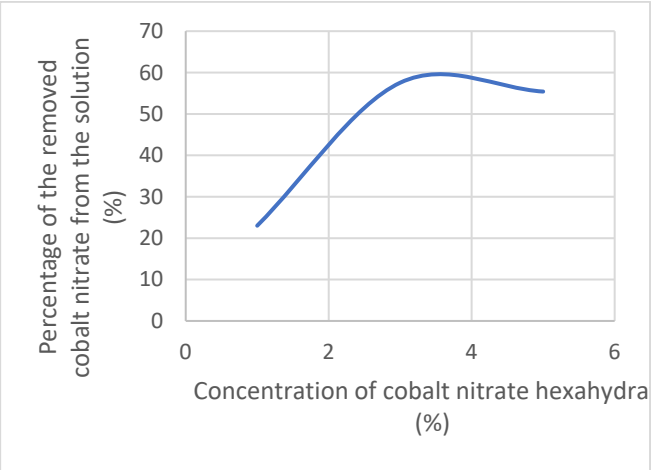

Fig. 3: The graph of percentage of the removed cobalt nitrate from the solution versus the initial concentration of cobalt nitrate hexahydrate solution for unwashed SPOEFB

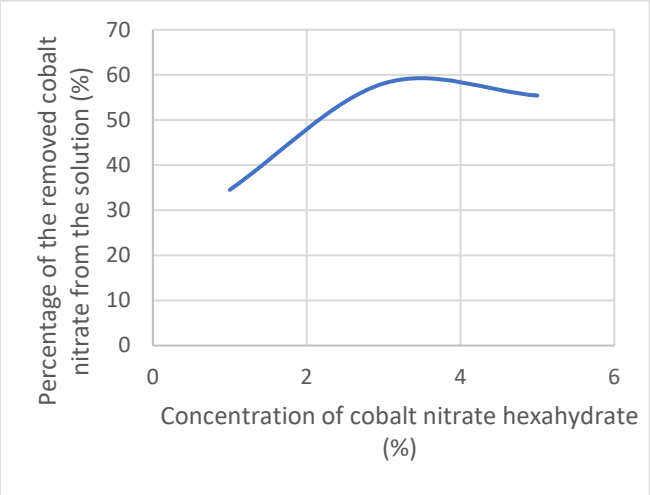

Fig. 4: The graph of percentage of the removed cobalt nitrate from the solution versus the initial concentration of cobalt nitrate hexahydrate solution for washed SPOEFB.

Meanwhile, the adsorption capacity of cobalt had been determined by using the formula as shown below.

$$Q = \frac{V(C_0 - C_f)}{W(1000)}$$

where q is the amount of cobalt being adsorbed at given time of t; C_0 is the initial concentration of cobalt nitrate solution; C_f is the final concentration of cobalt at a given time t, V is volume of cobalt nitrate hexahydrate solution (250 ml) and m is the mass of the biomass used (5g) (Hao, Zheng, Jiang, Zhang, & Wang, 2016).

Table 3: The adsorption capacity of cobalt nitrate for unwashed and washed SPOEFB

	Adsorption capacity of unwashed SPOEFB	Adsorption capacity for washed SPOEFB
1%	0.168	0.252
2%	2.781	2.807
3%	3.144	3.169

Based on data in Table 3, the graph of adsorption capacity against initial concentration of cobalt nitrate hexahydrate solution were plotted and displayed as shown in Figure 5 and Figure 6.

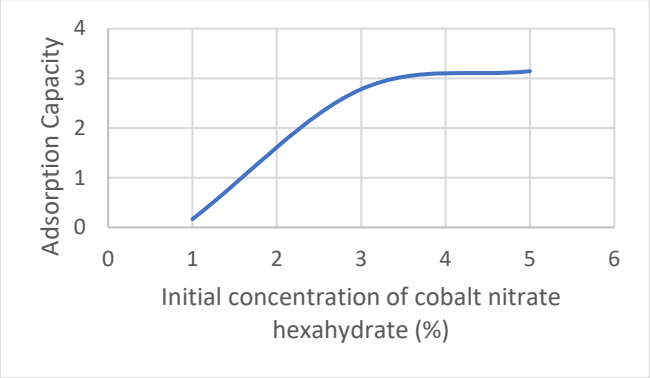

Fig. 5: The graph of adsorption capacity against initial concentration of cobalt nitrate hexahydrate solution for unwashed SPOEFB.

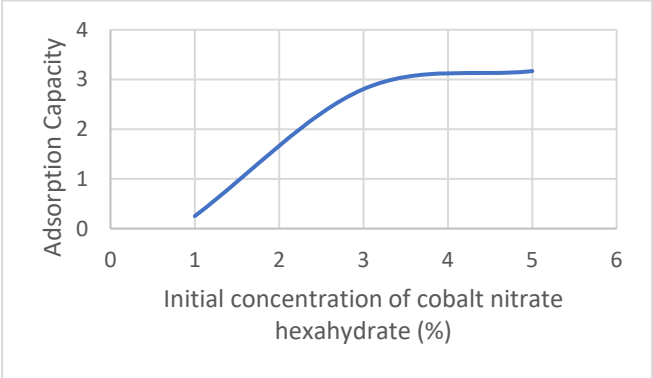

Fig. 6: The graph of adsorption capacity against initial concentration of cobalt nitrate hexahydrate solution for washed SPOEFB.

The comparison on the trend of adsorption capacity of cobalt nitrate hexahydrate between unwashed and washed were displayed as in Figure 7.

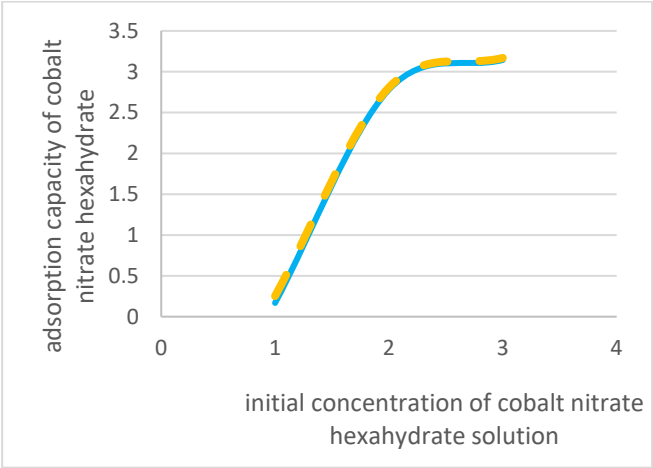

Fig. 7: The graph of adsorption capacity against initial concentration of cobalt nitrate hexahydrate solution for unwashed and washed SPOEFB.

B. Analysis from X-ray Diffraction laser (XRD)

This analysis was performed to verify the presence of cobalt nitrate on the SPOEFB after the impregnation process. The presence of cobalt nitrate is verified when the highest peak in the pattern is within the ranges of intensity for cobalt nitrate order Figure 4, Figure 5, Figure 6 and Figure 7 displayed the peaks resulted from XRD analysis on ash of unwashed cobalt-impregnated SPOEFB.

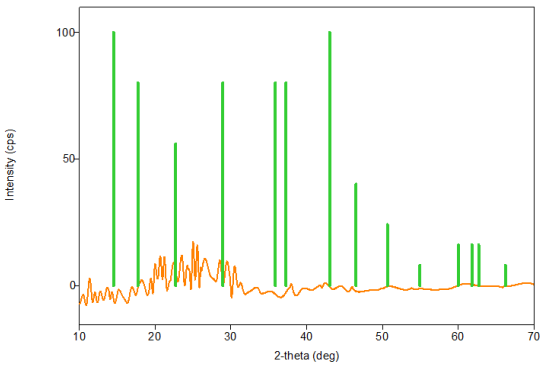

Fig. 8: XRD pattern for unwashed raw SPOEFB

From Figure 8, there were no peaks tally within the ranges of intensity for cobalt nitrate element. Thus, indicates that there is no

cobalt nitrate present on the SPOEFB before the impregnation process. Same goes with Figure .

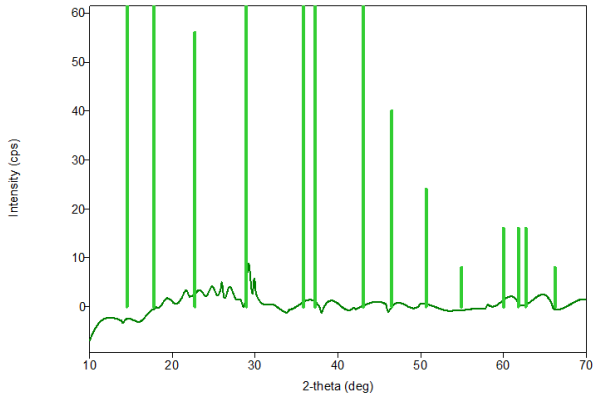

Fig. 9: XRD pattern for unwashed cobalt-impregnated SPOEFB

From Figure 9, the highest peak detected was within the ranges of intensity for cobalt nitrate element. Thus, indicates that there is cobalt nitrate present on the SPOEFB after being impregnated with 1% of cobalt nitrate.

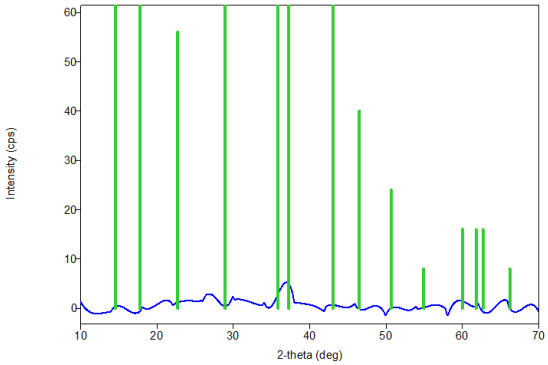

Fig. 10: XRD pattern for 3% unwashed cobalt-impregnated SPOEFB

From Figure 10, the highest peak detected also was within the ranges of intensity for cobalt nitrate element. Thus, indicates that there is cobalt nitrate present on the SPOEFB after being impregnated with 3% of cobalt nitrate. Figure 11 also displayed the quite similar pattern as Figure 10 which indicates that there is cobalt nitrate on the SPOEFB after being impregnated with 5% of cobalt nitrate

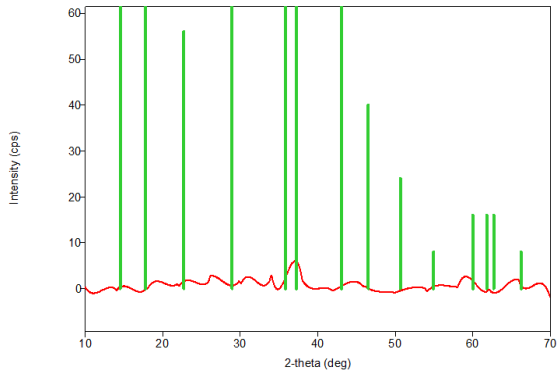

Fig. 11: XRD pattern for 5% unwashed cobalt-impregnated SPOEFB

Meanwhile, Figure 12, Figure 13, Figure 14 and Figure 15 displayed the peaks resulted from XRD analysis on ash of washed cobalt-impregnated SPOEFB.

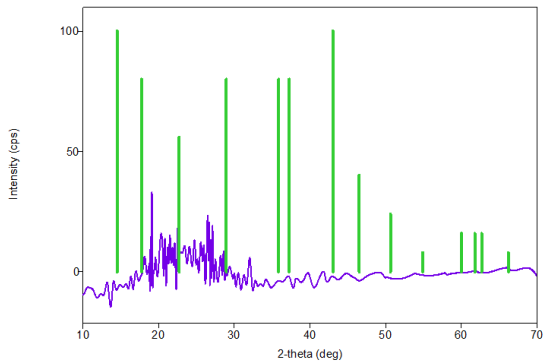

Fig. 12: XRD pattern for raw washed cobalt-impregnated SPOEFB

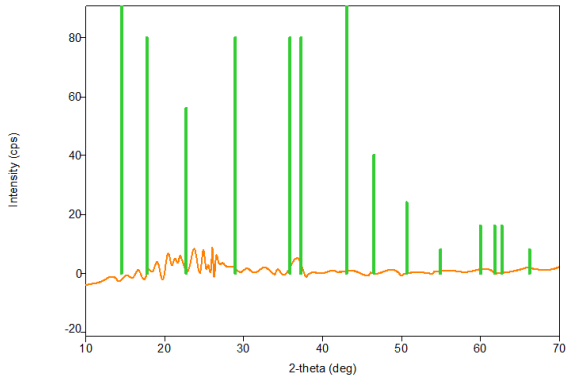

Fig. 13: XRD pattern for 1% washed cobalt-impregnated SPOEFB

From Figure 13, the highest peak detected was within the ranges of intensity for cobalt nitrate element. Thus, indicates that there is cobalt nitrate present on the SPOEFB after being impregnated with 1% of cobalt nitrate.

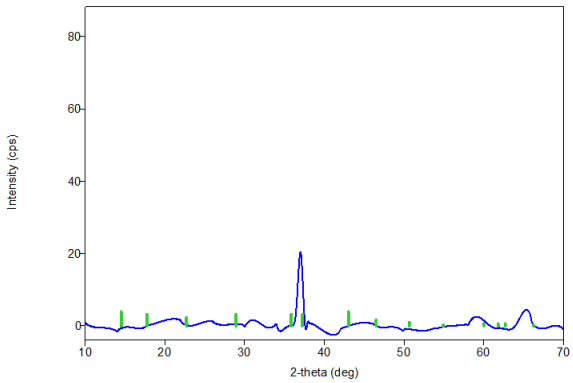

Fig. 14: XRD pattern for 3% washed cobalt-impregnated SPOEFB

Based on Figure 14, the highest peak detected also was within the ranges of intensity for cobalt nitrate element. Thus, indicates that there is cobalt nitrate present on the SPOEFB after being impregnated with 3% of cobalt nitrate.

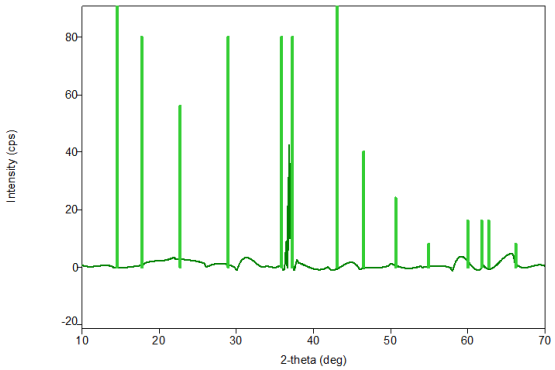

Fig. 15: XRD pattern for 5% washed cobalt-impregnated SPOEFB

Figure 15 also showed the highest peak was within the ranges intensity for cobalt nitrate element which indicates that there is cobalt nitrate on the SPOEFB after being impregnated with 5% of cobalt nitrate.

IV. Discussion

In this research study, there are two variables that had been applied. The first one is the effect of three different concentration of cobalt nitrate hexahydrate solution (1%, 3% and 5%) on the adsorption capacity of cobalt nitrate hexahydrate. Based on the results displayed in both Figure 3 and Figure 4, the adsorption capacity increased gradually as the metal initial concentration of cobalt nitrate hexahydrate solution increased. However, for the concentration 5%, the adsorption capacity of the cobalt nitrate was declining a little bit and its value compared to concentration 3% was not much difference. This might be because at higher concentration, the binding site had been gradually occupied. Thus, leads to the less cobalt to be adsorbed onto SPOEFB (Ideriah, David, & Ogbonna, 2012). That also implied that the cobalt nitrate had been attached more onto the active site at lower concentration compared to higher concentration of cobalt nitrate hexahydrate solution.

The second variable is the early treatment for SPOEFB before the impregnation process. Based on the graph in Figure 7, the adsorption capacity of cobalt nitrate onto unwashed and washed SPOEFB are not much difference. But the washed SPOEFB still the one that gave the higher adsorption capacity compared to unwashed SPOEFB as the washing helped in removing a little bit of the impurities on SPOEFB.

The presence of cobalt after the impregnation process had been e proven by the results from XRD analysis. A*ll Figure 9, 10, 11, 13, 14 and 15 showed the presence of cobalt element by observing the higher peaks that tally within the range for cobalt. Other than that, Figure 13, Figure 14 and Figure 15 had displayed the higher intensity peaks on washed SPOEFB compared to the unwashed SPOEFB. The high intensity peaks indicated that presence of cobalt nitrate on the washed SPOEFB is a little higher compared to the unwashed SPOEFB.*

V. Conclusion

The main purpose of this research study was achieved where the adsorption capacity of cobalt nitrate hexahydrate had been studied. The adsorption capacity increased as the concentration of cobalt nitrate hexahydrate increased but at high concentration (5%), the adsorption capacity slow down a bit and nearly to constant value. Besides that, the washed SPOEFB gave almost similar with the unwashed SPOEFB. The adsorption capacity a little bit higher when the SPOEFB were washed compared to the unwashed SPOEFB but that did not much differ. Other than that, most of the peaks resulted from XRD analysis showed the presence of cobalt in SPOEFB after the impregnation process. Thus, it is really recommended to treat the SPOEFB first before impregnating them with any metals. Maybe better with the other effective types of pretreatment that can give a great good effect on the impregnation process.

Acknowledgement

First of all, I would like to thanks my supervisor, Dr. Rusmi Alias and Universiti Teknologi Mara for the helps and the facilities provided during conducting my research study. Thanks also to the researcher En. Mohibah and others laboratory assistants for their kindness and commitment in assisting me during the experimental works.

References

Agricultural Ecosystems Research Group. (n.d.). Bioenergy Conversion Technologies. Retrieved December 17, 2016, from Wisconsin Grassland Bioenergy Network: http://www.wgbn.wisc.edu/conversion/bioenergy-conversion-technologies

Daud, F. A. (2014). A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. Energy Conversion and Management Vol. 87, 71-85.

H. Hassan, J. L. (2016). Recent Progress on Biomass Co-pyrolysis Conversion into High-quality of Bio-oil. Bioresource Technology Vol. 221, 645-655.

Hao, L., Zheng, T., Jiang, J., Zhang, G., & Wang, P. (2016). Removal ofAs(III) and As(V) from water using doped amino functionalized sawdust: Characterization, adsorptive performance and UF membrane separation. Chemical Engineering Journal 292, 163-173.

Ideriah, David, & Ogbonna. (2012). Removal of Heavy Metal Ions in Aqueous Solutions using Palm Fruit Fibre as Adsorbent. Journal of Environmental Chemistry and Ecotoxicology Vol. 4(4), 82-90.

Nor Aishah Saidina Amin, L. H. (2012). Bio-oils and Diesel Fuel Derived from Alkaline Treated Empty Fruit Bunch (EFB). International Journal of Biomass and Renewables Vol. 1, 6-14.

Simon Eibner, F. B. (2015). Catalytic Effect of Metal Nitrate Salts During Pyrolysis of Impregnated Biomass. Journal of Analytical and Applied Pyrolysis Vol. 113, 143-152.

Whyte, H. E., Loubar, K., Awad, S., & Tazerout, M. (2015). Pyrolytic Oil Production by Catalytic Pyrolysis of Refuse-derived Fuels: Investigation of Low Cost Catalysts. Fuel Processing Technology Vol. 140, 32-38.

Xiaoyien Lim, A. S. (2014). Influence of Red Mud Impregnation on The Pyrolysis of Oil Palm Biomass-EFB. Fuel Vol. 119, 259-265.