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Performance of Magnetic Palm Oil Empty Fruit Bunch Biochar for Removal of Waste Cooking Oil

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Abstract: Waste cooking oil is an end-product of oil used for frying or cooking in the manufacturing industry, restaurants and households. Unfortunately, improper disposal of the waste cooking oil in kitchen and sinks will solidify and block the sewer pipes. It may also forms a thin layer above the water that would reduce the dissolved oxygen concentration required for underwater living creatures. In order to remove waste cooking oil from the aqueous system, this research is conducted to develop a magnetic palm oil empty fruit bunch biochar. The magnetic biochar was prepared via co-precipitation of $FeCl_3$ and $FeSO_4$ for the formation of iron oxide. Batch experiments were conducted to analyse the performance of the magnetic biochar to remove the waste cooking oil. The magnetic biochar was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). Batch sorption studies were carried out at different parameters which is waste cooking oil concentrations of 0.25, 1.00 and 5.00 % with the magnetic biochar dose at 0.5, 1.0 and 1.5 g and 10, 60 and 120 seconds of contact time. The pH of solutions is in the range of 6.5 to 7.5. Reusability studies were also conducted on magnetic biochar to measure the adsorption capacity. The analysis from FTIR and SEM has proven that magnetic biochar from palm oil empty fruit bunch can act as adsorbent. From the result, the optimum performance of magnetic biochar in removing cooking oil waste is at 0.25 % concentration of waste cooking oil with 1.5 g magnetic biochar and 120 s contact time. The magnetic biochar towards zero waste production could be achieved as the magnetic biochar performance after 3 cycles of adsorption are still promising. This study proved that magnetic biochar could be used as a cost-effective and efficient adsorbent for oil removal applications.

Keywords: Palm Oil Empty Fruit Bunch, Magnetic Biochar, Waste Cooking Oil

1. Introduction

Waste cooking oil are oils that have been used for frying, cooking and other processing types in restaurants, food-manufacturing industry and households. Chemical reactions change the physical and

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chemical of cooking oil during these processes, including oxidation, polymerization, thermal degradation and hydrolysis. Consequently, many free fatty acids in waste cooking oil generating unpleasant odor and also causing corrosion of metal and concrete elements. This waste cooking oil has been classified as one of the municipal wastes since it can cause serious environmental problems [1]. As population growth, the quantity of cooking oil used has increased. However, specific technology and management developments remain behind, and causing a lot of oil spill into the drain. Oil pollution will affect groundwater resources, endangering aquatic resources and threatening human health [2]. Repeated use of cooking oil can increase the peroxide value and free fatty acids contained. Thus, continuous exposure to waste cooking oil will give hazardous impacts on the environment and also to human health. Therefore, it is necessary to separate and remove waste cooking oil before it is discharged to the environment. Many research has been done to solve waste cooking oil problems in aqueous solution with green solution by involving agricultural waste.

Most of the articles have stated that magnetic biochar as an efficient adsorbent for removing heavy metals and organic contaminants from aqueous solution and even from nuclear waste polluted water. Besides, several studies have indicated that reactive oxygen species produced by activated persulphate/hydrogen peroxide, using magnetic biochar as a catalyst could effectively degrade organic pollutants in aqueous solution [3]. Therefore, this study aims to produce magnetic biochar for the removal of waste cooking oil in aqueous solution, by using agricultural waste of palm oil empty fruit bunch. The implementation of palm oil empty fruit bunch biochar is investigated by variation of parameters including adsorbent dosage of palm oil empty fruit bunch magnetic biochar, contact time and concentration of waste cooking oil. This research will give new knowledge on the ability of palm oil empty fruit bunch to be used as magnetic biochar to separate the waste cooking oil from aqueous solution. It will be a great benefit to the environment as the oil trace in the water system may effectively be reduced by the modified agricultural waste.

1.1 Biochar from palm oil waste

Recently, many researchers are concerned to study biochar particles from palm oil waste because of the great attention to utilize the waste. Biochar is a substance like a charcoal which is produced by heating organic material with high temperature from biomass such as agricultural and forestry waste. It is the solid residue left after the heating of biomass under less oxygen conditions. As for the physical features, biochar are black, fine-grained, lightweight and highly porous. About 70.00 % of its composition consists of carbon. The production helps with the sequestration of carbon by storing the carbon present in the plant biomass [4]. Among other elements, the remaining percentage is nitrogen, hydrogen, and oxygen. Unlike the original feedstock for biomass, which primarily includes hemicellulose, cellulose and lignin, biochar is included in a category of materials called black carbon or charcoal but except black carbon from fossil fuels or non-biomass waste. Palm oil empty fruit bunch biochar is inexpensive and carbon rich material, which acts as adsorbent to adsorb diverse organic contaminants such as volatile organic compounds, aromatic dyes, oil, turbidity and a series of inorganic contaminants from aqueous solution. Recent biochar research is focused mainly on adjusting the biochar properties to increase their removal performance for organic and inorganic pollutants [5].

1.2 Magnetic biochar

The continuous growth in technology has always been a key factor for further improvement in any current product or technology in the world market. The development of magnetic biochar rose after the difficulty faced in the application of biochar in a vast area of interest. Magnetic biochar has a function for the separation of powdered biochar from aqueous solution. Generally, separation requires filtration, centrifugation and other time-consuming routes, which limit the practical application of biochar in aqueous solution. Introducing magnetic media, including Fe, Co, Ni and their oxides, into the biochar matrix is an efficient approach to enable the sorbent to be separated quickly from aqueous solution via magnetic separating technique [6].

Iron oxide, Fe_3O_4 is a strong black ore which forms opaque crystals and exerts powerful magnetism [7]. Ferric chloride with the chemical formula $FeCl_3$, has dark colour crystal with +3 as in iron oxidation state. Another name for ferric chloride is iron (III) chloride. It is an agent of iron coordination that acts as an astringent and Lewis acid. The solution of ferric chloride is colourless to light brown and has a slight scent of hydrochloric acid (HCl). Most metals and tissues are corrosive to it. It is non-combustible and is used extensively in the treatment of sewage and purification of water. It is deliquescent in its anhydrous shape. Partial hydrolysis also takes place as it absorbs water from the air and releases hydrochloric acid (HCl) which forms mists in moist air. It is a strong Lewis acid. Ferrous sulphate or the other name of iron (II) sulphate and iron sulphate is an iron salt. The chemical formula for ferrous sulphate is $FeSO_4$. Ferrous sulphate is the cheapest and best supplement of iron. Ferrous sulphate is formed when iron filings are mixed with a copper sulphate solution. Since iron is more reactive, it will push the copper and take its place. Figure 1 shows the schematic chemical reaction of $FeCl_3$ and $FeSO_4$ onto biochar.

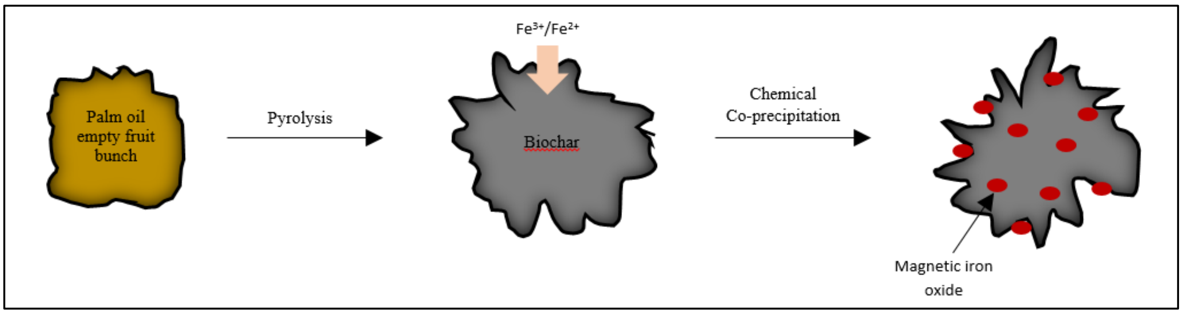

Figure 1: Chemical reaction of $FeCl_3$ and $FeSO_4$ onto biochar

2. Materials and Methods

2.1 Preparation of biochar and magnetic biochar

Palm oil empty fruit bunch are collected at Kluang Oil Palm Processing Sdn Bhd, Kluang, Johor. Five kilograms of palm oil empty fruit bunch were collected and stored in an airtight storage box. The excess of the fruit is removed from the palm oil empty fruit bunch. Then, it is washed with tap water followed with distilled water to get rid of any dirt particles [8]. Next, the palm oil empty fruit bunch was dried under the sun for three days to reduce the moisture content and undergoes further drying in the oven at a temperature of 120 ºC to prevent the growth of fungus. In order to synthesize biochar, the dried palm oil empty fruit bunch is grinded using a laboratory blender and then carbonized for 60 minutes at 400 °C. The carbonized product was impregnated with $ZnCl_2$ where the ratio of $ZnCl_2$ to C is 2:1. After that, the solution was filtered by using filter paper and placed in a crucible. Then, the carbonized product undergoes a pyrolysis process in a furnace PLF Series 140-160 (PROTHERM, Turkey) at 600°C and holding time for 120 minutes. With minimum existence of oxygen, the paralyzed samples were kept in a desiccator instantaneously after being taken out from the furnace. Then, the sample was washed with HCl (0.1 mol/L) for several times followed by deionized water until the pH was 6.0 – 6.5. After being dried, the biochar was sieved through 150 µm size by using Sieve Shaker EFL 300 and was kept in an airtight container.

For the production of magnetic biochar, 20 g of palm oil empty fruit bunch biochar was weighed and mixed with 200 mL of deionized water [9]. Meanwhile, 11.1 g $FeSO_4{\bullet}7H_2O$ and 20 g $FeCl_3{\bullet}6H_2O$ were mixed with 600 mL deionized water until completely dissolved. These two solutions were then mixed and stirred for 20 min at room temperature (23–26 °C). Thereafter, 10 M NaOH was added dropwise into the mixed suspension until the pH of the solution reached between the ranges of 10 - 11. Fe_3O_4 precipitation is produced on the surface of carbon materials under the alkaline environment. After being stirred for 1 hour, the mixtures are boiled for 1 hour to make sure that Fe^{2+} and Fe^{3+} could permeate into the biochar and the solution is filtered out. After the filtering process, the filtrate was washed with deionized water and ethanol several times. Finally, the solid particles were collected and dried at 70°C for 12 hours in a hot air oven. Figure 2 shows the overall process of magnetic biochar preparation and its application. Characterization of palm oil empty fruit bunch were investigated by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).

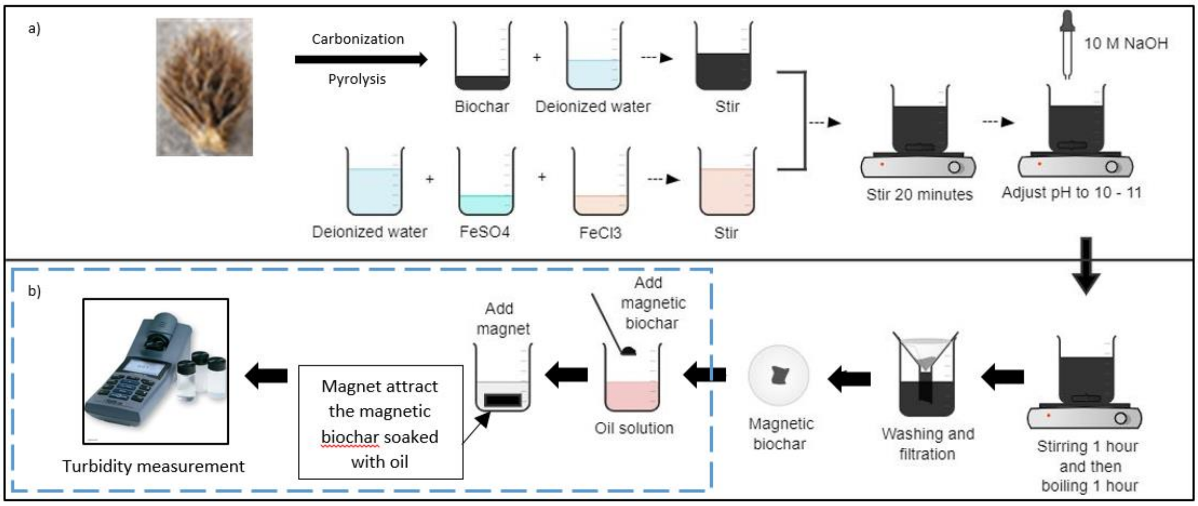

Figure 2: a) Schematic diagram of magnetic biochar procedure b) Schematic diagram of experimental procedure

2.2 Adsorption experiment

The parameters such as contact time, concentration and dosage of magnetic biochar, are varied in order to find the optimum condition for the magnetic biochar to get the maximum adsorption capacity. In order to evaluate the effect of palm oil empty fruit bunch magnetic biochar dosage, series of batch experiments are conducted at different waste cooking oil concentrations of 0.25, 1.00 and 5.00 %, prepared from the stock solution with the magnetic biochar dose maintained constant at 0.5 g, contact time is 10 second. pH of solutions was always in a range from 6.5 to 7.5. Also, different magnetic biochar doses of 1.0 and 1.5 g are tested to evaluate the effect of the magnetic biochar dose on the oil removal performance with the initial concentration kept constant at 0.25 %. The adsorption of oil was also studied at different contact time which is 60 and 120 second. After adsorption, magnetic biochar soaked with waste cooking oil is separated from the surface of water, conveniently by using a magnet. The excess volume of waste cooking oil in the solutions is directly measured by reading of turbidity. The percentage removal of waste cooking oil and adsorption capacity of magnetic biochar were calculated using equation 1 and 2 as shown below:

$$Percentage\ removal\ (\%) = \frac{T_i - T_f}{T_i} \times 100\% \qquad Eq.1$$

Where T_i is the initial turbidity of oil solution (NTU), T_f is the final turbidity of oil solution (NTU).

$$q = \frac{T_i - T_f}{m} \times V \qquad Eq.2$$

Where q is adsorption capacity in (mg/g), T_i is the initial turbidity of oil solution (NTU), T_f is the final turbidity of oil solution (NTU), m is the mass of magnetic palm oil empty fruit bunch biochar (g) and V is the volume of oil solution (L).

2.3 Recyclability experiment

The magnetic biochar derived from 0.25 % concentration of waste cooking oil, 1.5 g magnetic biochar and 120 second, showed a higher adsorption capacity than others and it was selected for the recyclability experiment. After adsorption in 0.25 % concentration oil, 1.5 g dosage of magnetic biochar for 120 second contact time, magnetic biochar was separated with a magnet and turbidity of the solution was measured. The adsorption cycle of magnetic biochar was conducted 3 times to evaluate the recycle efficiency.

3. Results and Discussion

Batch adsorption experiment is used for this study. Ferrous chloride and ferric chloride are used to create a magnetic medium by chemical co-precipitation method and biochar is added to improve the adsorption performance. The experiment is conducted at room temperature (23 – 26 °C).

3.1 Characterization of magnetic palm oil empty fruit bunch biochar

Based on Figure 3, magnetic palm oil empty fruit bunch biochar has peaked at 3165 cm^{-1} which indicates alcohol compound class with weak stretch of O-H group. In addition, the graph shows a strong peak at 2113 cm^{-1} that displays alkyne compound class with weak C≡C group. Next peak is 1990 cm^{-1} which illustrates that palm oil empty fruit bunch magnetic biochar has allene compound class with medium C=C=C group. 1800 cm^{-1} peaks represent a strong C=O group with conjugated acid halide compound class. Other peaks of 1077 cm^{-1} indicate that palm oil empty fruit bunch magnetic biochar has a strong stretch C-O group that is the primary alcohol compound class. Based on [10], the magnetic biochar contain peak at 2361 cm^{-1} which is grouped as C≡C stretch of alkynes while the transmittance of 1652-1497 cm^{-1} is identical to the hydroxyl O-H group.

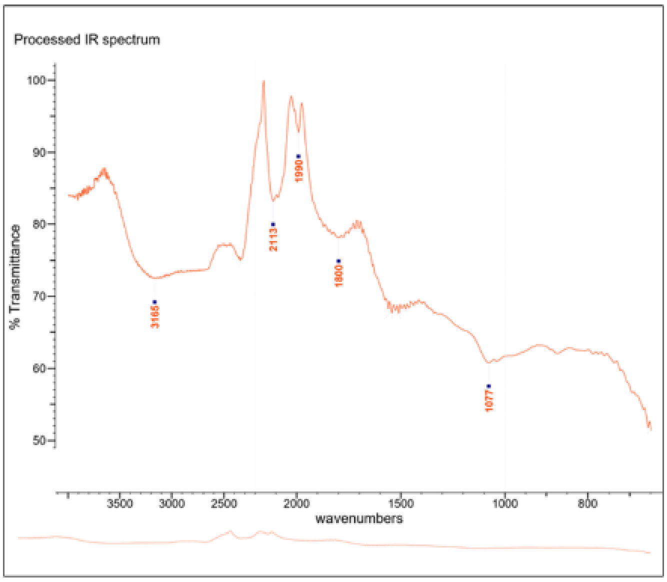

Figure 3: FTIR analysis of magnetic biochar

The analysis of the surface morphology of magnetic biochar based on Figure 4 showed the presence of large deep pores on the surface. The presence of large pores is associated with the presence of large quantities of resinous substances, hemicellulose, cellulose, and lignin in the palm oil empty bunch of fruit, which partially ferments at a high pyrolysis temperature, leading to the formation of stable large pores [11]. A well-developed porosity and uniform distribution of pores along its surface is shown by magnetic biochar. The formation on the surface of cavities and pores of nano dispersed oxide phases contributes to an increase in the specific surface and the formation of new spaces. In addition, these pores were produced by mixing palm oil empty fruit bunches with nano-Fe_3O_4 [11]. The mixing phase has a high shearing effect that interferes with the surface of a material until the pore is produced. A large surface area and high adsorption capacity are given by increasing the number of pores.

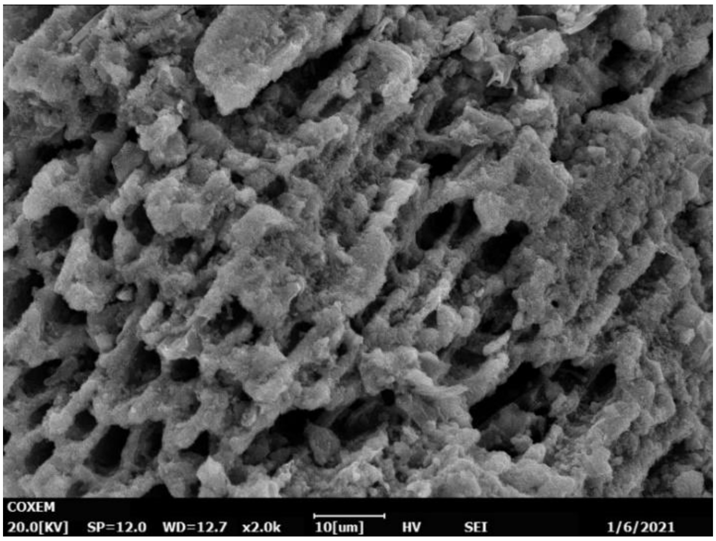

Figure 4: Surface morphology of magnetic biochar

3.2 Adsorption studies

Based on Figure 5, the highest percentage removal of 0.25 % waste cooking oil concentration were 99.14 %, 98.7 % and 97.59 % at 120 s, 60 s and 10 s contact time respectively, with 1.5 g dosage of magnetic biochar. The least percentage removal of 0.25 % waste cooking oil concentration were 75.59 %, 83.95 % and 84.44 % at 10 s, 60 s and 120 s respectively, with 0.5 g dosage of magnetic biochar. This results shows that the increase in contact time and dosage of magnetic biochar will increase the percentage removal of waste cooking oil.

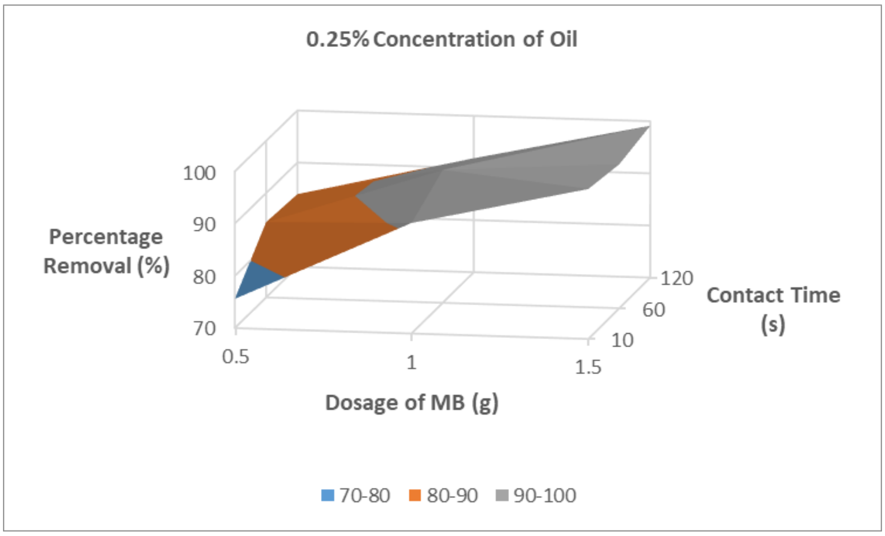

Figure 5: Graph of 0.25 % concentration

Figure 6 indicates the highest 1.00 % waste cooking oil concentration removal percentage was 99.06 %, 98.66 % and 95.51 % at 120 s, 60 s and 10 s contact time, respectively, with a magnetic biochar dosage of 1.5 g. In the meantime, 65.49 %, 85.49 % and 87.35 % were the minimum percentage removal of 1.00 % waste cooking oil concentration at 10 s, 60 s and 120 s respectively, with a magnetic biochar dose of 0.5 g. These findings show that the increase in contact time and magnetic biochar dosage would increase the percentage of waste cooking oil removal.

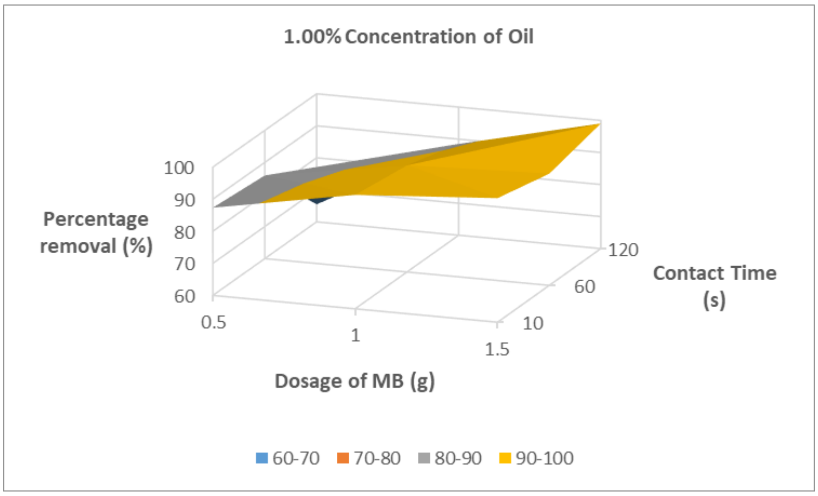

Figure 6: Graph of 1.00 % concentration

The highest percentage removal of 5.00 % waste cooking oil concentration was 98.83 %, 98.59 % and 96.76 % based on Figure 7 at 120 s, 60 s and 10 s contact time respectively, with a magnetic biochar dosage of 1.5 g. Meanwhile, 24.02 %, 28.03 % and 85.5 % were the minimum percentage removal of 5.00 % waste cooking oil concentration. All these three lowest percentage removal were results from 10 s, 60 s and 120 s respectively, with 0.5 g dosage of magnetic biochar. This results shows that the increase in contact time and dosage of magnetic biochar will increase the percentage removal of waste cooking oil.

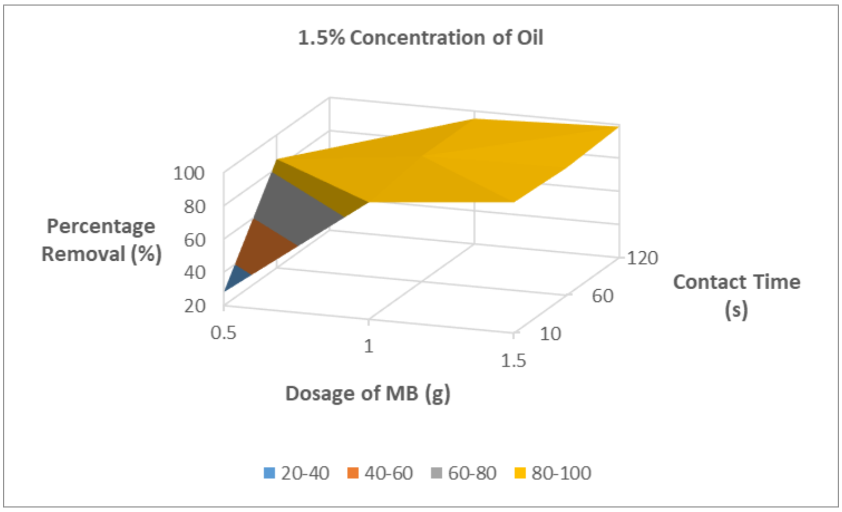

Figure 7: Graph of 5.00 % concentration

Figure 8 shows the recycle results of magnetic biochar from the highest percentage removal of the first cycle. The highest percentage removal from the first cycle was 99.14 % which were from 1.5 g magnetic biochar, 0.25 % concentration of waste cooking oil and 120 s contact time. Recyclability of magnetic biochar has been proven through experiment that it can be reused at all varied parameters which is concentration of waste cooking oil, contact time and dosage of magnetic biochar. Adsorption capacity was calculated for recyclability study at highest percentage removal and the results for the first cycle was 54.36 mg/g followed by 51.52 mg/g for second cycle and 47.42 mg/g for third cycle. However, the removal percentage of waste cooking oil and adsorption capacity of magnetic biochar were decreased as the cycle increased because the magnetic biochar has already adsorb waste cooking oil from cycle 1 and cycle 2. The magnetic biochar was already soaked with waste cooking oil from the first cycle.

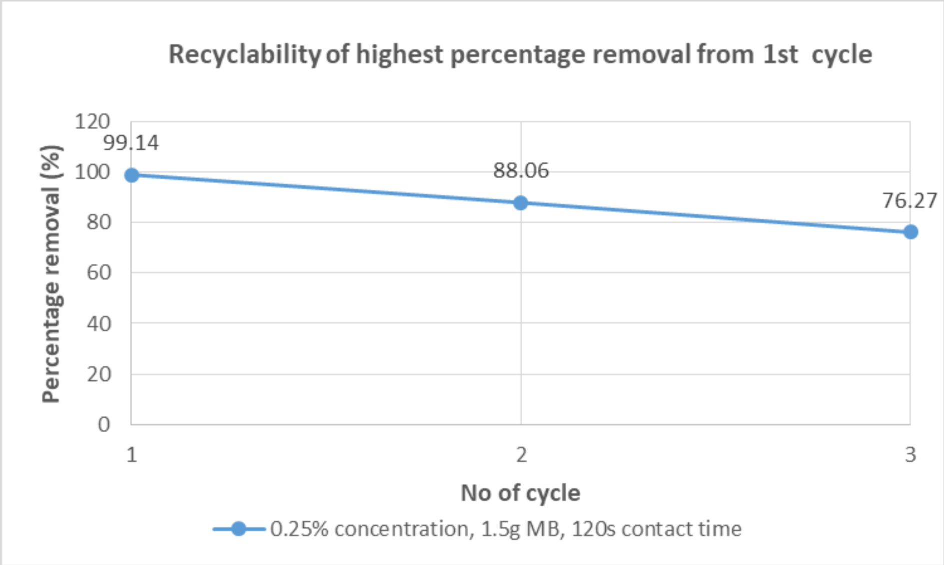

Figure 8: Graph of recyclability from 1st cycle

3.3 Summary

Generally, palm oil empty fruit bunch magnetic biochar were proven to be able to adsorb waste cooking oil in all varied parameter. Palm oil empty fruit bunch magnetic biochar also has been proven to be reused and effective for recyclability study. The most optimum results were high dosage of palm oil empty fruit bunch magnetic biochar, low concentration of waste cooking oil and high contact time. Higher dosage of magnetic biochar can adsorb more waste cooking oil since the higher dosage of magnetic biochar contains more surface area for adsorption of the waste cooking oil.

The removal efficiency increased as the dosage of magnetic biochar increased. Performance of removal was increased with a higher adsorbent dose due to the existence of more binding sites for the adsorption of waste cooking oil [12]. High concentration of waste cooking oil will affect the adsorption efficiency of magnetic biochar because magnetic biochar cannot adsorb more waste cooking oil since waste cooking oil viscosity and density were increased with increasing waste cooking oil concentration [13]. Increasing contact time will increase the percentage removal of waste cooking oil because magnetic biochar has enough time to adsorb waste cooking oil [14].

4. Conclusion

Palm oil empty fruit bunch were successfully synthesized into biochar and then to magnetic biochar by using the pyrolysis and co-precipitation method respectively. Efficiency of palm oil empty fruit bunch magnetic biochar in separating waste cooking oil from aqueous system was achieved with optimum performance of magnetic biochar is at 0.25 % concentration of waste cooking oil with 1.5 g magnetic biochar and 120 s contact time. It is proven that the palm oil empty fruit bunch magnetic biochar has a large surface area and good adsorption capacity. Magnetic palm oil empty fruit bunch biochar is also proven to be reusable and having an excellent recyclability in the waste cooking oil adsorption capacity as the results for first cycle was 54.36 mg/g followed with 51.52 mg/g for second cycle and 47.42 mg/g for third cycle. The results show that magnetic biochar from palm oil empty fruit bunch is a better option to tackle the problem of removing waste cooking oil from aqueous solution since it can be used in the environment, community and sewage treatment plan.

Acknowledgement

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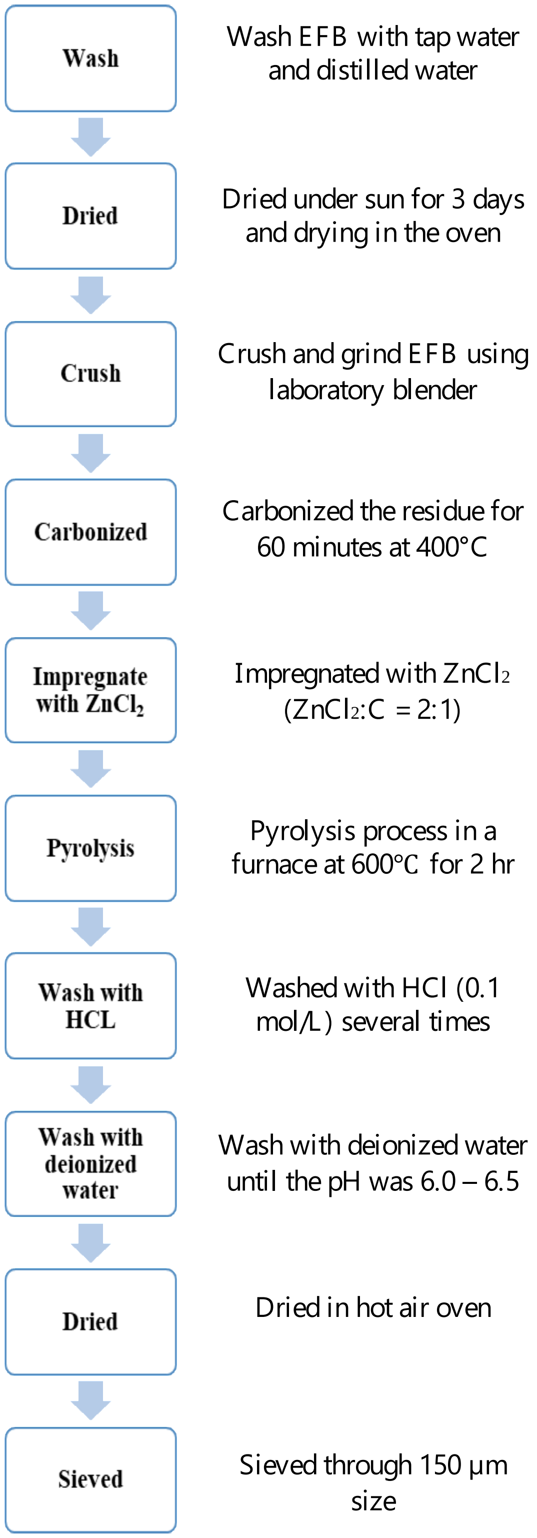
Appendix A


Wash
Wash EFB with tap water and distilled water
Dried
Dried under sun for 3 days and drying in the oven
Crush
Crush and grind EFB using laboratory blender
Carbonized
Carbonized the residue for 60 minutes at 400°C
Impregnate with $ZnCl_2$
Impregnated with $ZnCl_2$ ($ZnCl_2$:C = 2:1)
Pyrolysis
Pyrolysis process in a furnace at 600℃ for 2 hr
Wash with HCL
Washed with HCl (0.1 mol/L) several times
Wash with deionized water
Wash with deionized water until the pH was 6.0 – 6.5
Dried
Dried in hot air oven
Sieved
Sieved through 150 µm size

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