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Removal of Oil Waste by Iron Oxide Biochar Prepared from Sugarcane Bagasse

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Abstract: Nowadays, the dissolution of microsized oil droplets from water is strongly required by the environmental protection. Oil pollution has become a severe environmental issue and has attracted global concern. However, the oil released from household activities particularly cooking and bathing, could contaminate the surrounding environment and human health. The presence of contaminants in oil waste raises concerns as small quantities of organic chemicals have been shown to be carcinogenic to mammals and can pose a risk to both human health and aquatic organisms. Therefore, the presents study investigated the performance of iron oxide sugarcane bagasse biochar in the removal of oil waste from aqueous solution. The iron oxide sugarcane bagasse biochar is produced using co-precipitation method of iron chloride ($FeCl_3$) and iron sulphate ($FeSO_4$). Then, the magnetic biochar is characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). The efficiency of the magnetic biochar in removing oil waste are measured by performed a batch experiment with different iron oxide biochar dosages, oil waste concentration and contact time. At the end of the experiment, the iron oxide sugarcane bagasse biochar is separated by using a magnet. The optimum performance condition of the iron oxide sugarcane biochar is then undergone three cycles of adsorption process to determine the adsorption capacity. From the results of the adsorption experiment, the optimum separation of oil waste was achieved when contact with 0.25 % concentration of oil, 1.5 g of magnetic sugarcane bagasse biochar at 120 seconds with separation efficiency of 99.00 %. After performed three cycle of adsorption process, the iron oxide biochar still showing an excellence removing performance which towards zero waste production could be achieved at the highest adsorption capacity of 137.48 mg/g. The findings constitute that the iron oxide sugarcane bagasse biochar is efficient to be used in removal of waste cooking oil from aqueous solution. Thus, the prospect of iron oxide biochar utilization is promising as it is can customized for specific environmental applications.

Keywords: Magnetic Biochar, Sugarcane bagasse, Waste Cooking Oil

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1. Introduction

One of the most globally challenging tasks is an oil water separation. In practical, oils are restricted as floating oils, dispersed oils, surfactant-stabilized oil droplets, and surfactant-free micro scaled tiny oil droplets [1]. The discharge of oily wastewaters containing oil waste such as crude oil and cooking oil could lead to the loss of energy resources if not recovered as a usable and economical source of energy. To minimize the negative impact of the oily wastewaters on our environment and maximize the utilization of limited oil resources, oil removal/recovery from oily wastewaters is therefore of great environmental and socioeconomic importance. Removing or recovering of oil from discharged oily wastewaters is now a global challenge because the oil droplets of micro-sizes are extremely stable, resulting from the stabilization by natural and synthetic surfactants in the oily wastewaters [2].

Biochar is a kind of carbon-rich pyrogenic materials. It contains about 50.00 % cellulose, 25.00 % hemicellulose and 25.00 % lignin. Due to its prominent characteristics such as eco-friendliness, low castings, and the wide range of available feedstock material as well as mechanical and thermal stability which promote the application of biochar in various environmental areas. One of the main contributions of biochar is that it emphasizes the promising prospects of technology in the treatment of various wastewaters including industrial wastewater (dye, battery manufacture, and dairy wastewater), municipal wastewater, agricultural wastewater, and storm water [3]. Biochar can be used as an adsorbent to remove various pollutants in water and wastewater. Driven by the intense desire for low cost, facile procedure and higher efficiency, biochar-based technology attracts great attention of a growing number of researchers in the field of wastewater treatment [4]. Biochar is therefore seen as a promising alternative to water treatment technologies.

Magnetic nanoparticles are one of the existing remediation techniques based on a magnetically enhanced separation technology as an alternative to existing methods to separate the oil contaminants from the polluted solution. Magnetic nanoparticles have unique properties such as extensive surface area per volume substance and strong magnetic response. In addition, magnetic nanoparticles are rapidly developed scientific area due to the enormous potential of nanoparticle application in a wide range of biological, environmental, and technological fields. Furthermore, the efficiency of a magnetic nanoparticle can be improved by biochar. It is a carbon-rich solid material which has low-cost and environment-friendly, and biochar is attractive as an efficient absorbent with its large surface area, and powerful ion exchange. With its carbon storage capacity, it can help reduce greenhouse gases emissions. In recent years, magnetic biochar has been widely used in the removal of pollutants from water.

Sugarcane bagasse biochar is cheaper because the manual labour is far cheaper and easily available whenever and wherever it is needed in developing countries. Therefore, the cost-limiting factors such as collection, transportation and processing of sugarcane bagasse reinforce its utility in different biotechnological processes for such developing agricultural lands. This can help the industries to develop such technologies by having low investment. Whereas the public also can be live in better environment without disturbing the natural resources for their daily lifestyles. Individual contributions address the improvement of the magnetic biochar knowledge base, current information gaps, and future biochar research needs. The prospect of biochar utilization is promising, as magnetic biochar may be customized for specific environmental applications.

1.1 Sugarcane bagasse biochar

Sugarcane bagasse is the residual material derived from sugarcane after extracting cane juice. The bagasse will represent a predominately lignocellulosic feedstock. Compare with other agricultural residues, SCB is a carbon rich biomass which highly abundant and suitable for biochar production. Over 850,000 tons of bagasse generated in Florida in the United States are either burnt directly as fuel in sugar mills or disposed in landfills [4]. Huge quantity of sugarcane bagasse which is estimated at 30.00

% of the crop are generated during the sugar manufacturing process in all the tropical and subtropical regions on the worlds. It is practical to use this huge quantity of waste in the development of eco-friendly technologies [5]. Nevertheless, to satisfy the requirements of wastewater treatment, it is necessary to improve the catalytic performance of biochar through various modification and activation techniques [6].

In the process of remediating used oil aqueous solution, the use of biochar has been suggested. The practical applications of conventional biochar for contaminant immobilization and removal however need further improvements. Thus, recent consideration has focused on modification of biochar with novel structures and surface properties in order to improve its remediation efficiency and environmental benefits. Engineered biochar are commonly used terms to indicate application oriented, outcome-based biochar modification or synthesis.

1.2 Biochar magnetic nanoparticles

The multifunctional characteristics of biochar show its potential as an effective sorbent for contaminants in water and wastewater. Though, powdered biochar is harder to be separated from the aqueous matrix which makes practically unattractive for the users. Thus, to ease a better separation of biochar particles after treatment process, some attempts have been made to produce magnetic biochar sorbents. Engineered biochar has been produced by magnetic modification process to enhance its sorption of anionic contaminants. This is because the surface of biochar is mostly net negatively charged, therefore sorption of anionic contaminants is relatively low. The magnetic biochar that prepared by chemical co-precipitation of Fe^{3+}/Fe^{2+} normally has smaller surface area that non-magnetic biochar. However, the average pore diameter of the magnetic biochar was larger than that of non-magnetic biochar. Generally, magnetic biochar contained considerable proportion of iron oxide, which have small surface areas and abundant transitional pores (2-50 mm). Fe_3O_4 magnetic nanoparticles showed negligible demulsification effect, however, under both neutral and acidic conditions, APFS-coated MNPs could efficiently flocculate oil droplets mainly by electrostatic attraction and enabling magnetic separation. Whereas, under alkaline condition, MNPs can overcome electrostatic repulsion and be absorbed onto oil droplet surface via hydrophobic interaction, thereby exhibiting certain demulsification effect under magnetic field [6]. This study is mainly focused on the removal of oil waste by using iron oxide sugarcane bagasse bicohar.

2. Materials and methods

2.1 Experimental procedures

Sugarcane bagasse collected from a stall which selling sugarcane juices at Bukit Gambir, Johor. Then, it washed under running tap water as shown in remove contaminants and excess sugar. Then, they were and dried under sun for 3 days as shown in until constant weight achieved and stored in container for the next processing. 200g of dry sugarcane bagasse is then heat in a carbonization furnace PLF Series 140-160 (PROTHERM, Turkey) at a pyrolysis temperature of 400℃ with a fix residence time of 1 hours. Then the dried sugarcane bagasse impregnated with zinc chloride with ratio $ZnCl_2$ to C is 2:1[4]. Then, the sugarcane bagasse was filtered and carbonized at pyrolysis temperatures 600℃ for 2 hours. Then it was washed with 0.1 mol/L HCl and washed with deionized water until get pH 6-6.5. After that, the biochar was dried in oven with temperature 300℃ for 1 hour. The dried sugarcane bagasse was sieved through sieves size of 150 µm. The sugarcane bagasse biochar then stored in an airtight container for further use.

The iron oxide sugarcane bagasse biochar was prepared as shown in Figure 1. 20 g of sugarcane bagasse was dissolved completely in 200 ml deionized water. At the same time, 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 stirred using magnetic stirrer for 20 minutes with 400 rpm speed at room temperature (23–26 °C). Then 0.1 mol/L of NaOH was add dropwise into the mixture with vigorous stirring until the solution reached the pH 10-11. The mixtures were continued to stir and boiled for 1 hour. After boiled, the sample was filtered and wash with deionized water. Then the sample washed with ethanol for several time and lastly dried at 70℃ for 12 hours.

For the oil removal test, the turbidity of the waste oil solution was measured before and after the experiment in each set of experiment. The iron oxide sugarcane bagasse biochar together with the oily solutions then vigorously mix. Then a strong magnet is used to remove the oil from the aqueous solution. The percentage of removal of oil and the adsorption capacity is calculate using equation 1 and 2 shown below:

$$\text{Percentage Removal} = \frac{c_o - c_e}{c_o} \times 100\% \qquad \textit{Eq.1}$$

$$\text{Adsorption capacity} = \frac{Co - Ce}{m} \times V \qquad \textit{Eq.2}$$

Where, Co is initial turbidity of the waste oil solution Ce is final turbidity of waste oil solution (%), m is the mass of magnetic sugarcane bagasse biochar and V is the volume of oil solution.

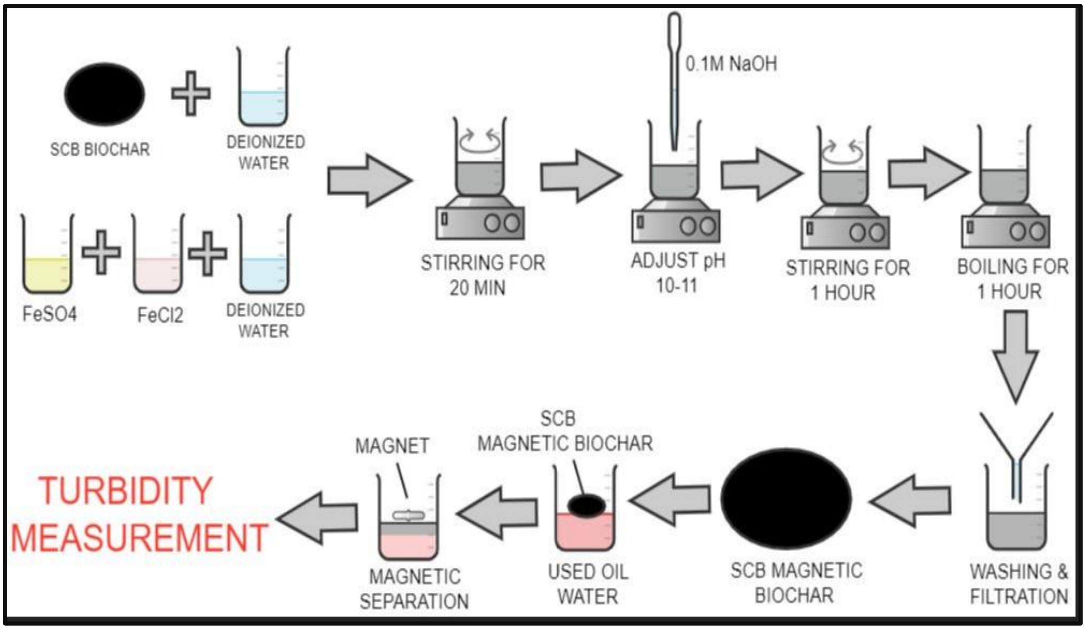


Figure 1: Preparation of iron oxide sugarcane bagasse biochar for turbidity measurement

2.2 Adsorption experiment

Batch experiment was conducted to determine the optimum operational parameters of dosage, contact time and concentration in separating the oil waste from aqueous solution as shown in Table 1. The experiments were performed at room temperature (26 ± 2ºC). The experiment is start by using three quantity 200-ml measuring beaker contacting with 0.5 g, 1.0 g and 1.5 g magnetic biochar with different concentration of waste oil solution (0.25 %, 1.00 %, 5.00 %) and shaking at 10,60 and 120 seconds at room temperature 25. At first 40 ml of waste oil aqueous solution pours into 3 beakers. Then iron oxide sugarcane bagasse biochar slowly adds to the solution and shake gently for the fixed time. The rate of oil removal from the aqueous solution determines by contacting by iron oxide sugarcane bagasse at various intervals of time. The attract waste oil and iron oxide sugarcane bagasse biochar was recycled for the second and also third beaker. The removal of oil was determined by measuring the turbidity before and after the experiment.

Table 1: Parameters of the adsorption experiment

No	Parameter	Variable Value
1	Concentration of oil (%)	0.25, 1.0, 5.0
2	Dosage(g)	0.5, 1.0, 1.5
3	Contact time(s)	10, 60,120

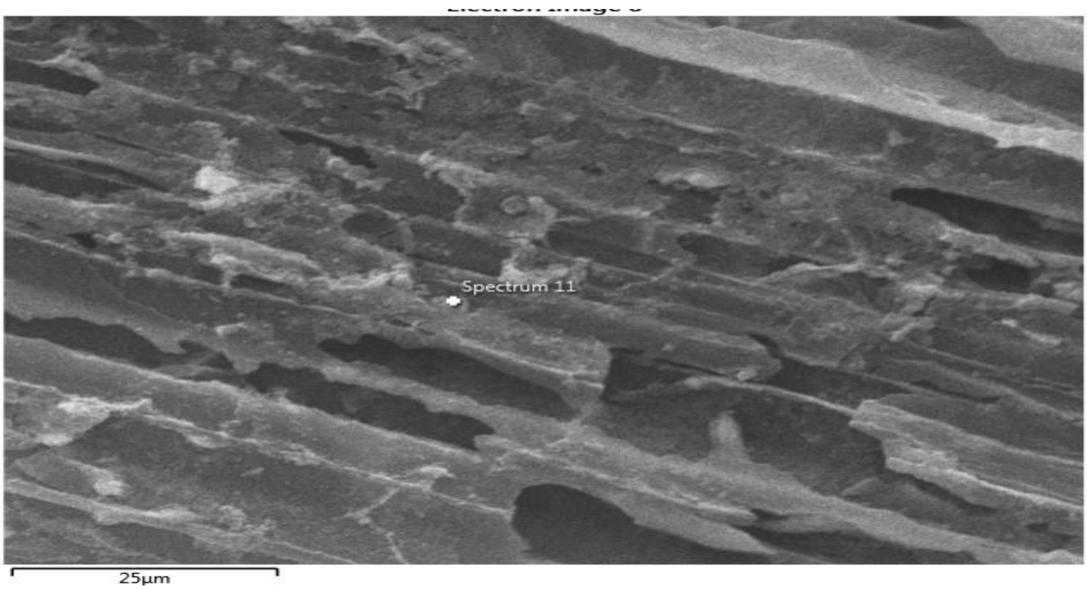
2.3 Recycled experiment

The iron oxide sugarcane bagasse biochar used in first cycle was reused for the second and third cycle for the recycled experiment. After each first cycle of experiment the iron oxide biochar was separated with a magnet and turbidity of the solution was measured. The adsorption cycle of iron oxide biochar was conducted 3 times to evaluate the recycle efficiency.

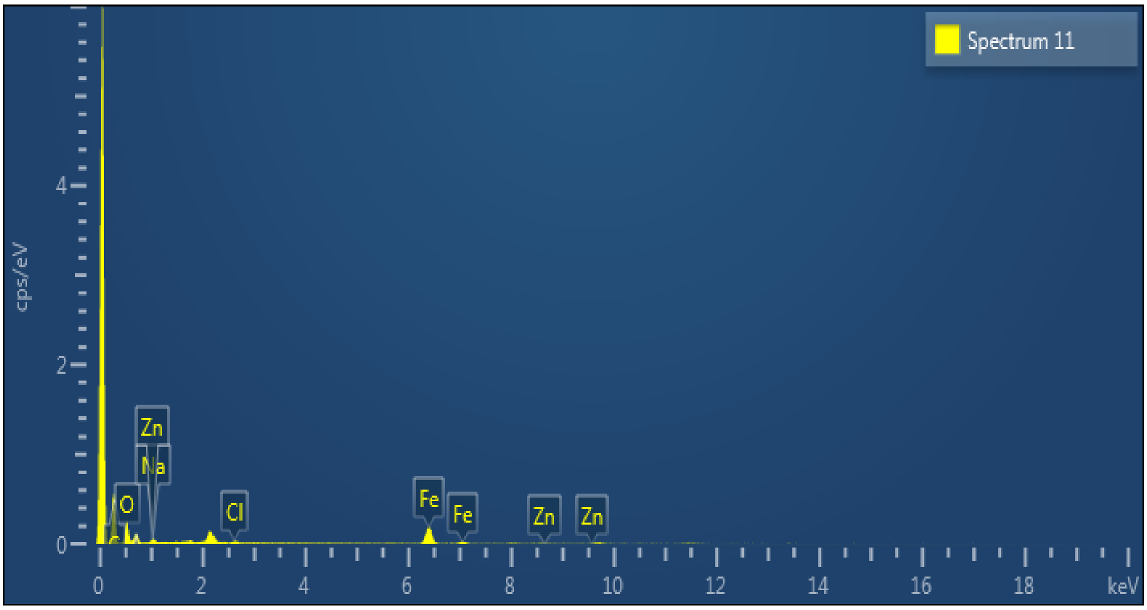
3. Results and discussion

3.1 Characterization of magnetic sugarcane bagasse biochar

The iron oxide biochar is characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). SEM images of the produced iron oxide sugarcane bagasse biochar are clearly shown in Figure 2(a), which was consistent with the structure observed by [8]. Porous structures and larger sized pores with some agglomerations could be observed at the surface of magnetic biochar. In addition, the porosity of the biochar and the size of the voids increased when the high temperature was applied as N2 and iron oxide particles were effective in creating well developed pores on the surface of the precursor, hence leading to novel iron oxide biochar with a large surface area and porous structure [7]. Moreover, the iron oxides formed on the surface of iron oxide sugarcane bagasse biochar ease the adsorption of oil. The presence of iron oxide affects the agglomeration of small particles on the surface of the biochar. A further EDX elementary composition analysis, as shown in Figure 2 (b), confirmed the presence of Fe, O, Zn, Na and Cl ions.



(a)



(b)

Figure 2: SEM image of (a) magnetic sugarcane bagasse biochar at 25 µm and (b) EDX analysis for magnetic sugarcane bagasse biochar

Iron oxide sugarcane bagasse biochar was analyzed using FTIR spectroscopy. Figure 3 shows that iron sugarcane bagasse biochar has several functional groups attached on the surface of biochar. Band 3712 cm^{-1} could be categorized to medium, sharp O-H stretching groups of alcohol, which indicated that existing functional groups containing hydrogen and oxygen due to the dehydration and decarboxylation reactions at the high temperature of pyrolysis. Peak located at 2341 cm^{-1} is a strong, broad N=C=O stretching isocyanate group. The new peak could be assigned at 1114 cm^{-1} which is a strong C-O stretching secondary alcohol and it indicated that this the porous carbon contained a small quantity from the carboxyl group [8]. However, the peak around 652 cm^{-1} is assigned to a strong C-Br stretching halo compound.

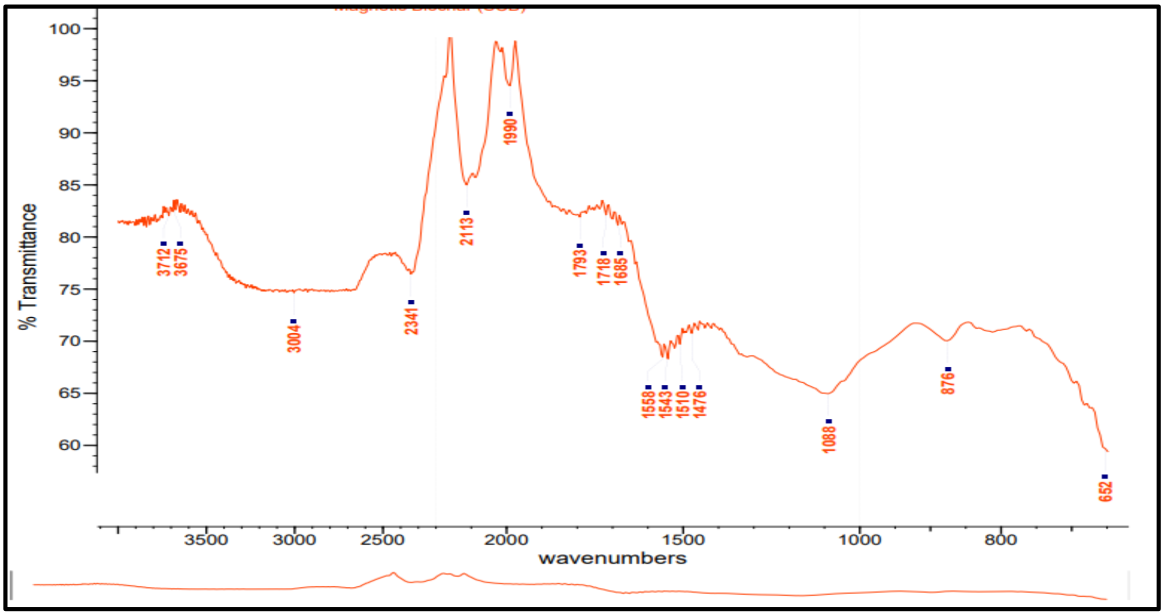


Figure 3: FTIR spectra of magnetic sugarcane bagasse biochar

3.2 Efficiency of the iron oxide biochar

The efficiency of waste cooking oil removal was determined with different concentration of oil, dosages of iron oxide sugarcane bagasse biochar and contact time. Figure 4 shows that 99.99 %, was the highest removal of 0.25 % oil concentration for 1.5 g of iron oxide sugarcane bagasse biochar at 10,60 and 120 seconds. Whereas 91.76 % is the lowest removal of 0.25 % oil for 0.5 g of magnetic sugarcane bagasse biochar at 120 seconds.When the mass of the iron oxide sugarcane bagasse biochar increases the percentage of oil removal also increase because an increase in iron oxide sugarcane bagasse biochar mass led to the increased surface area of iron oxide biochar and the number of adsorption sites available for adsorption [9].

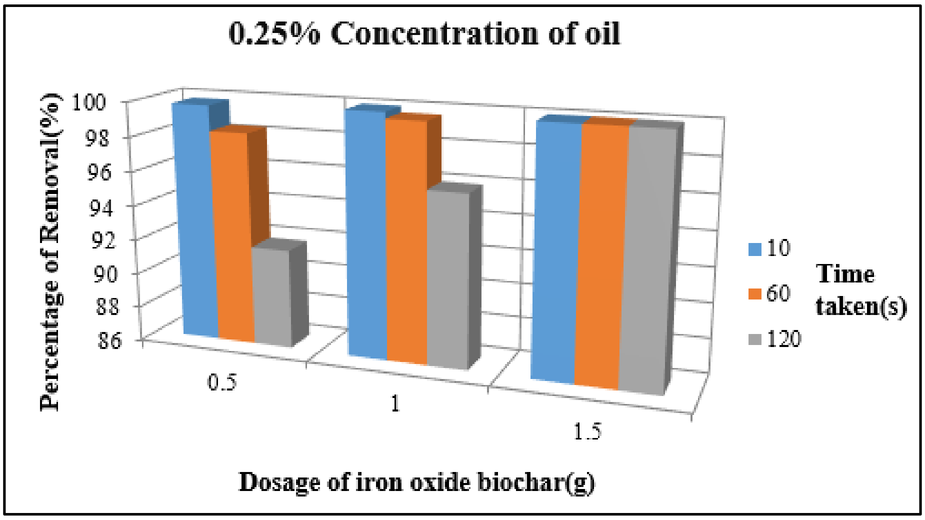


Figure 4: The effect of 0.25% concentration of oil, dosage of magnetic biochar and contact time with the percentage removal of oil

Based on Figure 5, the removal of 1.00 % oil concentration increases from 99.83 %,99.95 % and 99.99 % when contacted with 0.5 g of iron oxide sugarcane bagasse at 10, 60 and 120 seconds. At the same time, the removal of 1.00 % oil concentration decreased from 99.99 %, 99.99 % and 99.68 % when contacted with 1.0 g iron oxide sugarcane bagasse at 10, 60 and 120 seconds. This shows that the performance of iron oxide sugarcane bagasse must be increased with the time taken because the longer the time taken the greater the percentage of removal.

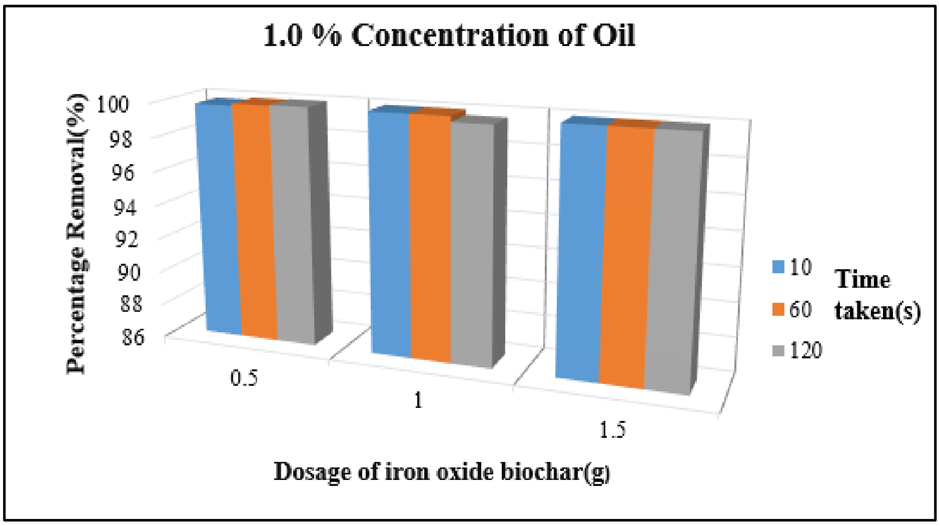


Figure 5: The effect of concentration of oil, dosage of iron oxide biochar and contact time with the percentage removal of oil

Figure 6 indicates, 99.99 % is the highest removal of 5.00 % oil concentration for 1.0 and 1.5 g of iron oxide sugarcane bagasse biochar at 10, and 60 seconds. Whereas 97.55 % the lower removal of 5.00 % oil concentration for 0.5 g of iron oxide sugarcane bagasse biochar at 120 seconds.This proves that 1.0 g and 1.5 g of iron oxide sugarcane bagasse is more efficient when contact with greater concentration of oil.

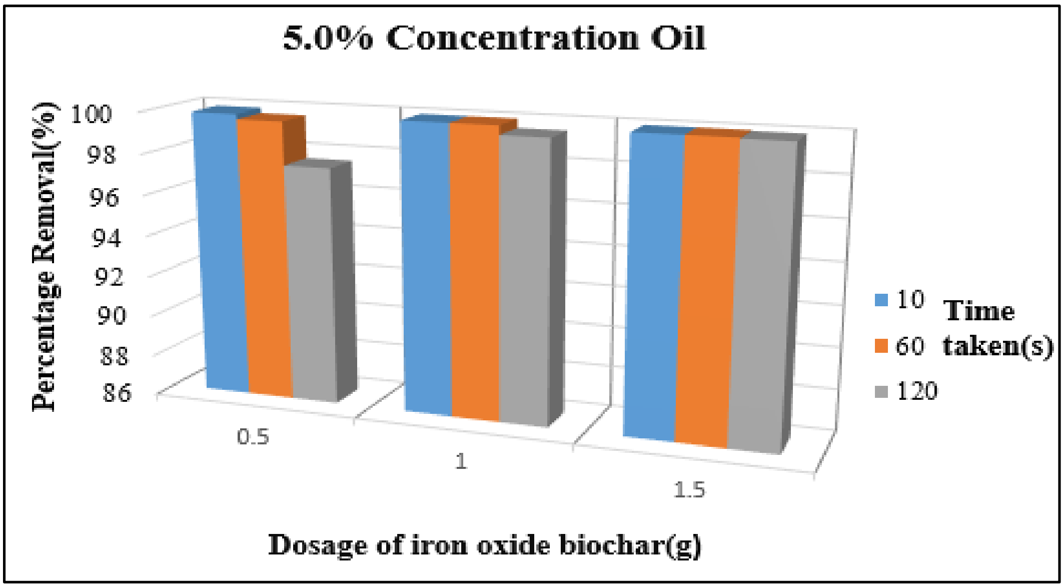


Figure 6: The effect of concentration of oil, dosage of magnetic biochar and contact time with the percentage removal of oil

3.3 Recyclability of the iron oxide biochar

The efficiencies of removal of waste cooking oil are decreased which 99.99 %,99.29 % and 98.84 % for 3 cycles of adsorption process when contacting with 0.25 % concentration of oil with 1.5 g of iron oxide sugarcane bagasse at 120 seconds, demonstrating the successful recycling of iron oxide sugarcane bagasse biochar adsorption process. This observation correlates well with the longer contact time of lower oil concentration and greater dosage of iron oxide biochar illustrating more secure anchoring of iron oxide sugarcane bagasse biochar at the oil-water interface [10].

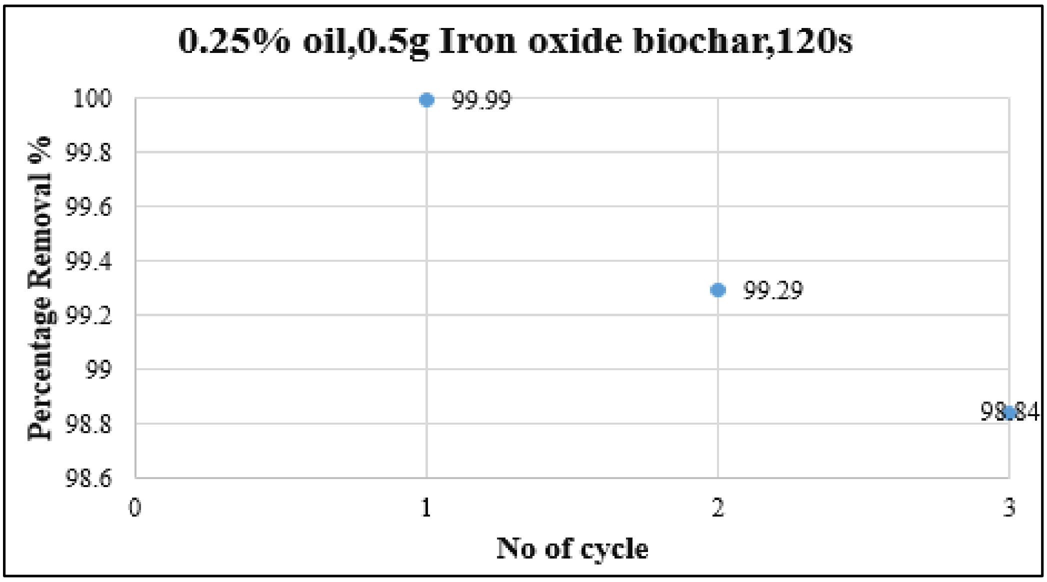


Figure 7: The effect of number of cycles with the percentage removal of oil

3.3 Adsorption capacity

Adsorption capacity is used to describe the amount of oil adsorbed by per unit mass of iron oxide sugarcane bagasse biochar. Adsorption capacity was calculated for recyclability study at highest percentage removal and the results for the first cycle was 55.0 mg/g followed by 49.97 mg/g for second cycle and 47.58 mg/g for third cycle as shown in Figure 8. After three cycles, the adsorption capacity of iron oxide sugarcane bagasse biochar was kept decreased because attributed to the bonding sites of iron oxide sugarcane bagasse biochar which being destroyed due to adsorption of oil in cycle 1 and cycle 2 [11]. Whereas the adsorption capacity increased with increasing the mass of the iron oxide sugarcane bagasse biochar due to the saturation of adsorption sites on the iron oxide sugarcane bagasse biochar at lower concentration of waste oil. From the results obtained get summarized that the iron oxide sugarcane bagasse was able to adsorb the waste oil under different dosage, contact time and concentration of oil. The iron oxide sugarcane bagasse biochar is more efficient when contacted with higher dosage of iron oxide sugarcane bagasse biochar with longer contact time. The higher the dosage and contact time, the greater the removal of waste oil because of more binding sites and perfect time for the adsorption of waste cooking oil. Unluckily, the higher concentration of oil is less suitable for the adsorption process because at higher concentration oil waste oil the density and viscosity will increase which will reduce the adsorption capacity [12].

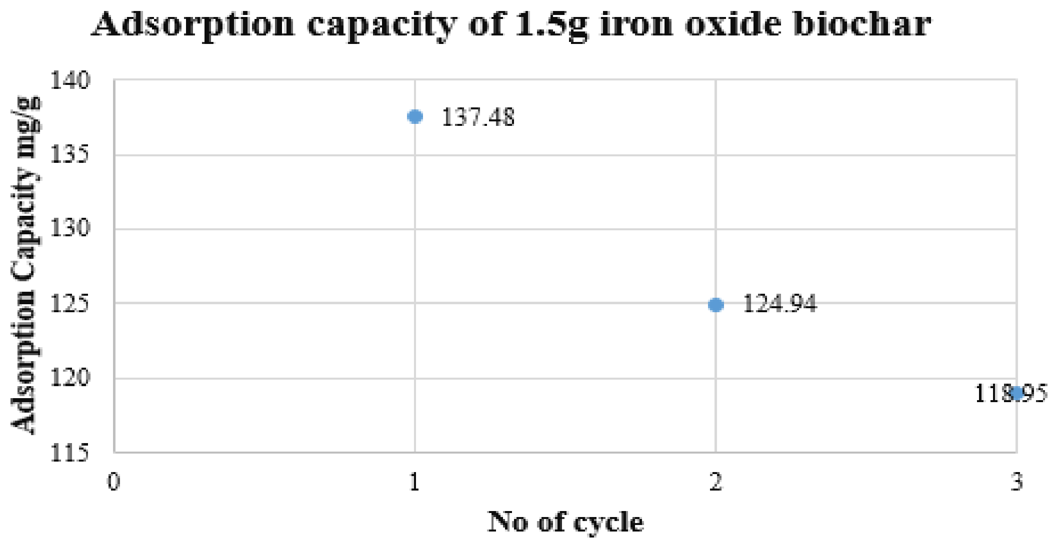


Figure 8: Adsorption capacity of iron oxide sugarcane bagasse biochar

4. Conclusion

In this study, the effective separation of oil waste was achieved when contact with 0.25 % concentration of oil,1.5 g of iron oxide sugarcane bagasse at 120 seconds with a separation efficiency of 99.00 %. The iron oxide sugarcane bagasse has the capacity to separate oil waste from water. Furthermore, the results from the recyclability test which proves that at 0.25 % concentration of oil, 0.5g iron oxide sugarcane bagasse at 120 seconds have better performances as 99.00 % of oil removal was achieved at the end of process. This shows that low-cost, biodegradable and naturally available cellulosic materials, leading to applications to oily wastewater treatment without generating secondary hazards to the ambient environment.

Acknowledgement

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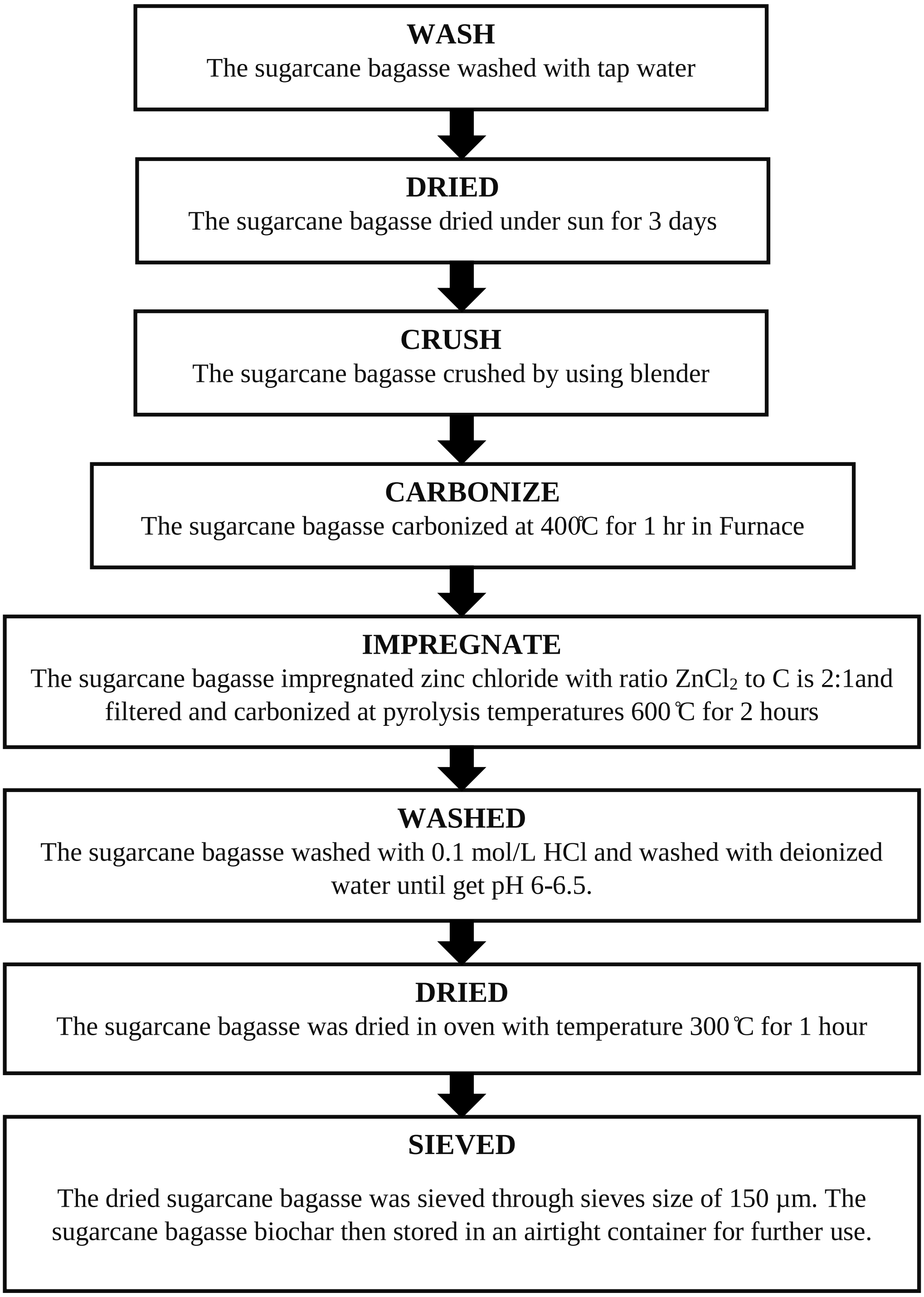
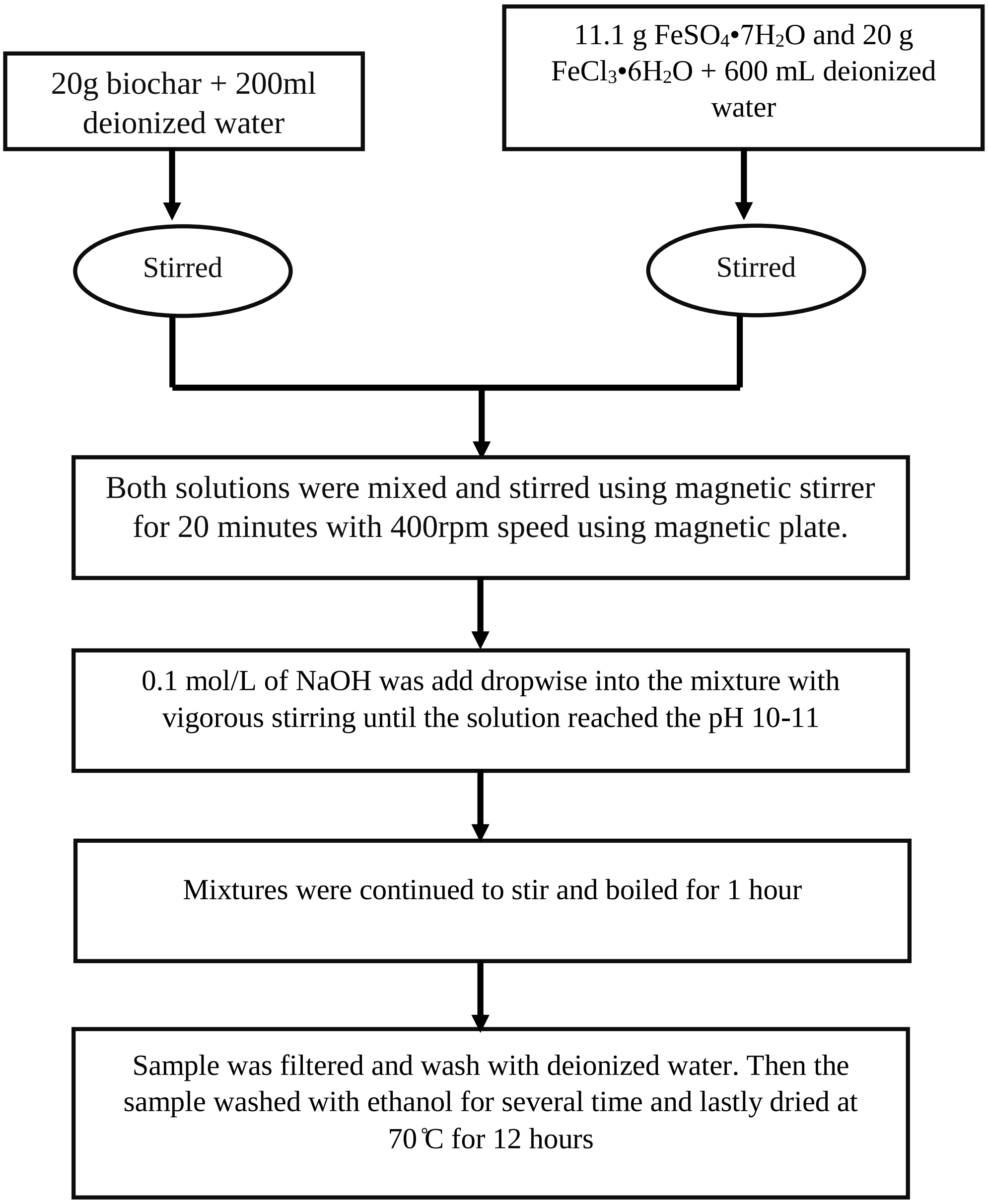
APPENDIX A


WASH
The sugarcane bagasse washed with tap water
DRIED
The sugarcane bagasse dried under sun for 3 days
CRUSH
The sugarcane bagasse crushed by using blender
CARBONIZE
The sugarcane bagasse carbonized at 400℃ for 1 hr in Furnace
IMPREGNATE
The sugarcane bagasse impregnated zinc chloride with ratio $ZnCl_2$ to C is 2:1and filtered and carbonized at pyrolysis temperatures 600℃ for 2 hours
WASHED
The sugarcane bagasse washed with 0.1 mol/L HCl and washed with deionized water until get pH 6-6.5.
DRIED
The sugarcane bagasse was dried in oven with temperature 300℃ for 1 hour
SIEVED
The dried sugarcane bagasse was sieved through sieves size of 150 µm. The sugarcane bagasse biochar then stored in an airtight container for further use.

APPENDIX B


20g biochar + 200ml deionized water
11.1 g $FeSO_4 \cdot 7H_2O$ and 20 g $FeCl_3 \cdot 6H_2O$ + 600 mL deionized water
Stirred
Stirred
Both solutions were mixed and stirred using magnetic stirrer for 20 minutes with 400rpm speed using magnetic plate.
0.1 mol/L of NaOH was add dropwise into the mixture with vigorous stirring until the solution reached the pH 10-11
Mixtures were continued to stir and boiled for 1 hour
Sample was filtered and wash with deionized water. Then the sample washed with ethanol for several time and lastly dried at 70℃ for 12 hours