Oil Spill Removal using Coconut Shell Based Composite Magnetic Activated Carbon

P F Megat Khamaruddin, M L Abdullah

Abstract: Activated carbon from coconut shell has been used as an oil adsorbent for various applications because of its high surface area, micro porosity and good sorption properties. However, the collection process after the sorption process is difficult due to its granular form. Impregnating the activated carbon with magnetic particle can solve the problem by removing the used adsorbent using magnet. The objectives of this study were to determine the optimum activation temperature and to compare the effect of immersion time. The study also investigated the effect of the iron to activated carbon ratio on oil removal capacities and the potential of reusability of the composite magnetic activated carbon. The activated carbon was produced by pyrolysis and activated at 600°C, 800°C and 1000°C. This was followed by the preparation of the composite magnetic activated carbon by co-precipitation method. The magnetic adsorbent was then characterised by using FTIR spectra and the surface characteristics was analysed using surface analyser. The highest oil removal were samples prepared at activation temperature of 800°C with the composite adsorbent oil removal was at 2 g/g which was 11.5% more than the activated carbon sample. Higher concentration of iron did not benefit the oil removal process as the higher the concentration of iron used, the less oil was adsorbed. Finally, the reusability of the composite magnetic activated carbon showed promising result.

Keywords: activated carbon, coconut shell, magnetic adsorbent, oil spill removal.

I. INTRODUCTION

An oil spill is an event when either crude oil or refined oil products are discharged directly on water or land. The spilled oil properties changes by a wide assortment of chemical, physical and biological process causing catastrophic impact to the environment.

There are many remediation methods of removing and controlling oil spill. Such as using booms containment, skimming, chemical dispersants, emulsion breakers, solidifiers, in-situ burning and biodegradation agents (either natural or assisted). Adsorption is a preferred method for oil removal due to its relatively lower processing cost. In the case of removing oil from the water surface, the adsorbent material should be oleophilic and hydrophobic. This means the material should attract oil and not water in order for it to be an effective oil spill removal material. There many natural materials that can be used as the oil sorption materials such as waste cotton, milkweed, kenaf [1], Ciba pentandra (L.) Gaertn. [2], barley straw, cotton grass, coconut husk and silk worm cocoon waste [3]. Peels of fruits was also used such as banana skins, potato peel and orange peels [4]. These materials were proven to be an effective oil removal material. The types of oil tested in these studies also varies such as diesel, crude oil, engine oil, vegetable oil and many others.

Coconut fruit is widely available in Malaysia where the solid and liquid endosperm is food to be eaten, for drinking or cooking whereas the other parts of the coconut fruit are thrown as waste. Coconut waste such as the endocarp is a well-known precursor to the production of activated carbon. It is known to be used to adsorb many pollutants either from gaseous phase or liquid. One of the pollutants is oil from aqueous systems [4], [5].

However, one of the major disadvantage faced when using activated carbon from coconut shell in powder form is the removal of it from the oily aqueous system. The removal work consumed so much effort and a time consuming task. To overcome this, there are studies that looked into using magnetic adsorbents [5], [6], [7] where the usage of magnet simplifies the removal of used adsorbents.

In this study, the coconut shell based activated carbon was impregnated with iron oxides using simple co-precipitation method to become a magnetic composite adsorbent to aid the removal process. The oil removal effectiveness was investigated and compared with the raw coconut shell and the activated carbon coconut shell. Hence, the objectives of this research were to determine the effect of activation temperature and immersion time on oil removal capacity, and to investigate the effect of the activated carbon to iron ratio on oil removal capacities. The potential of reusability of the adsorbent was also investigated. The oil used in this study was lubricating oil.

II. METHODOLOGY

A. Preparation of Coconut Shell and Iron Composite Activated Carbon

The coconut shells (CS) were dried at 110°C then carbonised under flowing nitrogen atmosphere at 600°C using a tubular furnace (MTI OTF 1200X series).
Next, the carbonised coconut shell was crushed into fine powder form using heavy duty grinder and sieved using 0.5 mm Analytical Sieve.

Basic activation method was used in this research by using potassium hydroxide (KOH). The KOH pellet (R&M Chemicals, 85% purity) was mixed with carbonised coconut shell with carbon to KOH of 1:2 for 24 hours using a hot plate that was set at 50˚C and 150 rpm for the stirring purpose. This followed with activation process in the same tubular furnace at 600˚C. The activated carbon was washed with deionized water until it obtained pH 6 to 7 and dried in an oven at 100˚C for about one hour. These steps were repeated for carbonisation temperature of 800˚C and 1000˚C. The samples (denoted as AC) were transferred to a beaker and ready to be used for the preparation of magnetic composite activated carbon.

Magnetic activated carbon was prepared using in-situ co-precipitation technique. The weight ratio of the activated carbon (activation temperature of 600˚C) to iron in the final composite material was fixed as 1:1. The activated carbon was first dispersed in 300 mL water that contained molar mixture of 2:1 ratio of FeCl₃·6H₂O (Merck) and FeSO₄·7H₂O (Merck). Forty-five (45) mL of ammonia solution (R&M Chemicals, 30%) was added into the beaker containing the mixture to precipitate the activated carbon-iron particles. The precipitate was then filtered and heated in the oven at 100˚C for 24 hours to remove the water and facilitate the binding of the iron particles to the surface of the activated carbon. Finally, it was washed several times till water pH was neutral. These procedures were repeated for coconut shell activated carbon with the activation temperature of 800˚C and 1000˚C. These samples are denoted as CMAC.

B. Characterisation of the Adsorbent

Infrared (IR) spectra were recorded on the FT-IR spectrometer to identify the functional groups of the CS, AC and CMAC. The FTIR model used was Spectrum One Model Perkin Elmer. The surface area and porosity measurements were performed using Micromeritics 3Flex surface analyser.

C. Oil Removal Capacity Experiment

The following procedures were repeated for these experiments. The first was the determination of oil removal capacities using lubricant oil for adsorbents prepared at different temperature. The type of lubricant oil used as 10W-40 (4T). Adsorption immersion time was manipulated for the second experiment. The third experiment was to determine the effect of three iron to activated carbon ratio on oil removal capacity. The ratio used was 1:1, 1:2 and 1:3. And the final experiment was to explore the possibility of reusability.

Distilled water was used as the aqueous system in simulating the oil spill where 60 mL was poured into a 100 mL beaker. Then, 20 mL of the tested oil was added. Five g (5 g) of the tested material was smeared over on top of the oily surface in the prepared beaker. The beaker was then weighed as the initial weight. Tested material used were raw grinded coconut shell as the control material (CS), activated carbon coconut shell (AC), composite magnetic activated carbon adsorbents (CMAC).

The sorbents were left for 30 seconds and it was recovered by using filter for CS and AC samples. Permanent external magnet was used to remove CMAC samples. It was then weighed for the second time and the weight of the water adsorbed by the sorbent was also noted to get the weight of the removed oil. The oil removal capacity was calculated by referring to the value of increment between the initial and the final reading in grams (g). All the sorption experiment was performed in duplicate at standard room temperature and pressure condition.

III. RESULTS AND DISCUSSION

A. Characterisation of Adsorbents

The FTIR spectra of CS, AC and CMAC are shown in Fig. 1. It was observed that there are multiple sharp peaks that appeared between 2321 to 2376 cm⁻¹ for all samples which was identified as the carbon dioxide spectrum [8]. Another peak that appeared for all three samples is at 668 cm⁻¹. This strong peak is due to the bending vibration of C-H functional deformation. The CS sample (Fig. 1(a)) shows the most complicated spectrum. A strong and broad peak appeared at 3377.09 cm⁻¹. This corresponds to the O-H functional group in the raw sample. However, this peak was not present in both the AC (Fig. 1(b)) and the CMAC sample (Fig 1(c)). This most likely suggest that most of the O-H functional group in the CS sample was due to moisture. This moisture was removed due to the high temperature during the drying stage for the AC and CMAC samples. The CS sample also shows a peak between 3000 to 2800 cm⁻¹ (Fig. 1(a)). This relates to the presence of alkyl group which was expected as CS is an organic compound. This group is one of the important functional group that indicates the its potential as an oil removal material [3]. Additional peaks in the range of 1600 to 1400 cm⁻¹ means there was a presence of aromatic compounds in the CS sample (Fig. 1(a)). Whereas the peaks in the range of 1300 to 1000 cm⁻¹, shows that either esters or ethers are present in the CS sample. This can be associated to the presence of plant wax. All these peaks were not seen for AC and CMAC samples. Table I shows the surface area, pore volume and pore size of all samples. The BET surface area for all the AC samples irrespective of the activation temperature, were smaller than the CMAC samples where the highest surface area was the 1000˚C CMAC sample at 2.968 m²/g. This is because the impregnation of the iron oxide in the activated carbon could change its surface, hence increasing the surface area. Similar trend was observed for pore volume and pore size of the AC and the CMAC samples prepared at 600˚C and 800˚C. However, for samples prepared at 1000˚C, the CMAC sample pore volume and pore size were smaller than the AC sample. This is probably due to the high activation temperature. It was also determined that there is a significant difference in pore volume (~47%) and pore size (~74%) higher for 800˚C CMAC compared to 1000˚C CMAC samples, even though the BET surface area for the latter sample was higher. It was also noted that the pore sizes for all samples falls within the mesopores region (2-50 nm) [9].
Fig. 1. FTIR spectra of (a) raw coconut shell (CS), (b) activated carbon (AC) and (c) composite magnetic activated carbon (CMAC).
Table- I. BET surface areas, pore volumes and pore sizes calculated by the BET equation.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C AC</td>
<td>0.819</td>
<td>0.00145</td>
<td>70.87</td>
</tr>
<tr>
<td>600°C CMAC</td>
<td>0.909</td>
<td>0.00264</td>
<td>116.24</td>
</tr>
<tr>
<td>800°C AC</td>
<td>0.999</td>
<td>0.00337</td>
<td>134.97</td>
</tr>
<tr>
<td>800°C CMAC</td>
<td>1.378</td>
<td>0.00484</td>
<td>140.37</td>
</tr>
<tr>
<td>1000°C AC</td>
<td>1.088</td>
<td>0.00266</td>
<td>97.78</td>
</tr>
<tr>
<td>1000°C CMAC</td>
<td>2.968</td>
<td>0.00254</td>
<td>35.46</td>
</tr>
</tbody>
</table>

Fig. 2 shows the nitrogen adsorption-desorption isotherms (at 77K) of the activated carbon (AC) activated at 600, 800 and 1000°C. Based on the shape, there is unrestricted monolayer-multilayer adsorption which is typical of Type II isotherm. The slight uptake at low relative pressure indicated significant amount of overlap of monolayer coverage and the onset of multilayer adsorption [10]. The plateau with a similar slope was observed for AC samples at 800 and 1000°C. This suggest a similar mesoporous surface area. It was also observed that all three curves have an adsorption ‘tail’ at high pressure and a desorption hysteresis loop due to adsorbate condensation in the mesopore. Comparatively, the highest adsorption was achieved by activated carbon prepared at 800°C. This finding is similar with [11].

The nitrogen adsorption-desorption isotherms for 600°C and 800°C CMAC samples however, is seen as closer to Type III isotherm with Type H4 hysteresis loop (Fig. 3). Type III isotherms have no inflection point at low relative pressure seen for samples in Fig. 2 except for 1000°C CMAC, which have a gradual curvature. Hence, this means there was no identifiable monolayer formation and the adsorption took place clustered around favorable sites on the surface of the adsorbent. The hysteresis loops were clearly observed for 800°C and 1000°C CMAC samples. This is commonly found in micro-mesoporous carbons. Comparatively, the highest adsorption was achieved by CMAC prepared at 800°C. The comparison of the quantity adsorbed for samples activated at 800°C for both AC and CMAC showed that the latter adsorbed more at high relative pressure (Fig. 2 and Fig. 3).

Fig. 3. Nitrogen adsorption isotherms of CMAC samples as a function of activation temperature.

B. Oil Removal of AC and CMAC Samples

Fig. 4 shows that the removal of lubricant oil at different activation temperature for all samples. The highest oil removal was 800°C AC sample at an average of 1.76 g/g, followed with 600°C AC sample and the lowest was 1000°C AC sample. This corresponds to the nitrogen adsorption isotherm and the pore volume value (Fig. 2). The pore volume for 800°C AC which was the highest when compared to the other AC samples (Table 1). Similar trend was also seen for CMAC samples (Fig. 4) where the oil removed was closer to 2 g/g. Between AC and CMAC samples activated at 800°C, the latter oil removal capacity was greater than AC for samples with a difference of approximately 11.5%. This difference is due to additional effect of the iron impregnated in the CMAC samples. According to [12], iron oxides is proven to be a highly hydrophobic and oleophilic particles. Hence, its presence in the CMAC samples enhances the adsorption capacity.

It was also noted that CS samples removed more of the lubricating oil than the samples activated at 1000°C. The probable reason was that the pore diameter for samples activated at 1000°C was smaller than the CS samples hence, it was unable to absorbed the lubricating oil. The other probable reason was the pores were damaged when the samples were activated at high temperature.
C. Effect of Immersion Time

This test was to study the oil removal capacity by varying the immersion time using samples activated at 800°C. The time used beside 30 seconds are 60, 90 and 120 seconds. From Fig. 5, it can be clearly seen that the sample immersion time affects the oil removal capacity. As the immersion time increases, the removal capacity increases. The oil removal capacity for the raw coconut shell was at the lowest compared to the two other samples which was 1.44 g/g when immersed for 30 seconds. At 60 seconds the value jumped to 2.46 g/g, then 2.79 g/g at 90 seconds and slows down to 2.83 g/g at 120 seconds. This trend was also observed for AC and CMAC samples. It was also noted that the oil removal capacity was reaching to its maximum as the difference between 90 sec. and 120 sec. was smaller compared to between 30 sec. and 60 sec. Similarly, to the earlier findings, it was observed that the CMAC samples were capable of adsorbing more lubricant oil at 3.09 g/g compared to AC at 2.95 g/g.

![Fig. 5. Lubricant oil removed at selected immersion time for CS, 800°C AC and 800°C CMAC.](image)

D. Effect of Activated Carbon to Iron Impregnation Ratio

This part of the research was to study the effectiveness of using different impregnation ratio of activated carbon to iron on oil removal using all the tested activation temperature samples. The additional impregnation ratio used were 1:2 and 1:3. Fig. 6 shows that the 1:1 ratio have the highest lubricant oil removal. When the ratio changed to 1:2 and 1:3, the oil removal capacity started to decrease. This may be due to the fact that the iron has invaded the pore of the activated carbon, thus reducing the space for oil to be removed. Although the effect for increasing the ratio of activated carbon to iron can increase the easiness to recover the adsorbent from the oil spill (Fig. 7), it is not the crucial purpose to the use of the adsorbent. Thus, it can be concluded that the best ratio to impregnate the AC to iron is 1:1.

E. Reusability Potential

The 800°C CMAC was used to study the reusability potential of the sample towards the oil removal. After the completion of the oil removal process, the sample was heated in a tubular furnace at the temperature of 500˚C for 1 hour, under nitrogen gas atmosphere for the separation of the removed oil and the sample. Fig. 8 shows the weight of the samples after the heating process (desorption) and the oil removed after subsequent cycles of usage. Even though the slope was not steep, it was noted that the sample weight after desorption increased slightly after each cycle. Which means that there was some accumulation of oil on the adsorbent after the desorption process. On the other hand, the slope for oil removed showed steep decline after second cycle and then slowly decreasing for the next subsequent cycles. This can be described as the oil removal capacity difference between two immediate sequence, which was calculated to decrease by 23% after the second cycle and then reduced and remain stable around 4% up to the fifth cycle. This means that the CMAC can be reused to remove oil up to 5 times and maybe more for lubricating oil.
Oil Spill Removal using Coconut Shell Based Composite Magnetic Activated Carbon

Fig. 8. Reusability potential of 800°C CMAC sample.

Another finding that can be assumed from this reusability result is that the removal of oil using the prepared samples is a physical adsorption process. This is proven by the removal of the oil from the adsorbents using heat. Hence, it can be safely assumed that the forces that hold the oil molecules onto the surface of the adsorbent is intermolecular forces (van der Waals forces) because the force weakens due to kinetic energy received by the molecules due to increment in temperature.

IV. CONCLUSION

This study has managed to prove that lubricant oil can be removed more efficiently using composite magnetic activated carbon based on coconut shell and it can be reused multiple times. The removal process of used adsorbent was found to be less tedious with the aid of magnet for the composite magnetic activated carbon.

ACKNOWLEDGMENT

The authors thanks Universiti Teknologi MARA for the financial assistance (RMI File No. 100-IRMI/GOV 16/6/2 (016/2018)).

REFERENCES


AUTHORS PROFILE

Putri Faizura Megat Khamaruuddin is currently a senior lecturer at Universiti Teknologi MARA and is a member of Integrated Separation Technology and Research Group (iSTRONG), Faculty of Chemical Engineering. She graduated with BEng. Chemical Engineering from Bath University, UK, M Tech. Environmental Management from Universiti Malaya, Malaysia and PhD Chemical Engineering from Universiti Teknologi PETRONAS, Malaysia. Her current research areas are in wastewater treatment, oil removal and separation, and environmental management.

Muhammad Luqman Abdullah was born on 24 April 1994 in Hospital Besar Ipoh. He received his first education in Sekolah Kebangsaan Jalan Panglima Bukit Gantang and continue in Sekolah Menengah Agama Izzuddin Shah. He then continued his study in Perak Matriculation College before getting his bachelor's degree in Oil and Gas Engineering at Universiti Teknologi Mara (UiTM), Shah Alam. He managed to be one of the best student's in SPM 2011. Now, he works as a researcher with Institute of Public Health, Ministry of Health Malaysia.