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Research on Oil Adsorption Capacity of Carbonized Material Derived from Agricultural by-product (Corn Cob, Corn Stalk, Rice Husk) Using in Oily Wastewater Treatment

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Abstract: Oily wastewater discharged from machinery producing, mining, storage service, marine transporting... is one of the polluting sources to receiving waterbody. Adsorption onto carbonized material derived from agricultural by-products are proved to be the promising treatment for this type of wastewater. Experiments implemented with the agro-wastes including: corn cob, corn stalk and rice husk with carbonizing temperature of 300-600 ^{o}C and retention time of 1-3h. According to the results of all carbonized materials, the decrease of oil adsorption accosiated with higher pyrolysis temperature, as well as longer retention duration. Under the same carbonizing conditions, the carbon derived from corn stalk have the higher adsorption capacity. The highest oil sorption capacity of 6.4 g/g is of corn stalk derived carbon with temperature of 300 ^{o}C, retention time of 1h; while the lowest one of 2.33 g/g is of material derived corn cob with temperature of 600 ^{o}C, 1h. The oil adsorption capacity is closely related to the porosity and oleophilic groups on the surface of the material. The results indicated that materials made from agricultural by-products, corn stalk in particular, are promising for oily wastewater treatment.

Keywords: Corn cob, corn stalk, rice husk, oily wastewater.

1. Introduction

In Vietnam, the redundant of agricultural by-products is one of the most serious problem. In present, the most common treating of these agro-wastes is to dispose as solid waste or, in lesser extent, to produce fuel, plant pot... The disposal of wastes causes the surrounding environmental pollution, discharging greenhouse gas as result of their biodegrading. The carbon derived biomass has advantage of low cost, abundant, environmental friendly, high C content, specific porosity of cellulose derived material, accordant with C based material production by carbonizing. The product is able to use for treatment wastewater, especially oil contaminated, occurring in industrial processing, maritime transporting [10]... There are many researchers targeting to remove oil by using agricultural by-products. Kumagai et. al (2007) investigated the oil adsorption by using carbonized rice husk. The result indicated that the biochar produced at 600 ^{o}C is able to use for oil adsorption [4]. Nwadiogbu et. al (2014) acetylated the corn cob to increase the hydrophobicity [6]. Suni et. al. (2004) used the by-product of peat excavation,

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cotton grass fiber to adsorb the oil [7]. Adsorption onto carbonized agricultural by-products are proved to be the most effective treating methods for organic compounds in wastewater, with the oil removal efficiency of about 99 % [8], inexpensiveness and ease of operation [1].

Among of agricultural wastes in Vietnam, rice husk, corn cob and corn stalk are the most common, significant high volume for producing low cost adsorbents. Therefore, this research aims to produce low cost carbon material from the aforementioned by-products in order to remove the oil in industrial wastewater.

2. Method

2.1. Precursor collecting and characterization

The agricultural by-products used in this study include: corn cob; corn stalk; rice husk. All samples are collected from waste disposal location in Luong Son district, Hoa Binh province and Hanoi. The sample is pretreated by dried in room temperature. The corn cob is grinded and sieved to achieve the particle of 3-5 mm diameter. The stalk is cut into pieces with average length of 20-30 mm. After that, all samples are stored in dried bottle.

2.2. Material carbonizing

The weighted samples are placed into horizontal reactor. Then, the carbonization implemented by using the furnace Emin SX2-5-12 (China) is occurred in different temperature and retention time. After the carbonization, the char sample is cooled by air, dried in 105 ^{o}C to remove the humidity. The carbon sample is weighted to determine the carbonization efficiency. The samples are denoted as X-Y-Z, whereas X: name of raw material; Y: carbonization temperature; Z: retention time.

2.3. Analytical method

Porous volume of carbon sample are determined according to distilled water pycnometer method [2]. The maximum oil absorption capacity of char sample is determined according to the method of ASTMF726-99 [5] using weight difference analyzing. Oil sample used is commercial DO with specific density in 15 ^{o}C of 820-860 kg/m^3, dynamic viscosity in 40 ^{o}C of 2 - 4,5 cSt (according to Saigonpetro Co. Ltd). The SEM image of sample is obtained by using Jeol 5300 (Japan). The IR spectrum is obtained by using Nicolet iS10 from Thermo Scienticfic, USA. TG-DTA of sample is collected by TGA209F1, from NETZSCH, Germany.

3. Results and discussion

3.1. Effect of carbonizing conditions

Effect of carbonizing temperature:

Figure 1 showed the TGA result of precursor samples, there is dramatically change in precursor mass within temperature of 300-600 ^{o}C, with value of about 50%. This could be explained by the thermal degradation of hemicellulose and cellulose [9]. In concluded, the carbonizing temperature used in this research is about 300 - 600 ^{o}C, which could cause significant change in structure of samples.

Figure 2 illustrated the effect of carbonizing temperature to the quality of chars. In general, compared at similar carbonizing conditions, the oil adsorption and pore volume of char derived from corn stalk is the largest, then followed by rice husk and corn cobs. At temperature of 300 ^{o}C, retention time of 1h, the oil adsorption capacity and pore volume of char derived from corn stalk, rice husk and corn cob are 6.4 g/g, 6.9 mL/g; 5.7 g/g, 6.7 mL/g and 2.3 g/g, 2.6 mL/g, respectively.

The result indicated that, for 3 precursors, the increase of carbonizing temparature leads to the decrease of oil adsorption capacity as well as pore volume of each chars, but with different trends. At same retention time (1h), the oil adsorption capacity corn stalk derived char reaches the maximum of 6.4 g/g at 300 ^{o}C, decreased constantly to the minimum of 3.9 g/g reached at 600 ^{o}C. The trend of pore volume change of corn stalk chars is fluctuated. It reaches the highest of 6.9 g/L at 300 ^{o}C, then dramatically decreased to the lowest of 4.1 g/L at 500 ^{o}C, followed by the increase to 4.6 g/L at 600 ^{o}C. There are similar variability trends between oil adsorption and pore volume of corn cob as well as rice husk carbon samples. The highest value of oil adsorption capacity and pore volume of rice husk derived chars are 5.7 g/g and 6.7 g/L at 300 ^{o}C, followed by the constant decrease and reached the lowest of 3.4 g/g and 3.6 g/L at 600 ^{o}C, respectively. There is slightly decrease of oil adsorption capacity and pore volume of corn cob chars with the upturn of carbonizing temperature. The highest of them are 2.3 g/g and 2.6 g/L at 300 ^{o}C, while the lowest of 1.7 g/g and 2.2 g/L are reached at 600 ^{o}C.

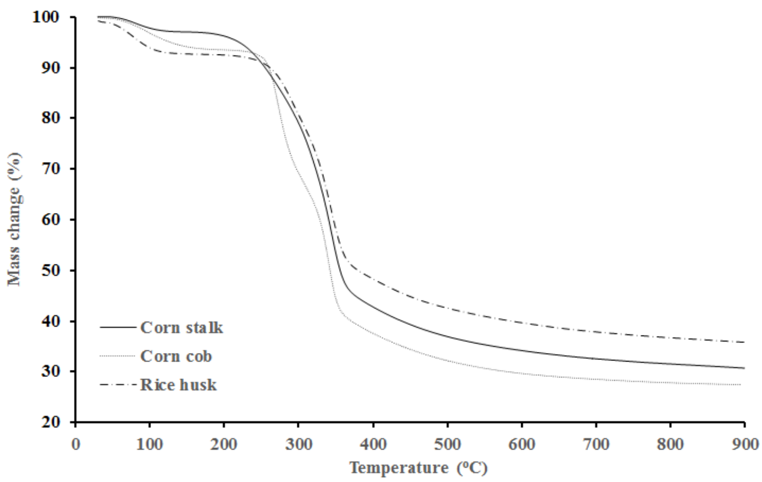

Figure 1. The TGA result of precursor samples.

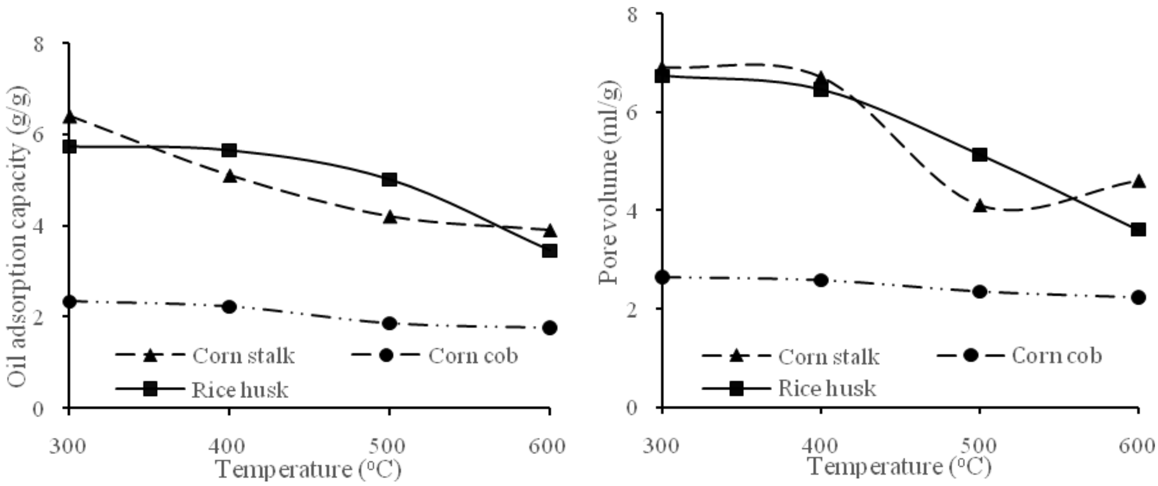

Figure 2. Effect of carbonizing temperature.

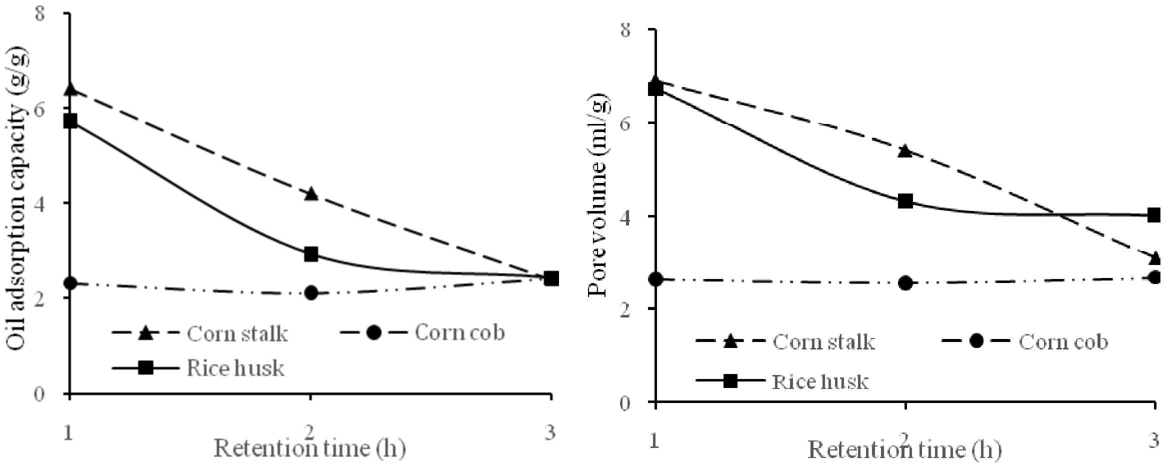

Figure 3. Effect of retention time.

Effect of retention time

Figure 3 showed the effect of carbonizing retention time. Similar to temperature, the retention time of carbonization effects significantly to the character of biochars derived from corn stalk and rice husk; negligible with ones from corn cob. In general, the longer retention time is, the lower value of oil adsorption capacity and pore volume of chars. For all chars, the highest value of them are reached at 1h of retention time, while the lowest achieved at 3h of retention time. The oil adsorption capacity of corn stalk chars at 1h and 3h of retention time are 6.4 and 2.4 g/g, while the value the pore volume are 6.9 and 3.1 mL/g, respectively.

According to the result, the effect of carbonizing conditions (temperature, retention time) to oil adsorbing characters of chars (oil adsorption capacity; pore volume) is significant. To better understand the structure of pore system and functional groups on surface, which contribute to oil adsorbing characters, the SEM and FT-IR experiments are implemented.

3.2. Discussion

As indicated from the aforementioned result, the samples produced at carbonizing condition of 300 ^{o}C and 1h have the best character for oil adsorption. Therefore, these samples of all precursors are chosen for further research in order to investigate the appearance structure of pore, functional group.

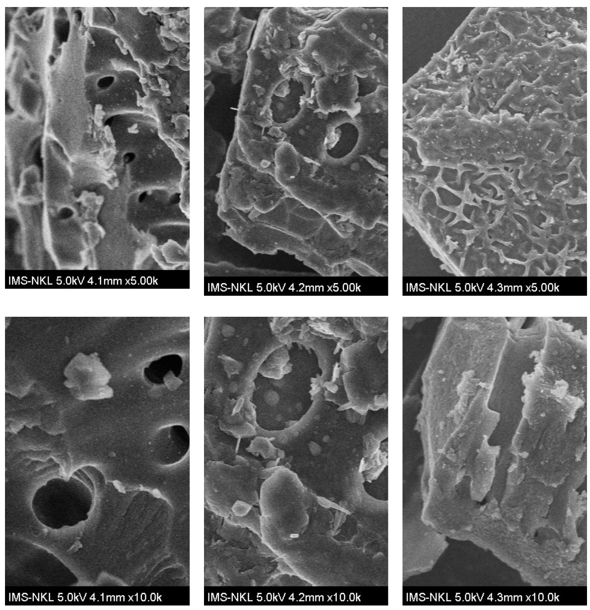

Figure 4. The SEM image of chars produced at 300 ^{o}C, 1h. (Corn cob (a, d), Corn stalk (b, e), rice husk (c, f)).

The result of SEM indicated that, with all of the char samples, the diameter of pore are about 1 - 4 µm. The pore diameter of corn cob, corn stalk and rice husk derived char are about 1 - 2, 2 - 4 and 2 µm, respectively. The oil droplet in water has the diameter of about 0.5 - 5 µm. Therefore, the pore of char samples are favorable for oil adsorption. The diameter of pore of char samples is classified as macro-pore originated from the precursor. Gray et. al. (2014) suggested the shrinkage of pore structure increase with the upturn of temperature [3], resulting the destructive of macro-pore. This could explain the reason of decrease of oil adsorbing character of char sample with elevation of carbonizing temperature.

The large pore of corn stalk could be one of the reasons explaining for the highest value of pore volume, as well as oil adsorption capacity. However, the diameter of pore of rice husk char is relatively small although the oil adsorbing character of this char is comparable with one of corn stalk char. It can be explained by the structure of pore. As illustrated in SEM results, the pore structure is complicated, crisscrossed by the system of hollow shaped pore. This could increase the pore volume of char, create more adsorption site of oil.

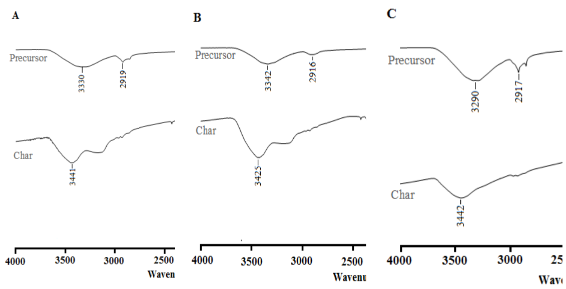

Figure 5. The IR spectrum of precursor and char samples (A: Corn cob; B: corn stalk; C: rice husk).

The result of FTIR spectra are performed in Figure 5 and 6. In general, the spectra graph of all precursors are relatively similar, which peaks include: 3330-3350 cm^{-1} (-OH stretching of hydroxyl group, phenol, acid carboxylic), 2850-2950 cm^{-1} (-C-H stretching of aliphatic), 1450-1650 cm^{-1} (-C=C- stretching of aromatic), 1650 - 1750 cm^{-1} (-C=O group of ester (ascribed to hemicellulose, acid carboxylic, aldehyde), 1036 - 1075 cm^{-1} (-C-O stretching in cellulose, hemicellulose and primary alcohol), 750 - 800 cm^{-1} (-C=C- bending of aromatic), 550 - 650 cm^{-1} (C is out of plane -C-H band, alkanes, -Si-O-Si- especially for rice husk sample), 480 - 590 cm^{-1} (-OH out of plane bending) [3, 6].

Compared to the result of precursors, one of char samples produced at 300 ^{o}C, 1h indicate the significant difference, especially for corn cob and corn stalk derived chars. Beside the peaks of –OH stretching of hydroxyl group, -CH stretching of aliphatic similar with ones of precursor sample, the peaks of –CH deformation in –O-C=O-CH_3 appear intensity at about 1359 – 1440 cm^{-1} [6]. This could be the result of hemicellulose and cellulose degradation in temperature of about 200 – 350 ^{o}C [8].

The result indicate that, the increase of carbonizing temperature leads to the diminishing of functional group abundance and diversity [3]. Except for rice husk derived samples, there is a significant increase of –CH aliphatic peak, which is of interest as positively correlating with hydrophobicity in biochars. However, the peaks representing for hydrophilicity of biochars such as –C=C- of aromatic, -C=O and –OH of ionisable hydroxyl group, show negligible change.

From all of the result reported, it could be concluded that:

i. The higher carbonizing temperature is, the longer retention time is, then the lower value of oil adsorbing character of chars (oil adsorption capacity, pore volume).

ii. The pore structure and chars are favorable the adsorption of oil.

iii. Except for rice husk chars, the carbonization results into the increase of hydrophobicity of biochar, while there is slightly change in hydrophilicity.

For further investigation, the oleophilic fluid produced in carbonization should be investigated. According to Kumagai et al (2007) [4], there is evident that this fluid contributes to the oil adsorption. Furthermore, the water uptake capacity of biochar causes negative effect to apply the biochar for oil adsorbing. The result of maximum water uptake capacity of chars derived from corn stalk, corn cob and rice husk (which is not showed in this article) are relatively high. The future investigation would include the research of lower water uptake capacity.

4. Conclusion

The experiments indicated the oil adsorption capacity of biochars derived from agricultural by-products such as corn stalk, corn cob and rice husk. The highest oil adsorption capacity of char samples are obtained at temperature of 300 ^{o}C, retention time of 1h. The increase of carbonizing conditions result in the downturn of oil adsorption of chars. The oil adsorption character of corn cob and rice husk chars are much better than one corn cob, showing the promise material for oil adsorbent. Further research is needed to investigate the oleophilic fluid as well as the method to decrease the water uptake capacity.

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Nghiên cứu khả năng hấp phụ của vật liệu than hóa có nguồn gốc từ phế liệu nông nghiệp (lõi ngô, thân ngô, vỏ trấu) nhằm sử dụng trong xử lý nước thải nhiễm dầu

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Tóm tắt: Nước thải nhiễm dầu mà được xả thải từ quá trình chế tạo cơ khí, khai thác mỏ, lưu giữ kho bãi, vận chuyển đường biển... là một trong những nguồn ô nhiễm đưa vào thủy vực. Quá trình hấp phụ lên vật liệu than hóa có nguồn gốc từ phế liệu nông nghiệp được coi là phương pháp xử lý có triển vọng đối với loại nước thải này. Các thí nghiệm được tiến hành với các phế phẩm nông nghiệp bao gồm: lõi ngô, thân ngô và vỏ trấu với nhiệt độ than hóa từ 300-600 ^{o}C, thời gian lưu từ 1-3 h. Dựa trên các kết quả thu được từ tất cả sản phẩm than hóa, nhiệt độ than hóa càng cao, thời gian lưu càng lâu thì khả năng hút dầu càng thấp. Ở cùng điều kiện than hóa, mẫu than có nguồn gốc từ thân ngô có khả năng hút dầu cao hơn các mẫu than có nguồn gốc từ lõi ngô và vỏ trấu. Mẫu than thân ngô được chế tạo ở 300 oC, thời gian lưu 1h có dung lượng hấp phụ dầu cao nhất ở mức 6,4 g/g; trong khi dung lượng hấp phụ dầu thấp nhất đạt 2,3 g/g thuộc về mẫu than từ lõi ngô mà chế tạo ở 600 oC, 1h. Dung lượng hấp phụ dầu có mối tương quan chặt chẽ với độ xốp và nhóm chức ưa dầu trên bề mặt than. Các kết quả chỉ ra rằng sự hấp phụ dầu lên vật liệu được chế tạo từ phế liệu nông nghiệp, đặc biệt là thân ngô, là phương pháp khả quan trong xử lý nước thải nhiễm dầu.

Từ khóa: Lõi ngô, thân ngô, vỏ trấu, nước thải nhiễm dầu.