Adsorption of Petroleum Hydrocarbon by Modified Biomass Carbon

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Abstract. In order to improve the oil adsorption performance of biomass carbon, a new oil removal absorbent was prepared by modifying natural material. Hydrophobic agent is used as modifier to graft biomass carbon. The structural characteristics and microstructure of biomass carbon treated by modifiers are characterized by FTIR spectroscopy and SEM observation. The results showed that self-made biomass charcoal has good floatability, and biomass carbon treated by the hydrophobic agent has a higher oil adsorption capacity than those of untreated ones. Peanut shell carbon and corn cob carbon modified by nano-SiO₂ dispersant obtained the best results with an oil absorption rate of about 1.5 g/g and an oil retention rate of about 95%. As determinate by GC/MS, the modified biomass carbon before and after the adsorption of marine oil, the alkane changed significantly, indicating that the adsorption capacity of oil is very obvious.

Keyword: Adsorption, Materials, Experimental method, Carbonized

1. Foreword

Oil pollution is one of the most common pollutants in the Marine environment [1]. According to statistics, 6 million to 10 million tons of oil and petroleum products enter the ocean through various channels every year [2]. At present, one of the most common and effective methods to deal with oil spill pollution is physical adsorption, that is, adsorption material adsorption method [3]. The adsorption materials can be divided into three categories: inorganic mineral materials, organic synthetic materials and natural biomass materials [4,5].

Moreover, natural biomass materials as a non-toxic, biodegradable material, has excellent environmental performance [6,7]. As incited considerable research interest from industries and institutions [8,9], biomass material has poor hydrophobicity and suspended shortcomings. Thus, it is difficult to use in direct adsorption of in seawater oil spill [10]. A mixed acid (oleic acid, stearic acid and capric acid) was used by BANERJEE to esterification modification sawdust with n-hexane and H₂SO₄ used in preparation of the sorbing material. It thereby has a higher adsorption capacity of crude oil than unmodified sawdust [11]. Moreover, Wang Yanmin demonstrated that a new modified raw sawdust was prepared by pyrolysis at 260°C for 8 h, and the new material soaked up 2.5 times more pure oil than unmodified sawdust [12].
The fiber surface of natural biomass materials is rich in hydrophilic hydroxyl, which seriously affects its oil absorption ratio, suspension performance, oil retention performance and reusability [12]. However, the current modification methods mainly focus on the modification of fiber structure, and few natural biomass materials is hydrophobically modified. In this study, selects the north main crops straw as raw material, hydrophobic reagent was used to prepare biomass carbon to improve the performance of oil adsorption. The modified biomass carbon was characterized and analyzed by Fourier-transform infrared spectroscopy (FTIR) and Electron microscope.

2. Materials and Methods

2.1. Materials

Peanut stalks, corn stalks, peanut shells, fruit tree branches, soybean stalks and corn cobs were obtained from local farms in Shandong province. The liquid paraffin, nanometer silica dispersant and trimethoxy silanol were obtained from from Yantai shuangshuang chemical co, Ltd., China. The methyl methacrylate and fluorinated nanometer silicon dioxide solution was obtained from Tianjin rujinte chemical co, Ltd., China.

2.2. Experimental method

2.2.1. Sample pretreatment

Firstly, the materials were defoliated and washed with water to remove the dirt on the surface. Then, it was cut into short rods with a length of 2~3cm and placed in the electric blast drying.

2.2.2. Coking process

In order to improve the carbonization rate and obtain ideal results carbonized, the short rods will be in strict accordance with the temperature and time given in Table 1 for biomass charcoal fire. After firing, the samples were removed and cooled to room temperature for subsequent testing.

| Sequence number | Species       | Carbonization temperature ℃ | Fire time min |
|-----------------|---------------|-----------------------------|--------------|
| 1               | Maize straw   | 410                         | 5            |
| 2               | Peanut straw  | 415                         | 6            |
| 3               | Soybean straw | 440                         | 10           |
| 4               | Corncob       | 405                         | 5            |
| 5               | Peanut shell  | 420                         | 7            |
| 6               | Fruit trees   | 440                         | 10           |

2.2.3. Modified process

Five hydrophobic reagents are selected to modify biochar respectively. The modification process is as follows:

- **Liquid paraffin**: a certain amount of solution and 0.5 g biomass charcoal were mixed, and it completely immerse into the solution for 1min, and then dry it in a ventilated place.

- **Nano-SiO$_2$ dispersants**: 0.5 g biomass charcoal was taken and completely immersed in the reagent for 30 s. Then, it was suspended above the container for 60 s. After baking at 60 °C in an oven for 10 min, the samples were removed.

- **Trimethoxysilane**: 3 g NaOH solid was dissolved into 20 mL water, and 0.5 g biomass charcoal was soaked in it for 3min and drying. Then put into trimethoxysilane for 30s and place it in a ventilated place for drying treatment.

- **Methyl methacrylate**: take an appropriate amount of solution and biomass charcoal were mixed in the beaker for 1min, then remove it.

- **Fluorinated nano-SiO$_2$ solution**: soak the biomass charcoal in the solution for 30 s and then remove it.
2.2.4. Rough screening of oil absorption performance and floating performance

(1) Preliminary treatment

40 mL of seawater was injected into 37 containers (36 of which were experimental group and 1 was control group) respectively, and 0.6 g of medium-fired F180 marine oil was added to each container, with a mass of 44.42 g after refueling.

Fig. 1 shows the extent of oil diffusion in the control group within 2 hours. After 2 hours, the color of the mixture of oil and water in the container remained unchanged, and the oil did not spread. The experiment began when the color of the experimental group and the control group reached the unity.

Figure 1. Oil diffusion in the control group

(2) Coarse sieve experiment

To 36 containers of oil-water mixture into different charcoals, static after 8 hours after classics agitate. Then, remove the oil-water mixture of carbon, to the weighing of solution, observe whether surface residual oil and observe the solution color change. Moreover, to judge the oil absorbency, watch the amount of residue at the bottom of the container to judge the performance of floating.

2.2.5. Accurate screening of oil absorption and flotation properties

A certain amount of marine fuel and 300 mL seawater were mixed into a 1L measuring cup with a constant temperature magnetic stirrer. Then, set the temperature at 17.5 ℃ to simulate the temperature of sea water. When the oil is stirred evenly into a mixture of oil and water, start the experiment.

Next, a small part of modified biomass charcoal was taken out, and the measured mass was denoted as the starting mass. Keeping the rotation of the oil-water mixed solution to simulate sea waves, putting the biomass carbon into the oil-water mixed solution, fishing out the biomass carbon after 5 minutes. And standing above the cup mouth for removing excess water and oil. Then weighing the fished biomass carbon and recording the biomass carbon as m2. After putting the fished biochar in an inclined tray and standing for 15 min, the measured mass is recorded as m3. Finally, Q (oil retention rate) and K (oil absorption rate) are calculated according to formulas (1) and (2).

\[ K = \frac{m_1 - m_2}{m_1} \, (g/g) \]  
\[ Q = \frac{m_1 - m_3}{m_1 - m_2} \times 100\% \]

3. Results and Discussion

3.1. Results carbonized
Table 2 shows the calculation results of carbonization rate of biochar. According to the calculation results, it can be judged whether the 6 kinds of biochar meet the expected carbonization rate of 40%.

| Serial number | Species        | Mass after carbonization /g | Volume /cm³ | Density g/cm³ | Coking rate % |
|---------------|----------------|-----------------------------|-------------|--------------|--------------|
| 1             | maize straw    | 2.58                        | 52          | 0.050        | 36.9         |
| 2             | corncob        | 2.66                        | 24          | 0.111        | 38.5         |
| 3             | peanut straw   | 3.86                        | 29.6        | 0.131        | 55.3         |
| 4             | peanut shell   | 3.24                        | 48.7        | 0.067        | 46.2         |
| 5             | soybean straw  | 2.37                        | 19.8        | 0.120        | 33.9         |
| 6             | fruit trees    | 2.43                        | 15          | 0.162        | 34.7         |

From Table 2, it can be seen that the carbonization rate of peanut straw, soybean straw and fruit tree branches has a large deviation from the ideal carbonization rate. The density of fruit tree branches and soybean straw is high, but the volume is small when the mass is the same. There is still residual air in the furnace during the firing process. In addition, the volume of straw is small and the residual air is large, the combustion is more intense, thus affecting the carbonization rate. Moreover, peanut straw has less air residue, resulting in high carbonization rate.

3.2. Rough screening results of oil absorption and flotation properties

Table 3 to Table 8 showed the results of crude screening experiments for adsorption of oil by five biochars, respectively. From the experimental data, it can be seen that the modified biochar has better adsorption performance for petroleum than the unmodified biochar. The colour of the oil-water mixture stabilized in about 2 hours after the adsorption of the five biochars. And most of the bottom sediments began to appear in about 1.5 hours and stabilized after 2 hours. The colour of the solution did not change significantly during the long-term immersion for the following 8 hours. This shows that the combination of biomass carbon and hydrophobic materials can achieve the expected effect and have a good oil retention rate. Among them, nano-silica dispersant and liquid paraffin modified biochar group have the most obvious effect.

Table 3. Liquid paraffin modified group

| No. | species      | poor quality/g | Surface oil pollution | Color of oil/water mixture | Bottom residue quantity | Effect of ranking |
|-----|--------------|----------------|-----------------------|----------------------------|-------------------------|-------------------|
| 1   | peanut shell | 1.72           | No                    | Shallow                    | No                      | 5                 |
| 2   | corncob      | 2.34           | Yes                   | Shallow                    | No                      | 3                 |
| 3   | maize straw  | 1.83           | No                    | No                         | No                      | 6                 |
| 4   | fruit trees  | 1.52           | Yes                   | Shallow                    | No                      | 4                 |
| 5   | soybean straw| 1.27           | Yes                   | Shallow                    | A few                   | 2                 |
| 6   | peanut straw | 1.94           | No                    | Shallow                    | No                      | 1                 |

Table 4. Methyl methacrylate modified group

| No. | species      | poor quality/g | Surface oil pollution | Color of oil/water mixture | Bottom residue quantity | Effect of ranking |
|-----|--------------|----------------|-----------------------|----------------------------|-------------------------|-------------------|
| 1   | peanut shell | 2.41           | No                    | No                         | No                      | 3                 |
| 2   | corncob      | 1.68           | No                    | No                         | No                      | 3                 |
| 3   | maize straw  | 2.39           | No                    | Shallow(A slight)          | No                      | 3                 |
| 4   | fruit trees  | 0.97           | Yes                   | Shallow(A slight)          | No                      | 1                 |
| 5   | soybean straw| 1.53           | Yes                   | No                         | No                      | 3                 |
| 6   | peanut straw | 1.21           | Yes(a few)            | Shallow(A slight)          | No                      | 2                 |

Table 5. Nano-silica dispersant modified group

| No. | species      | poor quality/g | Surface oil pollution | Color of oil/water mixture | Bottom residue quantity | Effect of ranking |
|-----|--------------|----------------|-----------------------|----------------------------|-------------------------|-------------------|

| No. | species      | poor quality/g | Surface oil pollution | Color of oil/water mixture | Bottom residue quantity | Effect of ranking |
|-----|--------------|----------------|-----------------------|----------------------------|-------------------------|-------------------|
3.3. Accurate screening of oil absorption and flotation properties

Table 9 shows the results of the fine screening experiment of five kinds of biochar adsorbing oil.

| No. | Name of straw charcoal (The modification reagent)  | m₁     | m₂     | m₃     | K     | Q     |
|-----|--------------------------------------------------|--------|--------|--------|-------|-------|
| 1   | Nano- SiO₂ dispersant modified corn stalk char    | 1.00   | 2.17   | 2.08   | 1.17  | 92.31 |
| 2   | Nano- SiO₂ dispersant modified peanut shell carbon| 1.47   | 3.81   | 3.69   | 1.59  | 94.87 |
| 3   | Liquid paraffin modified peanut straw charcoal   | 1.03   | 1.94   | 1.86   | 0.88  | 91.21 |
| 4   | Modified soybean straw charcoal with liquid paraffin | 1.08  | 1.68   | 1.62   | 0.56  | 90.00 |
| 5   | Corn cob carbon modified by nano- SiO₂ dispersant | 1.60   | 3.90   | 3.78   | 1.44  | 94.78 |

As can be seen from Table 10, the oil absorption rates of peanut shell carbon and corn cob carbon modified by nano-silica dispersant reach 1.59 and 1.44 respectively. Moreover, the oil retention rate
has reached over 94.5%, achieving very ideal results. And only a small amount of powdered carbon
was observed at the bottom. This shows that the bio-carbon modified by hydrophobic agent has good
floatability, oil absorption rate and oil retention rate.

3.4. Sample characterization

3.4.1. Infrared spectrum characterization to compare the effect of water repellent agents on the
structures and properties of the biomass charcoal, FT-IR spectra were employed on the respective
untreated biomass charcoal and animal glue binder treated by nano silica dispersant. The results are
shown in Figure 3 to Figure 6.

Fig.2 depicts the FTIR results of the unmodified corn cob carbon and the treatment of corn cob
carbon by nano silica dispersant. After the modified, the peak value in the characteristic absorption
zone of 3200cm\(^{-1}\)~3600cm\(^{-1}\) changes greatly, the frontal width increases. The O-H stretching vibration
decreases. The peak value decreases near 2875cm\(^{-1}\), producing -CH\(_3\), =CH\(_2\), and ≡CH, enhancing
hydrophobicity and lipophilicity. There was a strong fluctuation at 2000cm\(^{-1}\)~2800cm\(^{-1}\), which was
also relatively reduced at the peak. And the value was smaller than that of unmodified corn cob carbon,
indicating that a small number of C≡C, C≡N triple bonds were generated. At 1600 cm\(^{-1}\)~2000 cm\(^{-1}\), the
functional groups were mainly C=C, RHC=O, and R\(_2\)C=O double bonds. The generation of double
bonds and triple bonds was mainly reflected by the increase of surface hydrophobic functional groups.
In the fingerprint absorption band area, C-C-C deformation vibration occurred at 400cm\(^{-1}\)~500 cm\(^{-1}\),
C-C bond stretching vibration occurred at 800cm\(^{-1}\), and C-O stretching vibration occurred near
1000cm\(^{-1}\)~1240cm\(^{-1}\). It was once again verified that modification was conducive to the improvement
of hydrophobicity and hydrophilicity.

![Figure 2. FTIR of unmodified (a) and modified (b) corncob charcoal](image)

As seen Fig.3, FTIR of modified and unmodified peanut shell carbon has a small change at the
peak value of 3200 cm\(^{-1}\)~3600 cm\(^{-1}\), indicating O-H stretching vibration. C=C, RHC=O, and R\(_2\)C=O
double bonds were formed at 1600 cm\(^{-1}\)~2000 cm\(^{-1}\), and fat peaks appeared at 1000 cm\(^{-1}\)~1240 cm\(^{-1}\),
the peaks became smaller, and C-O stretching vibration occurred. In the fingerprint absorption band area,
C-C-C deformation vibration occurred at 400cm\(^{-1}\)~500cm\(^{-1}\), C-C bond stretching vibration occurred
at 800cm\(^{-1}\), and C-O stretching vibration occurred nearby. The modified corn cob carbon and
peanut shell carbon have similar changes in front and peak at 3200 cm\(^{-1}\)~3600 cm\(^{-1}\), 1000 cm\(^{-1}\)~1240
cm\(^{-1}\), 800 cm\(^{-1}\), and 400 cm\(^{-1}\)~500 cm\(^{-1}\). It indicates that the nano-SiO\(_2\) dispersant increases the surface
hydrophobic and hydrophilic functional groups of the two kinds of biomass charcoal.
3.4.2. Electron microscope observation to compare the effect of water repellent agents on the micropore structure of the biomass charcoal, Electron microscope observation were employed on the respective untreated biomass charcoal and animal glue binder treated by nano silica dispersant. The amount and microporous structure of biochar did not change after modification, while the surface area changed significantly, indicating that the fiber chain structure of biochar would be destroyed after modification, so that the surface area of biochar would change significantly.

3.4.3. Gas chromatographic analysis with nano-SiO$_2$ dispersant of the modified corn cob and peanut shell carbon adsorption was carried out on the Marine oil. The use of biomass charcoal adsorption oil before and after the oil meteorological chromatograms Through the comparison, biomass charcoal for oil has a very good adsorption effect, especially for the paraffin oil with special adsorption effect significantly. C$_9$H$_{20}$ absorbed about 28 million, C$_{10}$H$_{22}$ about 20 million, C$_{15}$H$_{32}$ about 21 million. It is more favorable for adsorption of oil containing short chain alkanes.

4. Conclusion
1) The preliminary screening experiments show that the modification of biochar by hydrophobic agents can obviously improve the oil adsorption effect.

2) The biomass charcoal has good floatability. The nano-SiO$_2$ dispersing agent and the liquid paraffin modified group both achieved good adsorption effect, among which the peanut shell carbon and corn cob carbon modified by the nano-SiO$_2$ dispersing agent achieved the best effect in the comparison experiment in the 36 groups, with the oil absorption rate of about 1.5g/g and the oil retention rate of about 94%.

3) The functional groups of corn cob carbon and peanut shell carbon modified with nano-SiO$_2$ dispersant were changed compared with the unmodified two kinds of straw charcoal through infrared spectrum characterization and determination, so that they had better adsorption effect on oil.

4) Through the determination of meteorological chromatography, before and after the adsorption of Marine oil by corn cob carbon and peanut shell carbon modified with nano-SiO$_2$ dispersant, the alkane in the oil changed significantly, indicating that the adsorption capacity of oil was very obvious.

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