SORPTION ABILITY OF MODIFIED NANO-CARBON MATERIALS

Abstract. In this work expanded graphite (EG) and carbonized rice husk (CRH) were obtained by heat treatment at different temperatures and by using different activating conditions. The samples were tested as sorbent for oil in water. The oil removal efficiency of carbonized rice husks and expanded graphite, were studied as an adsorbent for the removal of emulsified oils from wastewater. Results showed that the oil removal efficiency increased to 10-15% in the case of EG samples after base leaching. As concerns as the carbonized rice husk samples the adsorption capacities are similar and no particular variation with the activation temperature are detected. As a general result the carbonization process induced an increase of the adsorption capacities. Samples were purified and characterized by SEM-EDAX, FTIR, elemental analysis, Proximate analysis and ICP MS.

Keywords: Carbonized rice husk, expanded graphite; Oily wastewater, Adsorbent; Oil removal efficiency.

Introduction

Oil and oil-derivative are the most dangerous water contaminants in Kazakhstan. The oil pollution causes serious environmental problems to aquatic organisms and humans due to the high toxicity of many oil components [8]. The removal of oil and oil-derivative from wastewater by adsorption on solid sorbents is one feasible option to purify waters. To this aim we have prepared solid carbon-based sorbents by heat treatment of natural graphite and rice husk [1]. The aim of my internship at IRC-CNRS was the characterization of these materials and the collection of preliminary data about their oil adsorption capacity.

1. MATERIALS AND METHODS

Sample preparation

Natural graphite (NG) of the Zavalievsky deposit of Ukraine has been used (Zavalievsky Graphite Ltd., Ukraine, Kiev). Natural flake graphite, grade GTO-92, consist of 92.8 wt.% in carbon. Rice husk (RH) has been recovered from a deposit of the filed Kyzylorda in Kazakhstan. EG has been produced at al-Farabi University of Kazakhstan by a heat treatment method (Fig. 1). This is a very simple method in which a mechanical mixture of natural graphite and crystalline zinc nitrate hydrate (Zn(NO₃)₂ x 6H₂O) has been heated in air in a muffle furnace for 20 minutes at variable final temperature. The experimental conditions are listed in the Table 1.

![Figure 1 - Scheme of the synthesis of the expanded graphite](https://example.com/scheme)

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63
The RH carbonization has been performed at the Institute of Combustion Problems in Kazakhstan. 15 g of RH were carbonized in a home-made reactor (Fig. 2) under argon atmosphere at different temperatures for 1 h (Table 2).

![Figure 2 - Schematic diagram the RH carbonization setup. 1. argon cylinder, 2. mass flowmeter, 3. temperature controller, 4. carbonization rector, 5. iron crucible](image)

<table>
<thead>
<tr>
<th>Samples labels</th>
<th>Percentage of components, wt. %</th>
<th>Final temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG350(80/20)</td>
<td>20% NG 80% Zn(NO₃)₂·6 H₂O</td>
<td>350</td>
</tr>
<tr>
<td>EG 400(80/20)</td>
<td>20% NG 80% Zn(NO₃)₂·6 H₂O</td>
<td>400</td>
</tr>
<tr>
<td>EG 600 (80/20)</td>
<td>20% NG 80% Zn(NO₃)₂·6 H₂O</td>
<td>600</td>
</tr>
<tr>
<td>EG 800(80/20)</td>
<td>20% NG 80% Zn(NO₃)₂·6 H₂O</td>
<td>800</td>
</tr>
<tr>
<td>EG 500(70/30)</td>
<td>30% NG 70% Zn(NO₃)₂·6 H₂O</td>
<td>500</td>
</tr>
<tr>
<td>EG 600 (70/30)</td>
<td>30% NG 70% Zn(NO₃)₂·6 H₂O</td>
<td>600</td>
</tr>
<tr>
<td>EG 1000(80/20)</td>
<td>20% NG 80% FeCl₃·6 H₂O</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 1 - Experimental conditions for expanded graphite synthesis

Table 2 - Experimental condition for carbonized RH synthesis

<table>
<thead>
<tr>
<th>Samples labels</th>
<th>Carbonization temperature, °C</th>
<th>Carbonization time, hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRH600</td>
<td>600</td>
<td>1</td>
</tr>
<tr>
<td>CRH700</td>
<td>700</td>
<td>1</td>
</tr>
<tr>
<td>CRH800</td>
<td>800</td>
<td>1</td>
</tr>
<tr>
<td>CRH900</td>
<td>900</td>
<td>1</td>
</tr>
</tbody>
</table>

Washing. The samples have been purified at the IRC-CNR of Naples. 0.3 g of EG 600(70/30) and CRH 600 have been stirred with 50 mL of distilled water for 30 minutes and filtered on a Millipore FHUP 0.45 μm filter membrane. The solid has been recovered and allowed to dry at 105 °C overnight[2,8].

Base leaching. Base leaching treatment was performed in order to remove Zn oxide impurities from the graphitic surface. This treatment was performed on the two EG samples obtained with 70:30 ratio at 500 and 600 °C. These samples have been selected since they exhibited the highest carbon content among the EG samples obtained by using zinc nitrate as activation agent. The base treatment was performed on 0.4 g of material by adding 50 mL of 5M sodium hydroxide (NaOH) solution under stirring at the temperature of 90 °C for 2 h. After cooling to room temperature, the solid was recovered by filtration and washed until neutrality (about 200 ml of water)[3,8].

2. RESULTS AND DISCUSSION

Oil adsorption test.

Oil adsorption tests have been performed accordingly to the procedure reported in [5]. To this aim small boxes with a capacity of ~2 mL have been prepared by using a stainless steel metal grid (~100 μm pore dimensions) (Fig. 3a). Each box has been filled with 0.1 g of sample (sample granulometry above 300 μm) and dipped for 5 minutes in a 100 mL beaker containing 50 mL of water and 1 g of oil (Figs. 3 b,c). After the oil adsorption, the box was allowed dripping for 24 hours (Fig. 3d). After that time the box with the sample was dried at 60 °C overnight. In the oil adsorption tests a commercial carbon black (CB N110 type) was also used for comparison[4,5].
The oil sorption capacity was calculated as follows [7]:
Oil sorption capacity (g/g) = (S_a - S_b)/S_0
Where S_a is the initial mass of the sorbent, S_b is the weight of the spent sorbent (sorbent containing adsorbed oil at the end of the sorption test).

The results of the washing process are reported in Table 3.

<table>
<thead>
<tr>
<th>Name of samples</th>
<th>Water, ml</th>
<th>Time of mix, min</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG600(70/30)</td>
<td>50</td>
<td>30</td>
<td>93.5</td>
</tr>
<tr>
<td>CRH 600</td>
<td>50</td>
<td>30</td>
<td>94.2</td>
</tr>
</tbody>
</table>

The results of ICPMS analyses of the liquids recovered after washings are reported in the table below (Table 4).

<table>
<thead>
<tr>
<th>sample</th>
<th>EG 600(70/30)</th>
<th>CRH600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>67.45</td>
<td>165.8</td>
</tr>
<tr>
<td>Mg</td>
<td>522.1</td>
<td>936.6</td>
</tr>
<tr>
<td>K</td>
<td>236.3</td>
<td>15830</td>
</tr>
<tr>
<td>Ca</td>
<td>707.5</td>
<td>1047</td>
</tr>
<tr>
<td>Mn</td>
<td>13.82</td>
<td>46.6</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Zn</td>
<td>1636</td>
<td>5.648</td>
</tr>
<tr>
<td>As</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Sr</td>
<td>4.096</td>
<td>11.64</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Mo</td>
<td>0.6923</td>
<td>0.6515</td>
</tr>
<tr>
<td>Cd</td>
<td>0.7217</td>
<td>0.6565</td>
</tr>
<tr>
<td>Ba</td>
<td>1.515</td>
<td>0.703</td>
</tr>
</tbody>
</table>

The results of base leaching are reported in Table 5. It is worth of note that after this purification step about 40% of material (inorganic matter) was removed.
Table 5 - base leaching results

<table>
<thead>
<tr>
<th>Name of samples</th>
<th>NaOH, mL</th>
<th>Time of stirring, h</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG500(70/30)</td>
<td>50</td>
<td>2</td>
<td>62.6</td>
</tr>
<tr>
<td>EG600(70/30)</td>
<td>50</td>
<td>2</td>
<td>61.0</td>
</tr>
</tbody>
</table>

2.1 Materials morphology

SEM images in Fig. 4 show the typical structure of NG and of EG sample obtained at temperature 350 °C (EG350 (80/20)). As a result of thermal expansion graphite increases in volume due to the salts intercalation which leads to the formation of multilayer thermally expanded graphite.

Figure 4 - SEM images of natural graphite (NG, upper row) and expanded graphite obtained at the temperature of 350 °C (lower row) at different magnifications

The SEM imaging revealed that inorganic matter is present in EG350(70/30) sample, probably zinc or iron oxides (Fig. 5).

Figure 5 - SEM images of expanded graphite (EG350(70/30)) before NaOH treatment
SEM imaging was also performed on the expanded graphite after base leaching. The samples appear overall more homogeneous (Fig. 6).

![SEM images of expanded graphite (EG350(70:30) before (left panel) and after (right panel) leaching by NaOH](image)

SEM imaging on raw rice husk and carbonized rice husk at 600 °C (CRH600) are reported in figure 7.

![SEM images Rice husk (RH) and carbonized Rice husk (CRH600) at different magnifications](image)

Overall it can be observed that the carbonization process does not significantly alter the macroscopic morphology of the RH.

The results of oil sorption capacity are shown in Table 6 and Fig. 8.
The oil adsorption results indicated that EG samples after base leaching are the best adsorbents with an increase of 10-15 % compared to the not purified samples. It is noteworthy that as a general trend all the EG samples exhibit an adsorption capacity at least three-fold higher than NG.

As concerns as the CRH samples the adsorption capacities are similar and no particular variation with the activation temperature are detected. As a general result the carbonization process induced an increase of the adsorption capacities[6].

It is worth to note that the adsorption capacities estimated for the all heat-treated samples are quite higher compared to available literature data [7,8], as reported in Fig. 9 where oil absorption performances of acetic anhydride treated corn cobs, an abundant biodegradable agricultural waste, are reported.
3. Conclusions

In this work expanded graphite (EG) and carbonized rice husk (CRH) were obtained by heat treatment at different temperatures and by using different activating conditions. Samples were purified and characterized by SEM-EDAX, FTIR, elemental analysis, Proximate analysis and ICP-MS. The samples were tested as sorbent for oil in water.

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1 Кудайбергенов Кенес *, 1,2 Нысанбаева Гульнура *, 1,2 Огарбаев Ердос, 2 Мансуров Зулхайр, Р. Д. Каула, 2 М. Алфес, 2 В. Гаргулою 3

1 Казахский национальный университет им. аль-Фараби;  
2 Институт проблем горения;  
3 Академия гражданской авиации, 050012, Алматы, Республика Казахстан;  

СОРБЦИОННАЯ СПОСОБНОСТЬ МОДИФИЦИРОВАННЫХ НАНО-УГЛЕРОДНЫХ МАТЕРИАЛОВ

Аннотация. В этой работе расширенный графит (РГ) и карбонизированная рисовая шелуха (КРИШ) были получены термической обработкой при различных температурах и с использованием различных условий активации. Образцы были испытаны в качестве сорбента для нефти в воде. Эффективность удаления масла из карбонизированной рисовой шелухи и вспененного графита изучалась в качестве адсорбента для удаления эмульсийированных масел из сточных вод. Результаты показали, что эффективность удаления масла увеличивалась до 10-15% в случае образцов РГ после основного выщелачивания. Что касается образцов карбонизированной рисовой шелухи, адсорбционные способности аналогичны, и никаких особых изменений в зависимости от температуры активации не обнаружено. Как общий результат, процесс карбонизации вызвал увеличение адсорбционной емкости. Образцы были очищены и охарактеризованы с помощью SEM-EDAX, FTIR, элементарного анализа, микроскопического анализа и ICP-MS.

Ключевые слова: Карбонизованная рисовая шелуха, расширенный графит, масляные сточные воды, адсорбент, эффективность удаления масла.

1 Кудайбергенов Кенес *, 1,2 Нысанбаева Гульнура *, 1,2 Огарбаев Ердос, 2 Мансуров Зулхайр, Р. Д. Каула, 2 М. Алфес, 2 В. Гаргулою 3

1 Эл-арбаинатиындағыҚазУУ;  
2 Жаңа проблемаларын институты;  
3 Азаматтык авиация академиясы, 050012, Алматы, Казахстан Республикасы;  
4 Жаңа зерттәу институты -ЖЗИ, Неаполь, Италия

МОДИФИЦИРЛЕНГЕН НАНО-КОМПОРИТКЕТИ МАТЕРИАЛДАРЫНЫҢ СОРБЦИЯЛЫК КАСИЕТТЕРІ

Аннотация. Бұл жұмыста кенеңілген графит (EG) және карбонизацияланған құрғыш қауы (CRH) әр түрлі температурада термініл өңдеу және әр түрлі белсендіру әсілділ іздеу әрекетіне арқылы алынды. Сыңымалар судына мұайын сорбент ретінде сыңымды. Карбонизацияланған құрғыш қауы мен кенеңілген графит құрғыш құрғыш қауы әр түрлі температурада термініл өңдеу әрекетіне арқылы алынды. Нәтижелер корсеткіндемелер, мұнай сіңірудің тімділігі балық шаймаудағы кейін КГ ұлғарындағы 10-15% -ға дейін артты. Карбонизацияланған құрғыш қауы ұлғарындағы адсорбциялық қасыттығы бар және белсендіру температуросы анықталған өз.
Information about authors:
Kudaibergenov Kenes Sakimovich - PhD KazNU named after Al-Farabi, Acting Associate Professor, Deputy Head of the Department of Chemical Physics and Materials Science, kenes_85_85@mail.ru, Al-Farabi Avenue, 71, Almaty, Kazakhstan;
Nysanbayeva Gulnura Ryskulovna - PhD, 3rd year student of Al-Farabi Kazakh National University, Department of Chemical Physics of Materials Science, gulnur.83.29@mail.ru, 71 Al-Farabi Avenue, Almaty, Kazakhstan;
Nysanbayeva Gulnura Ryskulovna - Lecturer in Chemistry, Academy of Civil Aviation, gulnur.83.29@mail.ru, Akhmetsova, 44, Almaty, Kazakhstan;
Ongarbayev Yerdos Kalimullaevich - professor, Al-Farabi Kazakh National University, Department of Chemical Physics of Materials Science, 71 Al-Farabi Avenue, Almaty, Kazakhstan;
Mansurov Zulhair Aimukhamedovich - Professor, Al-Farabi Kazakh National University, Department of Chemical Physics of Materials Science, 71 Al-Farabi Avenue, Almaty, Kazakhstan;
Di Capua R. - PhD Institute of Research for Combustion-CNR, Naples, Italy;
Alfe M. - PhD Institute of Research for Combustion-CNR, Naples, Italy;
Gargiulo V. - PhD Institute of Research for Combustion-CNR, Naples, Italy

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