

## NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN  
SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2019.2518-1491.31>

Volume 3, Number 435 (2019), 63 – 70

<sup>1</sup>Kudaybergenov Kenes\*, <sup>1,3</sup>Nyissanbayeva Gulnura\*, <sup>1</sup>Ongarbayev Yerdos,  
<sup>2</sup>Mansurov Zulkhair, <sup>4</sup>R. Di Capua, <sup>4</sup>M.Alfe, <sup>4</sup>V.Gargiulo

<sup>1</sup>al-Farabi Kazakh National University, <sup>2</sup>Institute of Combustion Problems;

<sup>3</sup>Academy of Civil Aviation, 050012, Almaty, Republic of Kazakhstan;

<sup>4</sup>Institute of Research for Combustion-CNR, Naples, Italy

[gulnur.83.29@mail.ru](mailto:gulnur.83.29@mail.ru)

## 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-CNR 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 ( $\text{Zn}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ ) 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

Table 1 - Experimental conditions for expanded graphite synthesis

Samples labels	Percentage of components, wt. %		Final temperature, °C
EG350(80/20)	20% NG	80% $\text{Zn}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$	350
EG 400(80/20)	20% NG	80% $\text{Zn}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$	400
EG 600 (80/20)	20% NG	80% $\text{Zn}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$	600
EG 800(80/20)	20% NG	80% $\text{Zn}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$	800
EG 500(70/30)	30% NG	70% $\text{Zn}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$	500
EG 600 (70/30)	30% NG	70% $\text{Zn}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$	600
EG 1000(80/20)	20% NG	80% $\text{FeCl}_3 \times 6 \text{H}_2\text{O}$	1000

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.).

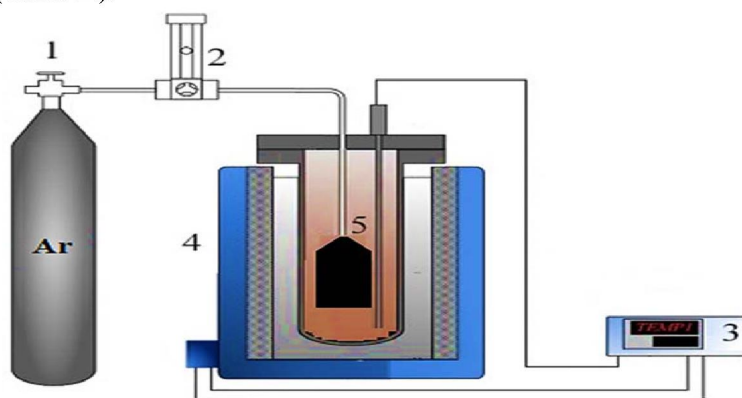


Figure 2 - Schematic diagram the RH carbonization setup. 1. argon cylinder, 2. mass flowmeter, 3. temperature controller, 4. carbonization reactor, 5. iron crucible

Table 2 - Experimental condition for carbonized RH synthesis

Samples labels	Carbonization temperature, °C	Carbonization time, hour
CRH 600	600	1
CRH 700	700	1
CRH 800	800	1
CRH 900	900	1

**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  $\mu\text{m}$  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  $\mu\text{m}$  pore dimensions) (Fig.3a). Each box has been filled with 0.1 g of sample (sample granulometry above 300  $\mu\text{m}$ ) 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 absorption tests a commercial carbon black (CB N110 type) was also used for comparison[4,5].

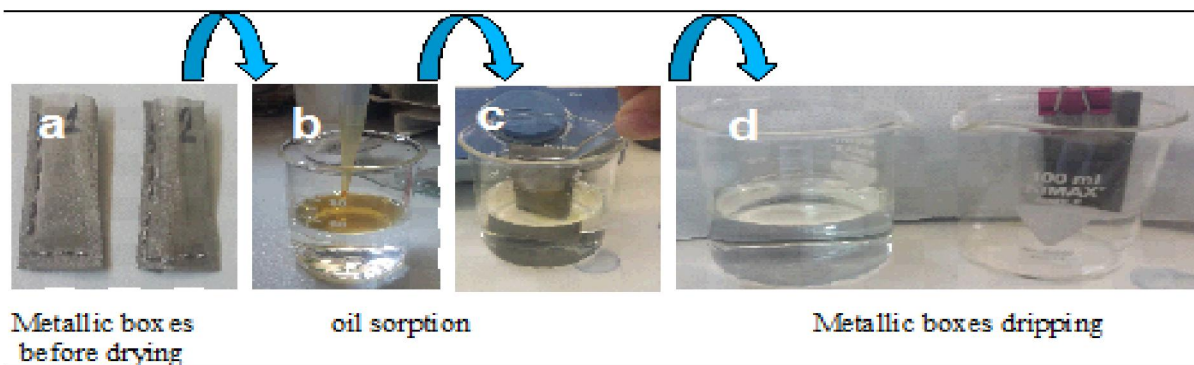


Figure 3 - Oil adsorption procedure

The oil sorption capacity was calculated as follows [7]:

$$\text{Oil sorption capacity (g/g)} = (S_{st} - S_0) / S_0$$

Where  $S_0$  is the initial mass of the sorbent,  $S_{st}$  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 3 - Washing results

Name of samples	Water, ml	Time of mix, min	Yield, %
EG600(70/30)	50	30	93.5
CRH 600	50	30	94.2

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

Table 4 - ICP-MS results (quantities are expressed in ppm)

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

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

Name of samples	NaOH, mL	Time of stirring, h	Yield, %
EG500 (70/30)	50	2	62.6
EG600(70/30)	50	2	61.0

## 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.

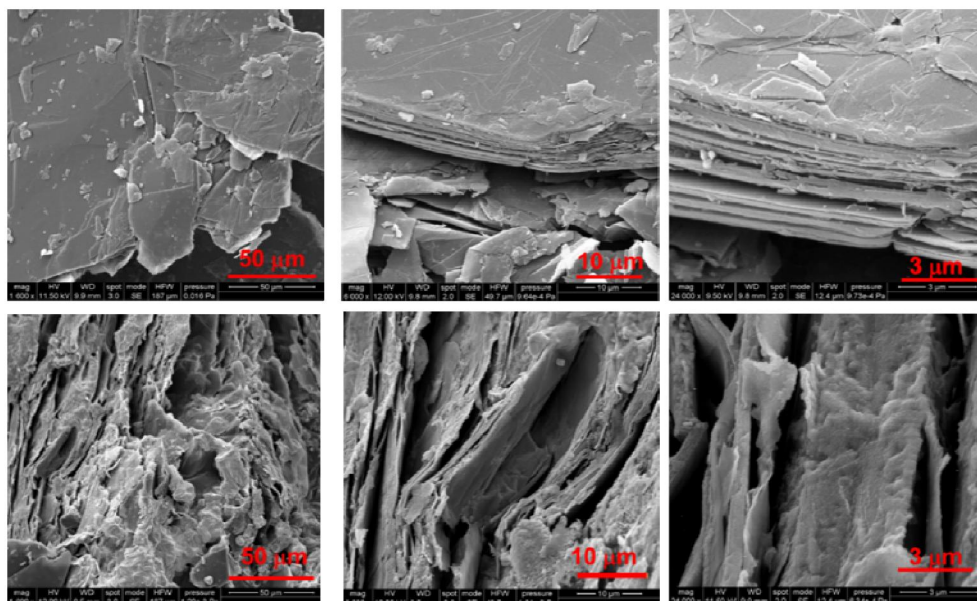


Figure 4 -SEM images of natural graphite (NG, upper row) and expanded graphite obtained at the temperature of 350 °C (lower row) at different magnifications

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

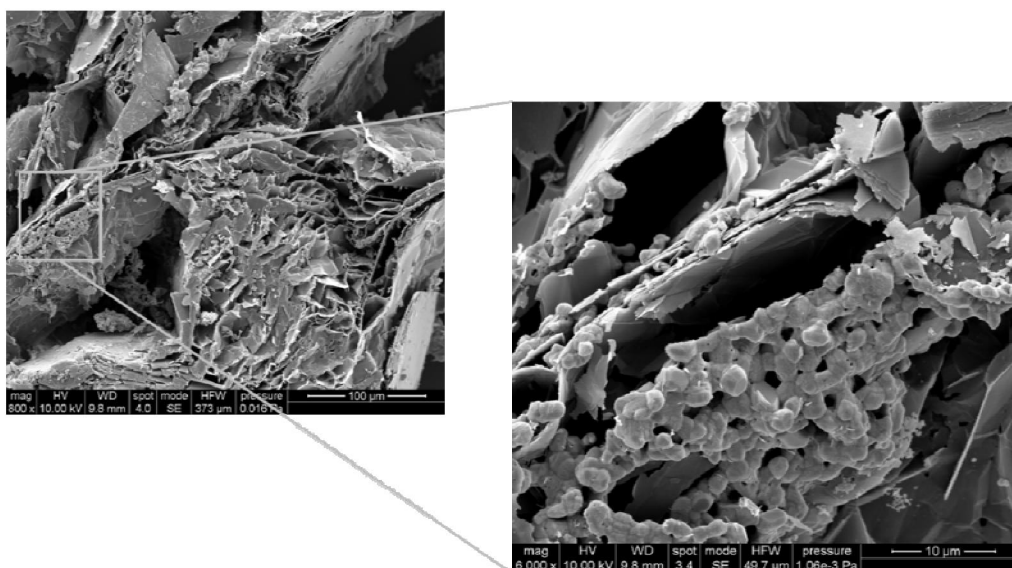


Figure 5 - SEM images of expanded graphite (EG350(70/30)) before NaOH treatment

SEM imaging was also performed on the expanded graphite after base leaching. The samples appear overall more homogeneous (Fig. 6).

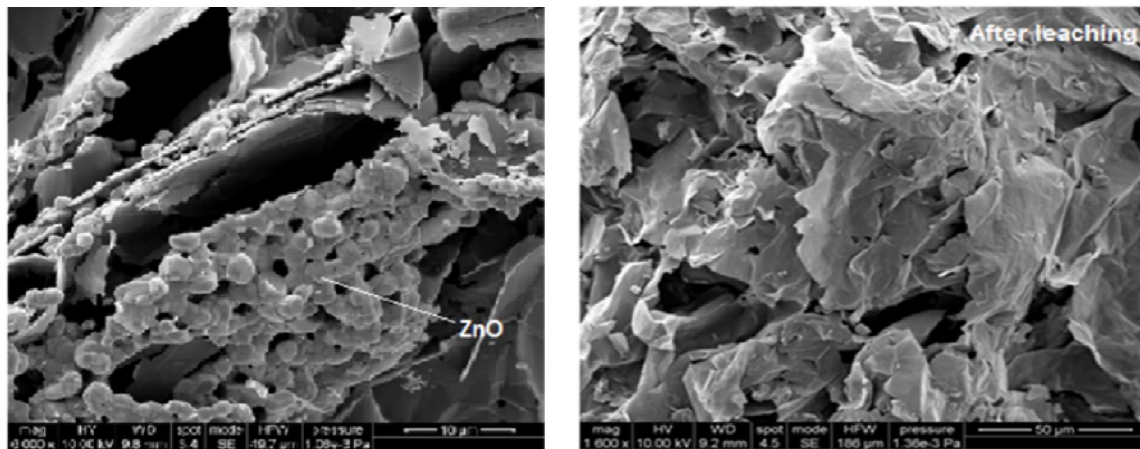


Figure 6 - SEM images of expanded graphite (EG350(70/30)) before (left panel) and after (right panel) leaching by NaOH

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

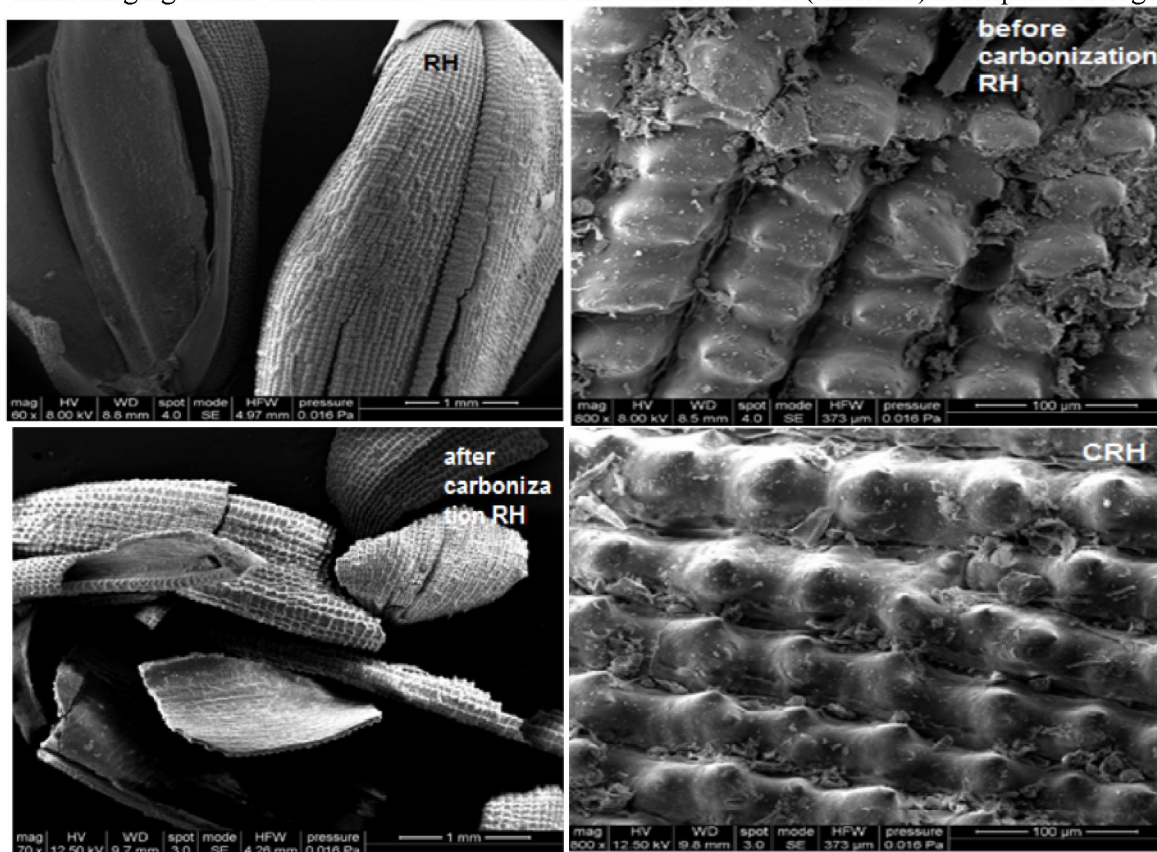


Figure 7 - SEM images Rice husk (RH) and carbonized Rice husk (CRH600) at different magnifications

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.



Sorbent	S <sub>st</sub> , Mass of the spent sorbent (sorbent+oil), g	S <sub>0</sub> , mass of sorbent, g	Oil sorption capacity, g/g
NG	0.42	0.10	1.8
EG 500(70/30) before leaching	0.99	0.10	6.0
EG 500(70/30) after leaching	0.87	0.10	7.1
EG 600(70/30) before leaching	1.1	0.10	5.6
EG 600(70/30) after leaching	0.78	0.10	6.2
RH	0.35	0.10	1.2
CRH 600	0.73	0.10	3.1
CRH 700	0.67	0.10	3.3
CRH 800	0.69	0.10	3.7
CRH 900	0.66	0.10	3.2
CB	0.56	0.10	2.6

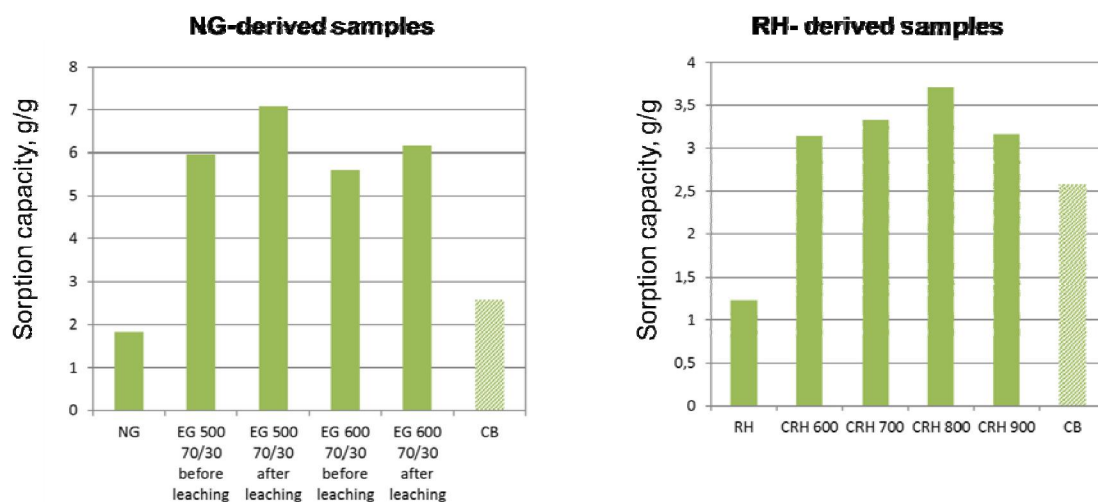


Figure 8. Comparison between NG-derived samples (left) and RH – derived samples (right). CB is also reported for comparison.

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 corncobs, an abundant biodegradable agricultural waste, are reported.

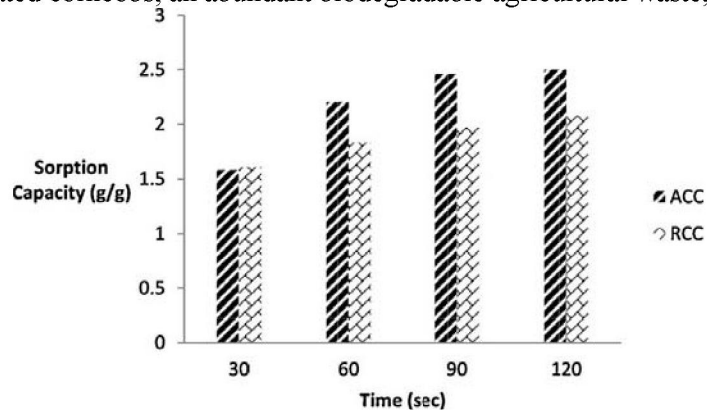


Figure 9 - Crude oil sorption capacity (g/g) of corncobs at different sorption time

### 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.

EG samples after base leaching are the best oil sorbents 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.

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It is worth to note that the adsorption capacities estimated for the all heat-treated samples are quite higher compared to available literature data.

<sup>1</sup>Құдайбергенов Кенес \*, <sup>1,3</sup>Нысанбаева Гүлнұра \*, <sup>1</sup>Оңғарбаев Ердоc,  
<sup>2</sup>Мансуров Зұлхайр, <sup>3</sup>Р. Ди Капуа, <sup>3</sup>М. Алфе, <sup>3</sup>В. Гаргиуло

<sup>1</sup>Қазақстанның миллиондык университеті им. аль-Фараби;

<sup>2</sup>Институт проблем горения;

<sup>3</sup>Академия гражданской авиации, 050012, Алматы, Республика Казахстан;

<sup>3</sup>Институт исследований горения-ИИГ, Неаполь, Италия

### СОРБЦИОННАЯ СПОСОБНОСТЬ МОДИФИЦИРОВАННЫХ НАНО-УГЛЕРОДНЫХ МАТЕРИАЛОВ

**Аннотация.** В этой работе расширенный графит (РГ) и карбонизированная рисовая шелуха (КРШ) 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 эмульгированных масел из сточных вод. Результаты показали, что эффективность удаления масла увеличилась 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, элементного анализа, проксимального анализа и ICP MS.

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

<sup>1</sup>Құдайбергенов Кенес \*, <sup>1,3</sup>Нысанбаева Гүлнұра \*, <sup>1</sup>Оңғарбаев Ердоc,  
<sup>2</sup>Мансуров Зұлхайр, <sup>4</sup>R. Di Capua, <sup>4</sup>M. Alfe, <sup>4</sup>V. Gargiulo

<sup>1</sup>Әл-арабиатындағы ҚазҰУ;

<sup>2</sup>Жану проблемалары институты;

<sup>3</sup>Азаматтық авиация академиясы, 050012, Алматы қ., Қазақстан Республикасы;

<sup>4</sup>Жану зерттеу институты -ЖЗИ, Неаполь, Италия

### МОДИФИЦІРЛЕНГЕН НАНО-КӨМІРТЕКТІ МАТЕРИАЛДАРЫНЫҢ СОРБЦИЯЛЫҚ ҚАСИЕТТЕРІ

**Аннотация.** Бұл жұмыста кеңейтілген графит (EG) және карбонизацияланған күріш қаузы (CRH) әр түрлі температурада термиялық өңдеу және әр түрлі белсендіру жағдайлары арқылы алынды. Сынамалар судағы мұай үшін сорбент ретінде сыналды. Карбонизацияланған күріш қаузы мен кеңейтілген графиттың сулардан эмульгирленген майларды алу үшін адсорбент ретінде зерттелді. Нәтижелер көрсеткендей, мұнай сіңірудің тиімділігі базалық шаймалаудан кейін КГ үлгілерінде 10-15% -ға дейін артты. Карбонизацияланған күріш қаузы үлгілерінде адсорбциялық ұқсастығы бар және белсендіру температурасы анықталған жоқ.

Жалпы нәтиже ретінде карбонизациялау процесі адсорбциялық мүмкіндіктерді арттырды. Үлгілер тазартылды және SEM-EDAX, FTIR, элементальды талдау, Шамамен талдау және ICP MS сипатталды.

**Түйін сөздер:** Карбонизделген күріш қаузы, кеңейтілген графит, су бетіндегі мұнай, адсорбент, эффективтілікті жою.

**Information about authors:**

Kudaibergenov Kenes Kakimovich - 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](mailto: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](mailto: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](mailto:gulnur.83.29@mail.ru), Akhmetova, 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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