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Oil Spill Cleanup from Sea Water by Porous Sorbents

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Abstract

Sorbents were produced on the basis of rice husk, rubber crump and apricot stone by carbonization. They all possessed a high sorption capacity for oil and oil products. With the use of these sorbents an oil overflow was experimentally removed from the surface of the river Syrdarya (Kyzylorda). Results showed that the oil sorption capacities of carbonized rice husk, rubber crumb and apricot stone were 18, 14 and 7 g/g, respectively. The material obtained by carbonization of rice husk has very good buoyancy characteristics, high oil sorption capacity and high hydrophobicity. The effects of contact time, water temperature, amount and type of sorbents on the oil sorption capacity of the carbonized sorbents were further studied on the basis of microstructure and morphology using optical digital microscopy and scanning electron microscopy (SEM). The results of the SEM and optical microscopy studies strongly indicate that carbonization is a suitable method for improving the porous structure of the sorbents particles compared to the virgin samples. This research provides the basis for the development of a new environmental material with optimal characteristics, providing efficient sorption of oil and oil products from an aqueous medium.

Introduction

The liquidation of oil spills on water surfaces aims to reduce the damage to the ecological and socio-economical resources, while reducing the time required for recovery of these resources and providing acceptable standards of cleanup [1]. The basic variants for removal are containment and pickup of spilled oil, spraying chemical dispersants, shoreline protection or natural purification. The physical removal of oil from the surface of the water reduces the threat to birds, mammals in coastal waters and on the coast. Dispersants help to break the surface slick, but getting into the coastal waters could threaten marine organisms.

Nowadays sorption methods are widely used for the removal of these contaminants from the surface of the water and soil with different sorption materials. For the production of oil sorbents, natural organic raw materials and waste products of plant origin are the most attractive. They are usually an integral part of the existing ecosystems and therefore they meet the most relevant environmental requirements. Different types of adsorbents including chrome shavings [2], raw cotton and sand [3], feathers [4], wool and sepiolite [5], peat [6], exfoliated graphite [7], vermiculite [8], silica aerogels, zeolites, organoclays [9] and nonwoven polypropylene [10] have been investigated in this context. Among various reports, most of these oil adsorbents were found to have high costs or poor buoyancy after oil sorption compared to agricultural waste materials.

Advanced oil sorbents are sorbents based on rice husk (RH) and apricot stone (AS) [11]. Their action is particularly effective in the removal of the heavy oil fractions. The main advantages of these sorbents are environmental friendliness, a wide range of available raw materials, very hydrophobic behavior and high oil sorption capacity at a relatively low cost [12].

Rice husks are an agricultural waste that incurs annually at 545 million tons [13]. Typically, rice husks consist of about 75% organic substances (cellulose, lignin, hemicelluloses), 15% amorphous SiO_2, 10% water and microelements [14].

This shows there is a real need to create a fundamentally new generation of sorbents for the purification of water on an industrial scale, based on the principles of nanotechnology [15].

In this paper we conducted studies to evaluate the properties of new sorbents on the basis of carbonized rice husk (RH), apricot stone (AS) and rub-

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ber crumb (RC). According to the results obtained, sorbents characteristics (sorption with varying oil viscosity, degree of purification of the water surface, as well as water absorption and buoyancy) show that rice husk based adsorbents have the greatest degree of absorption of oil from the water surface.

Materials and Methods

The samples were carbonized according to the procedure developed at R.M. Mansurova Laboratory of Carbon Nanomaterials at the Institute of Combustion Problems. Samples were washed with water to remove dirt, then oven-dried at about 110 ºC for 24 h. The dried samples were placed in a steel reactor and heated in a muffle furnace under CO_2 flow (100 ml/min) at 700 ºC for 1 h.

To carry out the process of adsorption of oil under real circumstances, one needs to know how much oil and water the sorbent absorbs simultaneously. Therefore, an in vitro reservoir with a large surface area was filled with water. The water temperature was varied depending on the real temperature of the water in the seas and rivers in winter and summer (8 ºC, 15 ºC, 23 ºC, 38 ºC). On the surface of water a slick of oil was applied. Two types of oil have been used - oil of the Kumkol and Kalamkas oil fields. On the oil slick 4 g layer of sorbent were sprinkled. Carbonized rice husk, apricot stone and rubber crumb were used as adsorbents. Sorption time was varied from 5 to 30 min, in order to find the optimal absorption time of the oil sorbents.

The microstructure of the sorbents was analysed with a SEM (Quanta 3D 200i, USA) at an accelerated voltage of 20 kV and a pressure of 0.003 Pa (performed by National Nanotechnological Laboratory of Open Type of Kazakh National University). The surface appearance of the carbonized sorbents was also observed with Optical Digital Microscopy (Leica DM 6000 M).

Results and Discussion

The experimental results of the relation between the oil sorption capacity and the water temperature are shown in Fig. 1 for the different adsorbents. The highest sorption capacity is observed at a temperature of 23 ºC. Similar data were obtained during the experiment on the sorption of water (Fig. 2). Also, the results show that the rice husk has the highest sorption capacity of the investigated sorbents.

During the experiment, some observations were made. At a water temperature of 8 ºC, which is possible in winter, the oil does not stay on the surface as a thin film; it is gathered in a small cake, some of which remains on the surface as a solid film. The rest settles down on the bottom, thereby making it impossible to complete the adsorption of oil from the surface.

The adsorption of oil by RH at 23 ºC was almost instantaneous. However, as the adsorption capacity is independent of the weight of sorbent during the experiment, it is necessary to use that amount of adsorbent which is able to cover the whole surface of the oil spill. Note that the temperature of the water affects the spreading ability of the oil on the surface. Hotter water facilitates the spread of oil, making it faster and larger.

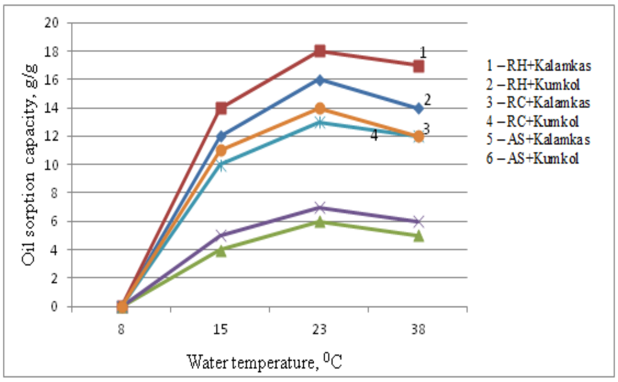


Fig. 1. Dependence of oil sorption capacity of sorbents on the water temperature.

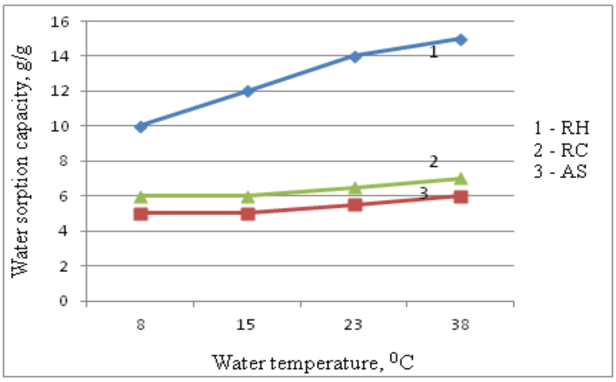


Fig. 2. Dependence of water sorption capacity of sorbents on water temperature.

When conducting experiments with apricot stone it was noticed that part of the sorbent falls to the bottom (3 g out of 9 g), thereby making it a very costly spill response. Furthermore, this sorbent needs longer time for adsorption (30 min). Rubber crumb absorbs oil well, not leaving any traces of fatty oil compared with the other absorbents.

Based on the results of the experiments diagrams were plotted, showing the dependence of the oil capacity on the type of sorbents, the time of adsorption and the amount of sorbent. It is shown that carbonized rice husk presents the best sorption capacity of all the available samples (Fig. 3).

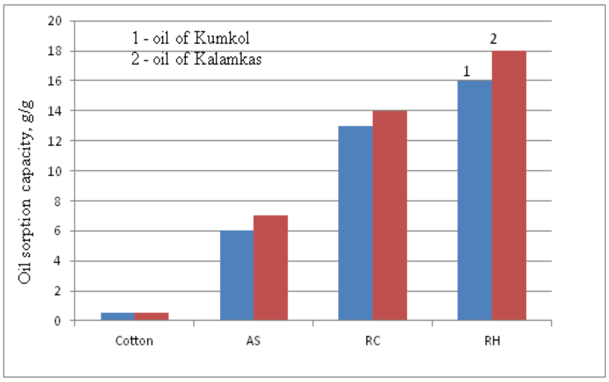


Fig. 3. Dependence of oil sorption capacity on the type of sorbents.

The effects of contact time on the sorption capacity of the sorbents was also studied. Figure 4 shows that the sorption capacity of the sorbents increased rapidly with contact time, then it reached an equilibrium. The equilibrium times for oil on RH, RC and AS were 10, 20 and 30 min, respectively. Summarizing these results, the carbonized rice husk required less time for the oil sorption than the other sorbents.

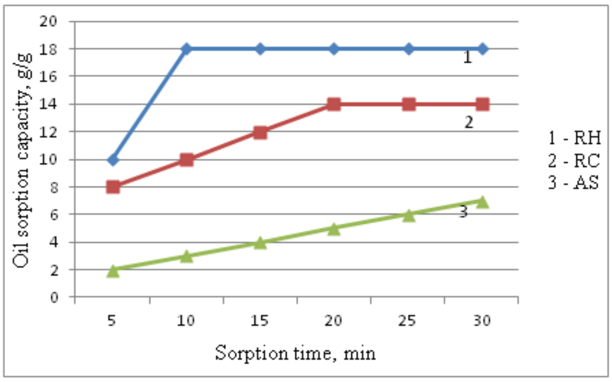


Fig. 4. Dependence of oil sorption capacity of sorbents on the sorption time.

Figure 5 shows a clear dependency between amount of adsorbed oil and the amount of sorbent. It is economically more advantageous to use rice husks as a sorbent, as in this case less sorbent is needed for the process than for the other materials. When using apricot stone, one must take into account the lower quantity of material available to adsorb the oil layer because of the loss due to the low buoyancy of this material.

An important parameter of the sorption process is the degree of desorption of the oil from the sorbent as it demonstrates the possibility of a return of oil to the production cycle. A variety of methods were considered for regenerating these materials.

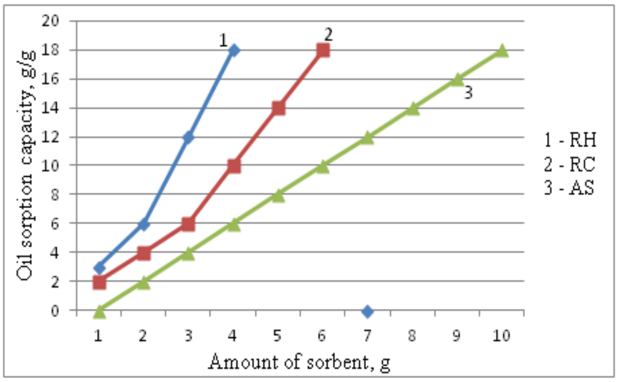
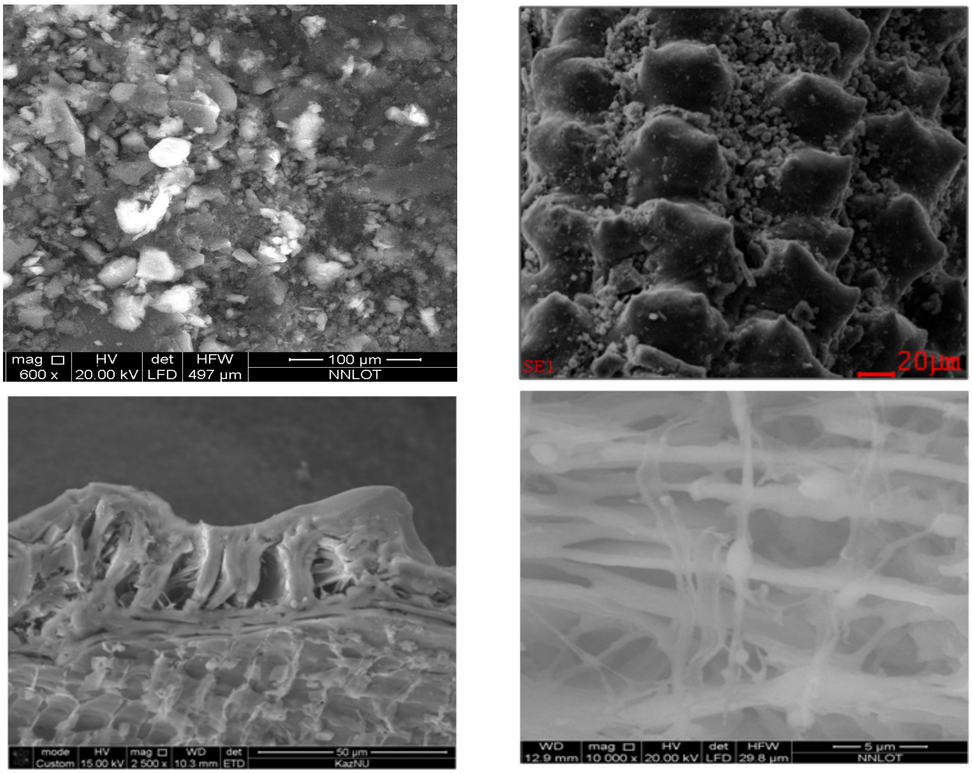


Fig. 5. Dependence of oil sorption capacity on the amount of sorbents.

The photographs in Fig. 6 depict the microstructure of carbonized rice husks (CRH). The SEM image of carbonized rice husks (Fig. 6 (a)) shows spherical silica particles of varying form on the organic matrix. Furthermore, the external wall of CRH shows the occurrence of a large number of button-like structures with small pores, which were not found in the virgin rice husk particles. The emerging of pores and button-like structures may be caused by the fast removal of volatile organic components from the particle [16]. A cross-section of CRH is shown in Fig. 6 (b) and illustrates the presence of pores and channels in the particles with diameters of about 5–10 µm. The emerging of channels during combustion of rice husk has been discussed earlier in [13]. The interior structure of CRH (Fig. 6 (c)) furthermore indicates the formation of backbone-like structures during combustion [17]. The particles underwent drastic changes in this process of high-temperature treatment. Pores increased both in number and size, new types appeared, two or more smaller pores merged into bigger ones, and the surface and volume of the pores changed.

The surface appearance of the CRH was also observed in optical digital microscopy. Figure 7 shows the optical microscopy images of the CRH. There are clear differences between the lower and the higher magnifications. In the lower magnification, some particles of carbon (Fig. 7 (a)) and amorphous silica (Fig. 7 (b)) can be seen. Figure 7 (c) shows the presence of pores with diameters of 5–15 µm on the surface of the particles.



(a) (b)

(c) (d)

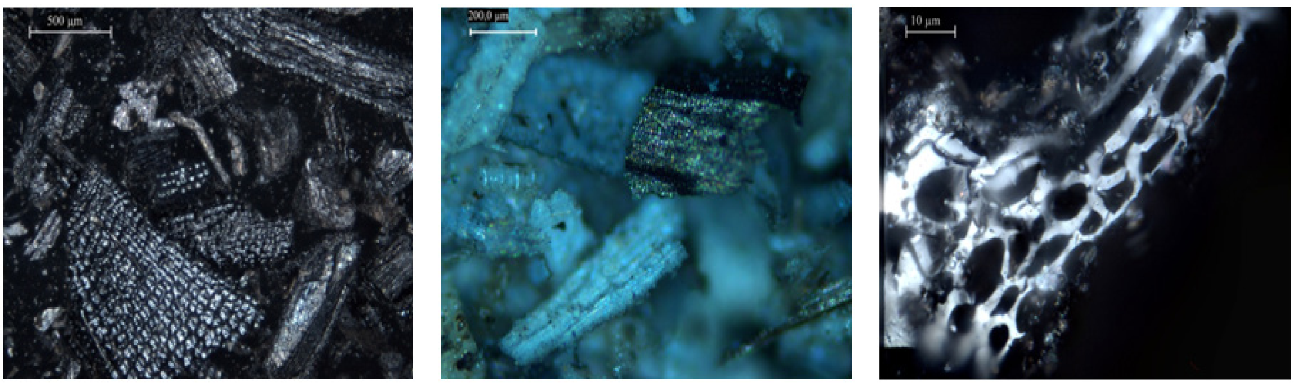
Fig. 6. SEM images of virgin and carbonized rice husk: (a) – virgin rice husk; (b) – external wall of CRH; (c) – cross-section of CRH; (d) – interior wall of CRH.

High oil sorption ability is determined by the porous structure of the adsorbents, as well as by the physical and chemical interactions of their functional groups with the crude oil components. One can see in the SEM and optical microscopy images that carbonization results in a drastically modified structure with higher porosity compared to the virgin husk samples.

Sorbent regeneration was carried out in a "Soxhlet" extraction apparatus. Therefore a weighed amount of used sorbent is taken and compacted in a special filter paper. The sample is then placed on top of the apparatus and the necessary amount of solvent, in this case benzene, is added. The process was conducted for 5–6 h until clarity of the benzene. To separate oil from the mixture the solvent was evaporated and the amount of residual oil was determined. The sorbent was subjected to a drying process for further reuse.

In the end we obtained a pure sorbent, which has the same capacity to adsorb and retain oil as the original one, and as such can be reused for any specific purpose.

The extraction process was also carried out by washing the sorbent with solvents, followed by filtration and treatment with hot water. This process is much more economical and requires less solvent and real costs in an industrial environment.



(a) (b) (c)

Fig. 7. Optical microscopy images of the CRH.

Pilot tests of these sorbents were conducted on the Syrdarya river [18]. Oil adsorption was carried out using the 3 types of sorbent that were previously tested and studied in the laboratory: carbonized rice husk, apricot stone and rubber crumb. Tests were carried out in Kyzylorda on the surface of the Syrdarya River under the supervision of an ecologist LLP "Timur Company". This physical-chemical method of oil spill has been tested and the environmental impact assessment shows that it is harmless to the environment.

Conclusions

Carbonized sorbents based on rice husks are an efficient absorber for heavy crude oil, since they possess a high porosity and reactive surface functionalities. Results showed that the oil sorption capacities of carbonized rice husk, rubber crumb and apricot stone were 18, 14 and 7 g/g, respectively. The results of optical digital microscopy show that carbonized rice husk consist mainly of carbon and amorphous silica (SiO_2). One can see in SEM and optical microscopy images that carbonization allows to obtain a drastically modified structure with higher porosity compared to the virgin husk samples. In conclusion, this study demonstrates the possibility to obtain effective petroleum adsorbents from rice husks, which are currently considered to be an agricultural waste.

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