Research note

Oil Sorption by Synthesized Exfoliated Graphite (EG)

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Abstract

In this paper a chemical method applied to synthesize exfoliated graphite (EG) is presented. In this method graphite intercalation compound (GIC) was firstly synthesized by chemical treatment of graphite flakes using a mixture of sulfuric and nitric acids followed by thermal shock of GIC at 1000°C to produce EG. The bulk density of synthesized EG was found to be as low as 4.5 kg/m3. X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were used for identification and characterization of different materials. According to the XRD observations, the GIC was identified as graphite bisulfate with stage 2, and residue GIC and EG had nearly the same diffraction pattern, but with distinctly lower intensity. In accordance with SEM results the residue graphite bisulfate was swelled in comparison with the graphite flake. The oil sorption capacity of synthesized EG in this work was studied by common static and dynamic tests and compared with other sorbents. The results show the superior capability of EG for oil spill cleanup.

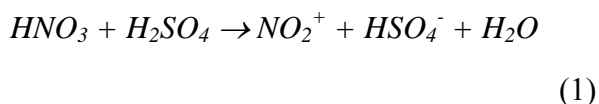**Keywords**: *Exfoliated graphite, Oil Spill, Sorption, Crude Oil*

1- Introduction

Exfoliated graphite (EG) is a well known material usually produced from various intercalation compounds submitted to a thermal shock. EG is an important industrial raw material in the manufacturing of flexible graphite sheets, which are widely used as gasket, seals and packing [1]. Recently it has been found that EG is also a good absorbent, especially for materials with large molecular size and weak polarity like oil and petroleum products [2,3]. The use of sorbents increased in oil spill cleanup and wastewater treatment due to their abundance as well as their low prices [4-6]. The crystalline structure of graphite flak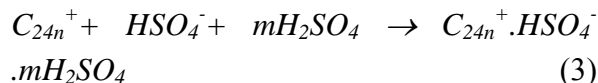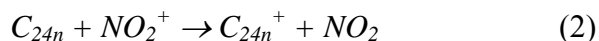e consists of layered planes of carbon atoms arranged in a hexagonal structure. There is strong covalent bonding within the basal planes and weak van der Waals bonding between the layers. Various species of molecules, atoms and ions are eligible to be inserted between the carbon planes in graphite crystal structures and create graphite intercalation compounds (GIC) [7,8]. The intercalation compounds of graphite can be classified into two main groups including covalent intercalation compounds and ionic intercalation compounds [9]. The first group includes graphite oxide, carbon monofluoride and tetracarbon monofluoride, while the second group includes graphite salts (e.g. graphite bisulfate

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and graphite nitrate), graphite-alkali metal compounds, graphitehalogen compounds, graphite-metal chloride compounds, etc. Properties of GICs are different from not only the host graphite, but also the guest intercalate. When GIC is exposed to a high temperature thermal shock, the intercalate species vaporize and therefore GIC decomposes. This phenomenon causes an over eighty-fold expansion in volume along the c-direction compared to the original graphite flake. This expansion produces worm-like structures known as exfoliated graphite (EG) [10,11]. Graphite reacts with a large number of acids to form ionic intercalation compounds. One of the graphite-acid compounds is graphite bisulfate or graphite hydrogen sulfate (H_2SO_4-GIC) [9]. H_2SO_4-GICs are graphiteacid compounds and widely used for the production of EG because of their high expansion volume ability through a thermal shock. Intercalation of H_2SO_4 can be done by chemical and electrochemical methods [12]. Intercalation of H_2SO_4 into a graphite structure has been reported by chemical oxidation in the presence of H_2O_2 [13]. Intercalations of H2SO4 into a graphite structure have also been carried out via electrochemical methods [3]. They have studied the effects of preparation conditions on the characteristics of EG. A mixture of H_2SO_4-HNO_3 has been used in order to synthesize thermally expandable graphite [14]. According to their work, nitric acid was ionized to give nitronium cations by the following reaction:

$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

$$(1)$$

The graphite matrix was then oxidized by nitronium cations and intercalating species could be inserted as intercalate between the layers of graphite as the following reactions [14]:

$$C_{24n} + NO_2^+ \rightarrow C_{24n}^+ + NO_2 \qquad (2)$$

$$C_{24n}^+ + HSO_4^- + mH_2SO_4 \rightarrow C_{24n}^+.HSO_4^- .mH_2SO_4 \qquad (3)$$

The product of reaction (3) is a graphite bisulfate, which consists of graphite layers with HSO_4^- ions and H_2SO_4 molecules between the layers. In these reactions, n is the stage index with the value of m equal to 2, according to the literature [15]. Although the industrial grade of EG is characterized mostly by bulk density, a more detailed characterization of the EG is required for new applications such as sorbents. In the present work, EG was synthesized using a mixture of sulfuric and nitric acids.

2- Experimental

2-1- Synthesis procedure of EG
Chemical intercalation of concentrated sulfuric acid (96%) was conducted in the presence of nitric acid (65%). Natural graphite flakes with an average flake size of 300 μm and 94% purity were used for the preparation of EG. The flakes of graphite were immersed in a mixture of sulfuric and nitric acids with a 4:1 ratio (the best ratio in our experiments) for 24 hours at room temperature. The prepared GIC was then rinsed with distilled water to reach pH between 3 and 4 and was kept in an oven at 100 °C for 1 h. The product at this stage is known as residue GIC and was converted to EG by thermal shock at 1000 °C for 5 s.

2-2- Identification and characterization techniques
Graphite flake, GIC, residue GIC and EG were identified by XRD (model Bruker D8 ADVANCE) at room temperature (40 kV, 35 mA, CuKα radiation, 1.5 °2θ/min scan speed). In order to prevent GIC from decomposition, it was wrapped with a thin film of polyethylene and then XRD analysis was done. Also, the surface morphology of the particles was studied by using SEM (model Philips XL30).

2-3- Sorption capacities of synthesized EG

Experiments have been conducted to clean up four oil samples, presented in Table 1, as pollutants from the surface of water. Also, the synthesized EG in this work, having a density of 4.5 Kg/m^3, has been used as sorbent. Simulated seawater (ASTM 1141) was used in this work. This is an aqueous solution of specific amounts of different salts, with a pH equal to 8.2 at room temperature (ASTM 1141, [16]). The experiments were carried out in static and dynamic modes. In the static mode a specified amount of oil pollutants was added to a 600-ml beaker containing 400-ml of simulated seawater. Then, one gram of EG was carefully weighted and added to the beaker. The required time for complete sorption of oil pollutant by EG is measured. In the dynamic mode, one gram of EG was wrapped in a cloth net then added to a 600-ml beaker containing 400-ml of simulated seawater and a specified amount of an oil pollutant. The system was shaken for 5 min at 90 cycles/min.. The wetted EG was removed from the pollutant water, drained for 2 min and then carefully weighted. The water content of the sorbent was determined by the ASTM D 95 distillation technique (ASTM D 95 [17]).

Table 1. Specification of sorbent materials

Property	Unit	Oil samples			
		Gas oil No.1 (GO1)	Gas oil No.2 (GO2)	Light crude oil (LCO)	Heavy crude oil (HCO)
Density at 30 °C	Kg/m^3	838.4	831.1	853.7	879.5
Kinematic viscosity at 40 °C	m^2/s	4.05E-6	3.63E-6	6.17E-6	1.25E-5

3- Results and discussion

3-1- X-ray diffraction pattern of different samples

XRD tests have been conducted on graphite flakes, graphite intercalation compounds (GICs), graphite residue and exfoliated graphite (EG). Samples were covered with a thin layer of polyethylene (10 μm) in order to protect them from decomposition. An XRD pattern of graphite flakes is presented in Fig.1. According to this figure, the sample mostly consisted of graphite with some small impurities, which was identified as a compound with the chemical formula of $Na_{0.5}$ *(Mg, Fe, Al)$_3$ (Si, Al)$_4$ O$_{10}$(OH).* Fig.2 presents an XRD pattern of GIC. As can be seen from this figure, some new diffraction peaks appeared after the acid treatment of graphite flakes. This means that graphite flakes are changed to another compound, identified as graphite bisulfate (graphite hydrogen sulfate) with the chemical formula $C_{48}^{+}.HSO_4^{-}.2H_2SO_4$. It can be easily concluded that *n* is equal to *2* by comparing the above mentioned formula with the general formula of $C_{24n}^{+}.HSO_4^{-}.2H_2SO_4$ [18]. This means that the synthesized GIC was graphite bisulfate with stage *2*. Fig.3 shows the diffraction pattern of residue GIC, which is nearly similar to that of the initial graphite flakes, but the peaks are broader and lower than those of the graphite flakes. The reason

may be related to the decomposition of graphite bisulfate when it is rinsed with distilled water. This is due to the fact that most intercalate species are removed during the decomposition of graphite bisulfate. Of course there is some intercalating between the layers, even after the washing step, and therefore the structure of residue GIC could not be determined accurately. This compound was completely different from graphite bisulfate, which had a definite layered structure. However, synthesis of residue graphite bisulfate could be well-approved by exfoliation due to thermal shock. The XRD result of EG is presented in Fig.4. According to this figure, the analyzed sample had a diffraction pattern very similar to that of graphite flakes. Since during thermal shock the intercalate species vaporize and cause the layers to separate, residue graphite bisulfate is changed again into graphite. Comparing Figs.1 to 4 it is concluded that the intensity of the diffraction peaks is lowered consecutively. In fact, atoms with ordered structure are responsible for XRD peaks, or in other words, the diffraction is not observed for a completely disordered structure. Therefore the intensity of the peaks is proportional to the degree of orderness of the atoms [19]. So it can be concluded that the amount of ordered atoms of the residue graphite bisulfate and EG should be less than those of graphite bisulfate, and this may be the reason for intensities reduction during the processing of the graphite flakes, as can be seen from Figs. 1-4. From Figs. 3 and 4 it is found that the intensity of GIC is a little lower than that of residue GIC. This may be due to the optical absorption of x-ray beams by the polyethylene film which is used to wrap the GIC sample. A comparison of X-ray diffraction patterns of GIC, residue GIC, and EG is presented in Fig.5. It can be seen from this figure that some new diffraction lines are created during chemical reactions. Since the intensity of diffraction peaks is proportional

to the amount of compound, when a material is changed to another one, some new diffraction lines appear and the diffraction lines of the initial compound are weakened.

3-2- SEM micrographs of different samples

SEM micrographs of graphite flakes, residue graphite bisulfate and EG are presented by Figs.6-9. According to Fig. 6, the surface of graphite flake particles is relatively flat. After the treatment of graphite flakes with a mixture of acids, graphite bisulfate with stage 2 was produced in which two graphene layers are separated by two intercalate layers. It is concluded from Fig.7 that graphite bisulfate is decomposed during the washing step, and residue graphite bisulfate is formed by the removal of most of the intercalate species. Of course the distances between the layers of graphene are more than those of graphite flakes due to the incomplete removal of intercalate species during the washing step. Manning et.al [20] synthesis a stable form of exfoliated graphite (EG) from the GIC fluorine–graphite using an atmospheric-pressure 27.12 MHz inductively coupled argon plasma. By using SEM images they identified nanotubular structures at the terminals of the EG.

The swelling of the graphite material observed in this figure is due to the partial expansion of graphite flakes along the graphite c-axis and the splitting of graphite layers. In Fig.8 an enlarged (one thousand-fold) image of a residue graphite bisulfate particle is presented. From this figure it can be concluded that the layers are separated as groups with dissimilar distance. After exposing residue graphite bisulfate to thermal shock at high temperatures, EG is prepared. A worm-like appearance of EG particles is obviously shown in Fig.9. The same results have been reported by Celzard et al. [1]. They found EG products as typical disc-like platelets, long, porous, distorted cylinders having a diameter of the order of 0.5 mm and a thickness ten times lower
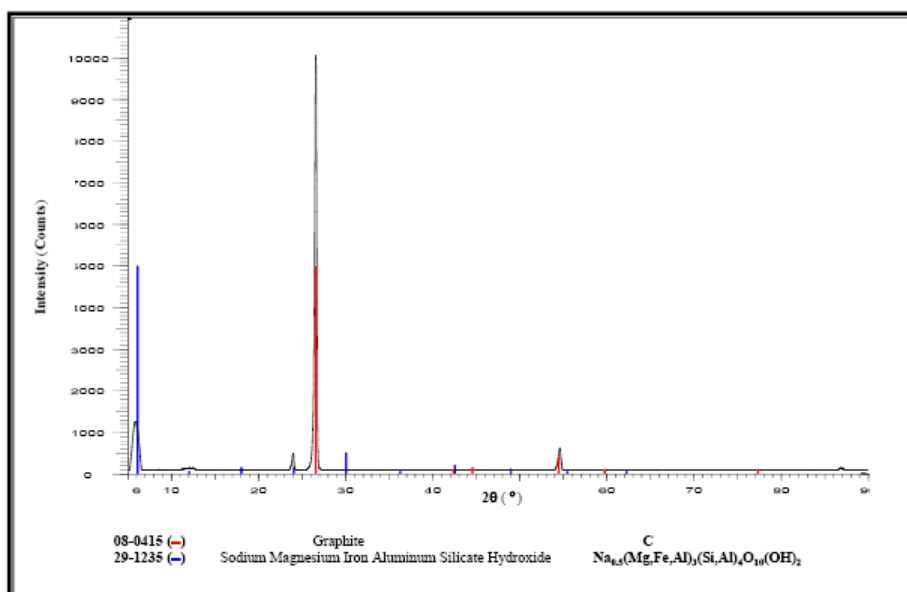
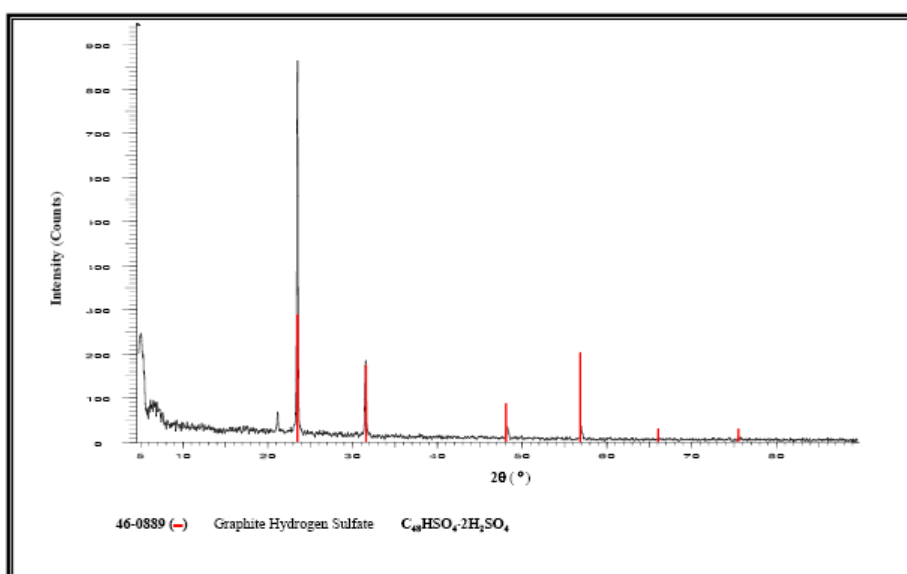**Figure 1.** X-ray diffraction pattern related to Graphite

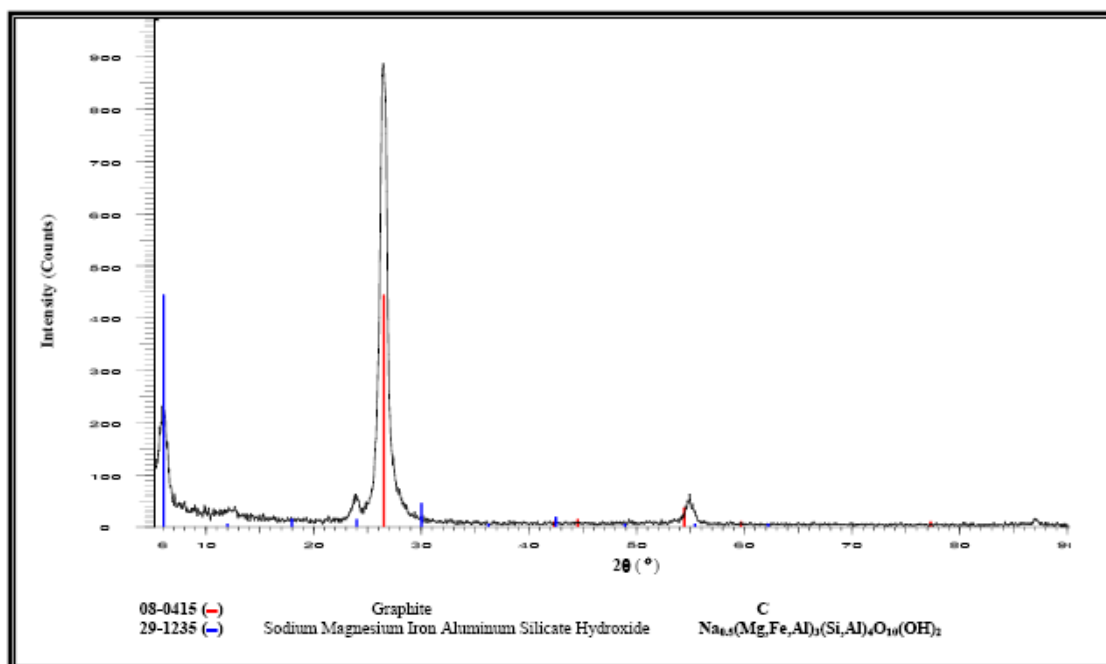
Figure 2. X-ray diffraction pattern related to GIC

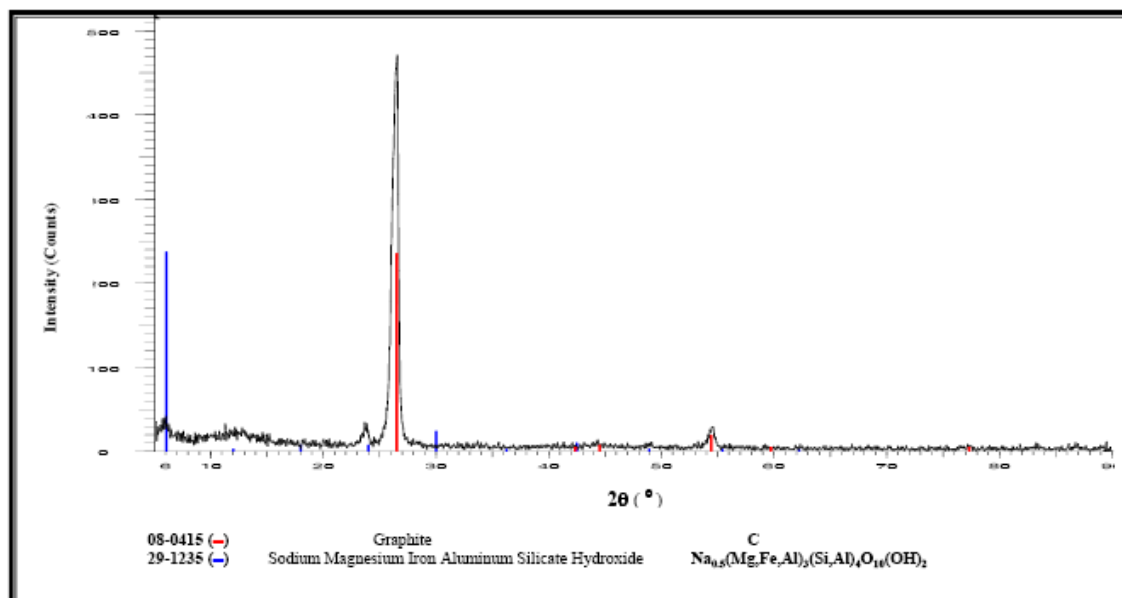**Figure 3.** X-ray diffraction pattern related to residue GIC
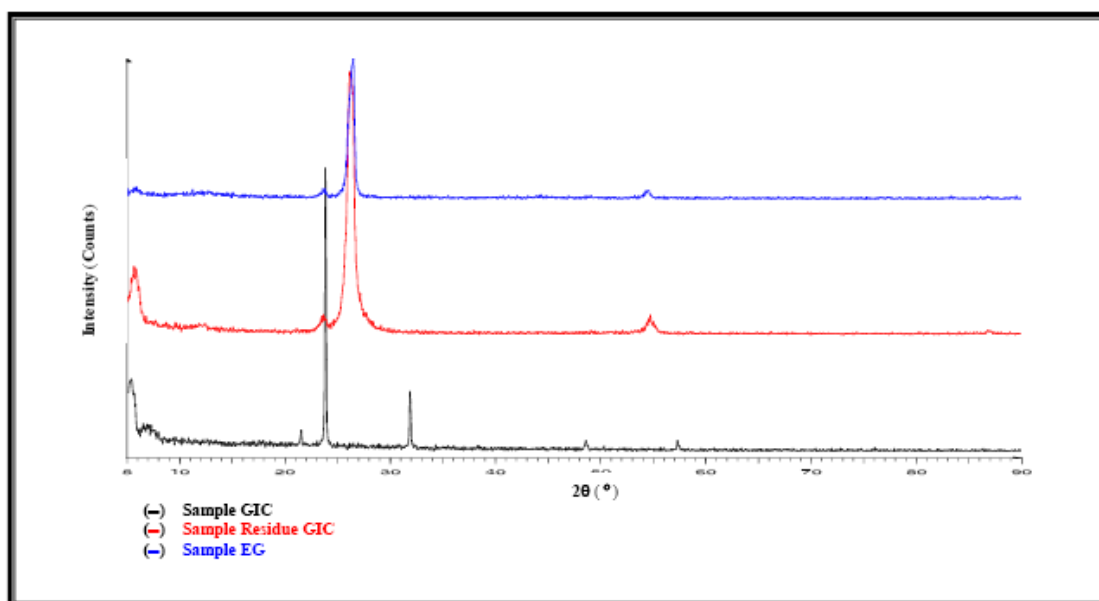

Figure 4. X-ray diffraction pattern related to EG
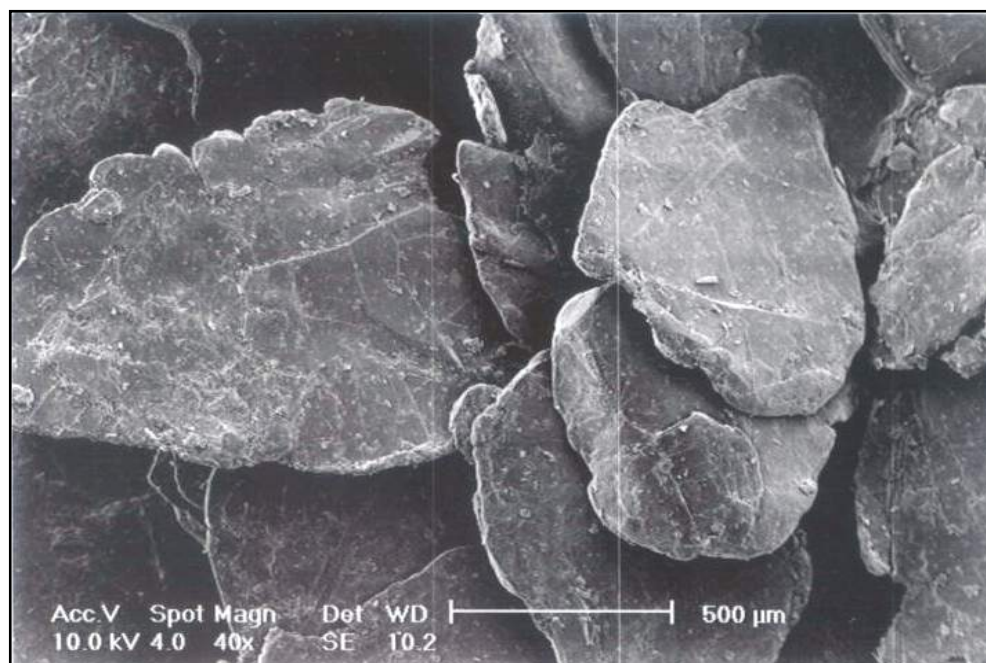
Figure 5.

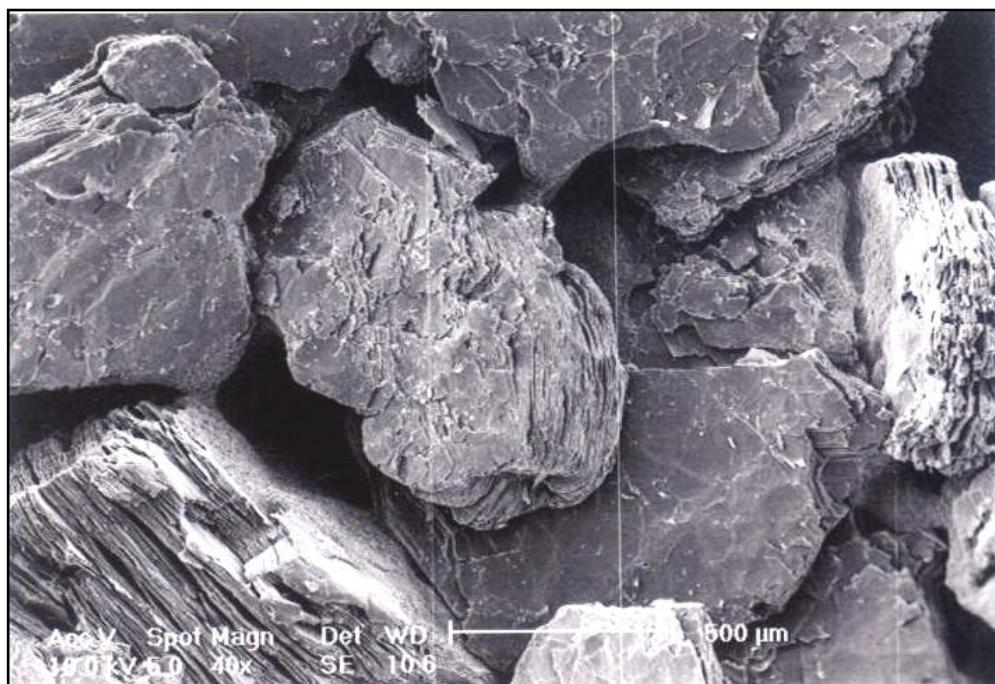**Figure 6.** SEM micrograph of graphite flakes used in synthesis of EG

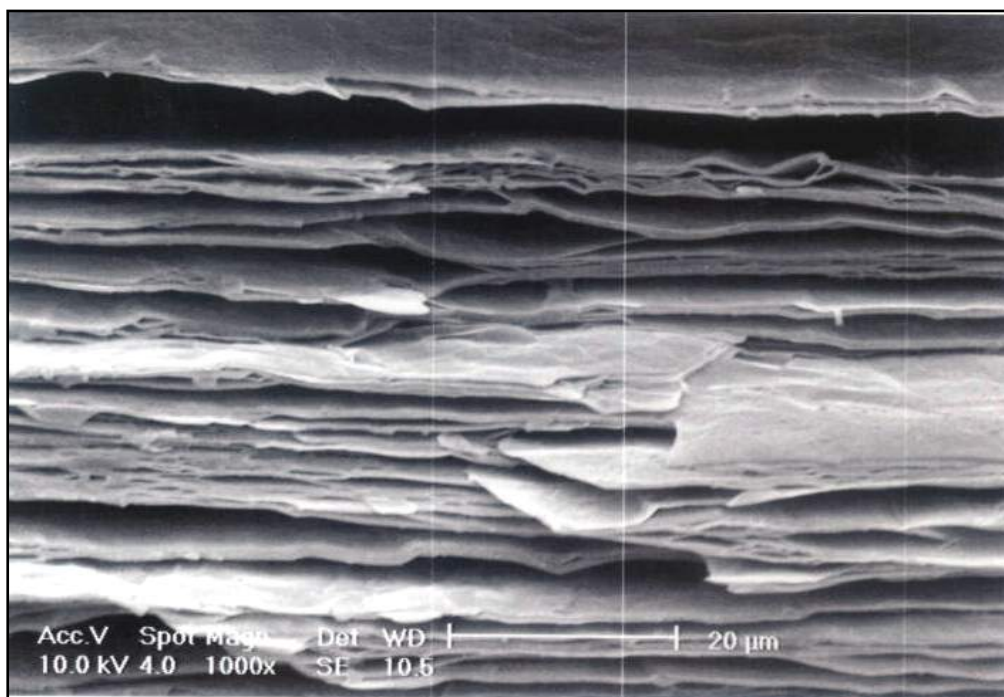**Figure 7.** SEM micrograph of residue graphite bisulfate

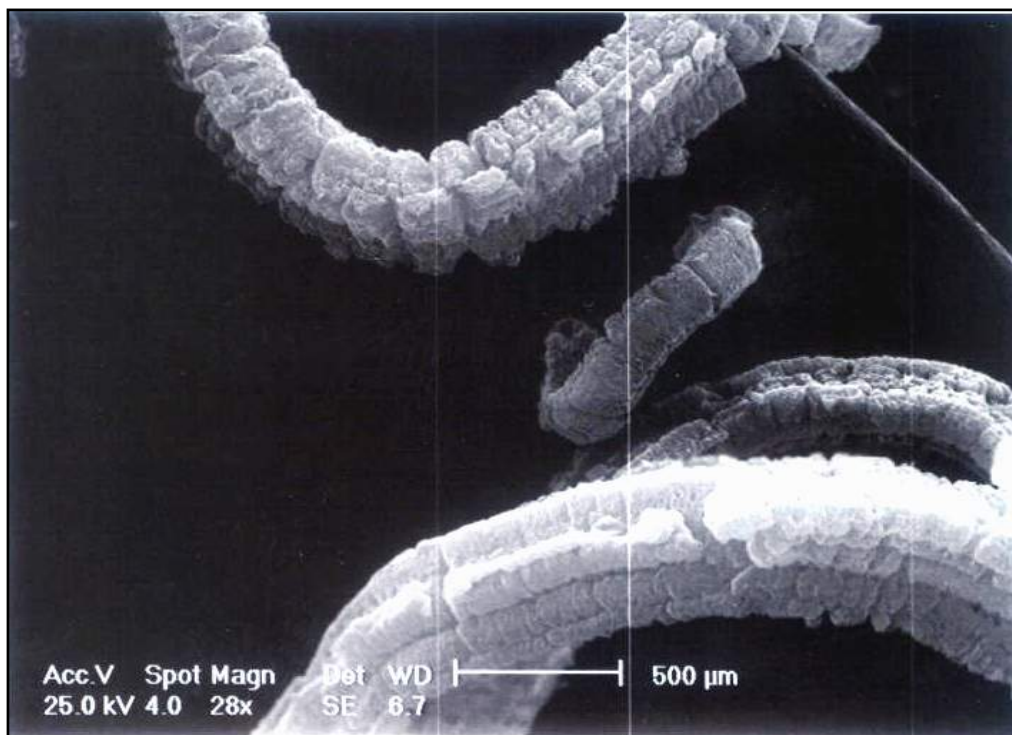**Figure 8.** SEM micrograph of distances between the graphene layers

Figure 9. SEM micrograph of EG particles

3-3- Sorption capacities of synthesized EG

3-3-1- Static tests

Sorption capacity of EG for different oils is shown in Fig.10. As can be seen, EG with a density as low as 4.5 kg/m^3 is capable of sorbing large amounts of oils from the surface of water. According to Fig.10 one gram of EG can sorb 87, 85, 75 and 70 grams of GO2, GO1, LCO and HCO consecutively. Also, Fig.10 shows that oil sorption into the pores of vermicular particles and empty spaces among the entangled particles of EG reduces as oil viscosity increases. Oil sorption time required for exfoliated graphite to sorb different oils is presented in Fig. 11. As can be seen, GO1 and GO2 are sorbed in 1 minute, while sorption of LCO and HCO are completed after 5 and 90 minutes respectively. The longer time required for sorption of HCO can be related to its high viscosity.

3-3-2- Dynamic tests

Oil sorption capacity of wrapped EG is shown in Fig. 12. It is concluded from the figure that net cloth has a negative effect on the oil sorption of EG. Oil sorption of EG is significantly reduced for heavy crude oil. It should be noted that oil viscosity can play two different roles. First, the rate of sorption within the pores and capillaries of EG is reduced as oil viscosity is increased. Second, the adherence on the surface of the material and within the pores during drainage is increased as oil viscosity is increased. According to the second effect, low density oils are released by the sorbent while being lifted out of water and during drainage. It results in lower oil sorption [21]. In our previous work a similar dynamic sorption method was employed to determine the oil sorption capacity of 3 sorbent materials [19] The results of recent experiments for EG are given by Figs. 13-16. Also, in these figures

the oil sorption capacities of EG and other sorbents (presented in Table 2) are compared. These figures show that EG has the highest oil sorption capacity, as much as 65-73 grams of different types of oils per each gram of its weight. After exfoliated graphite, polypropylene nonwoven web has a high oil sorption capacity and is eligible to sorb 7-9 grams of different types of oils per each gram of its weight. Bagasse with mesh 18-45 is capable of sorbing 5-6 grams of oils per each gram of its weight. Oil sorption capacities of bagasse with mesh 14-18 and rice hull are comparable and lower than the other sorbents.
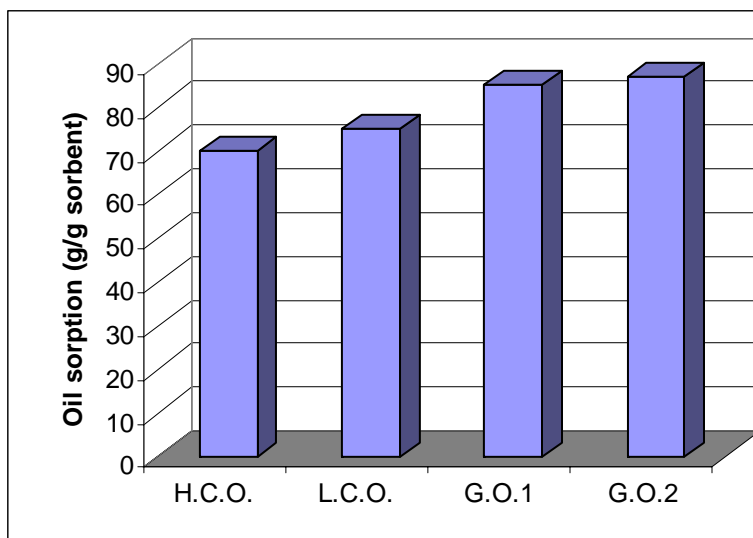
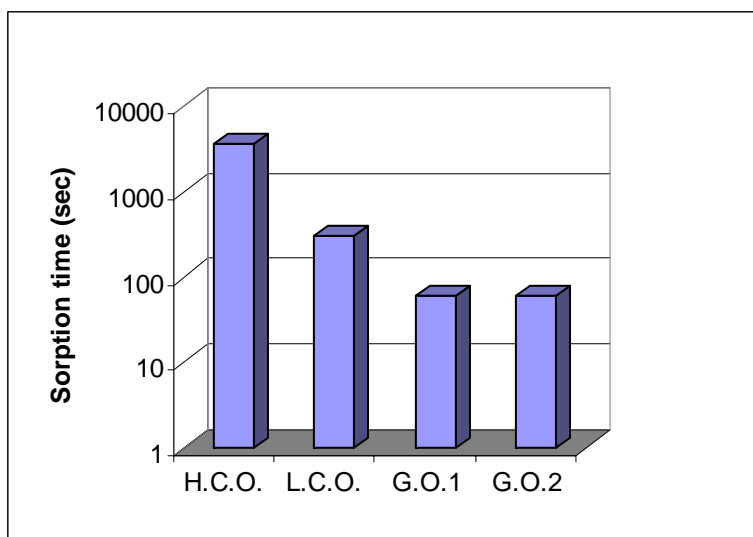**Figure 10.** Oil Sorption capacity of exfoliated graphite for different oils

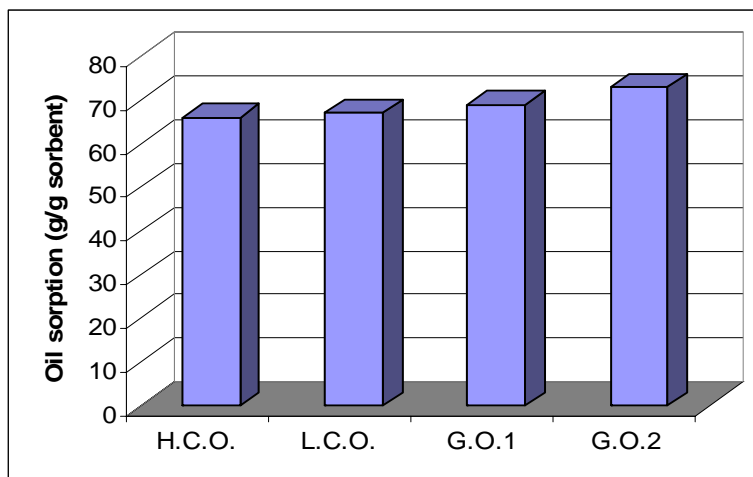**Figure 11.** Sorption required time of different oils after adding exfoliated graphite

Figure 12. Oil sorption of wrapped exfoliated graphite for different oils from water
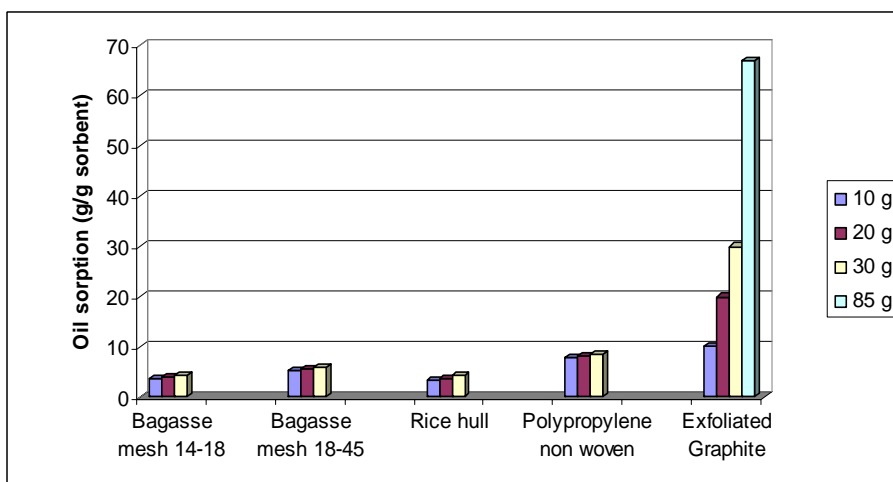

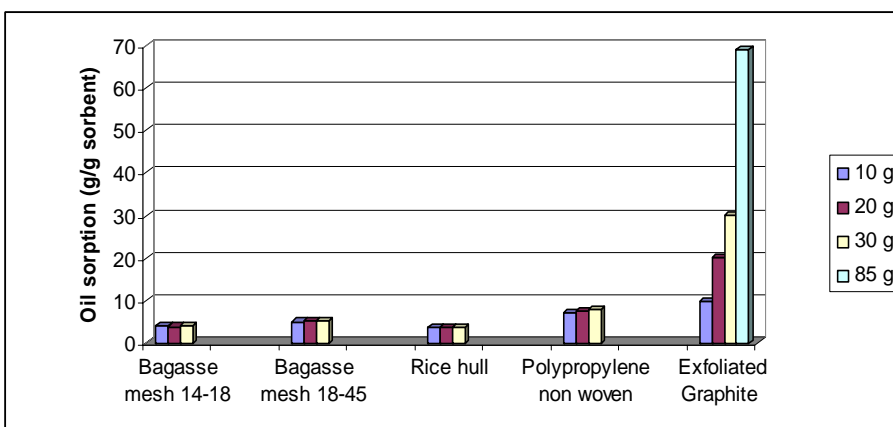**Figure 13.** Sorption capacity of different sorbents for light crude oil

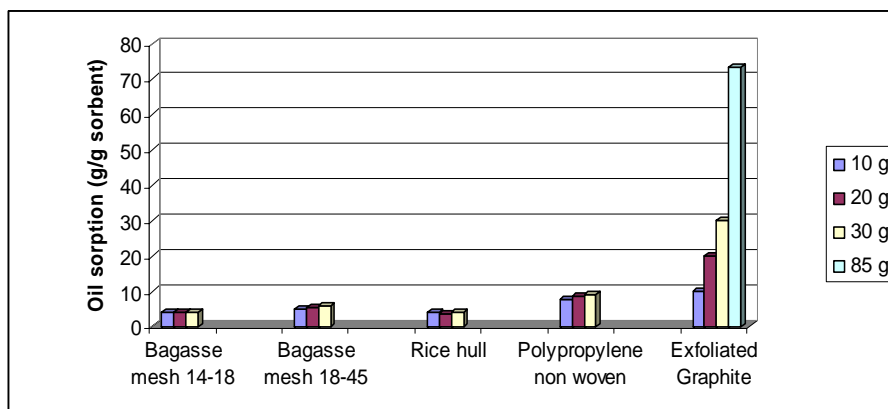**Figure 14.** Sorption capacity of different sorbents for Gas Oil No.1

Figure 15. Sorption capacity of different sorbents for Gas Oil No.2

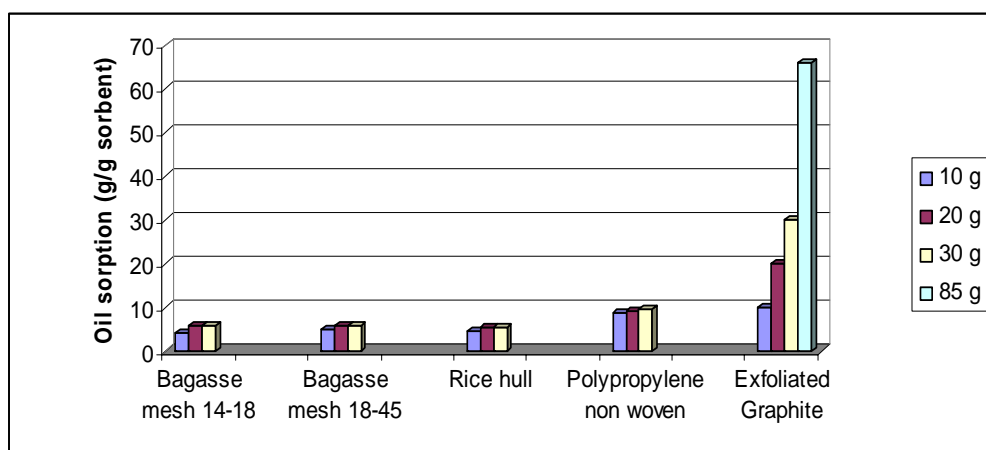**Figure 16.** Sorption capacity of different sorbents for heavy crude oil

Table 2. Specification of sorbent materials

Sorbent → Property ↓	Bagasse	Rice hull	Polypropylene (nonwoven web)
Mesh	14-18 & 18-45	10-14	-
Source	By product of sugar cane	A milling by product	-
Mass per area Kg/m^2	-	-	0.5933

Conclusion

In this research, the worm-like and low density (4.5 kg/m3) EG was synthesized by thermal shock of residue GIC. The GIC was identified as graphite bisulfate with stage *2* using XRD. It was observed that the intensities of diffraction peaks of graphite flake, graphite bisulfate, residue graphite bisulfate and EG were reduced consecutively. SEM micrographs are employed to approve exfoliation of graphite flakes due to treatment with a mixture of sulfuric and nitric acids. This treatment inserts some HSO_4^- ions and H_2SO_4 molecules between the layers of graphite. According to the results, the residue intercalate species between the layers of graphite was enough in order to cause the exfoliation along the normal to the basal plane of graphite. The results show that the synthesized EG in this work with low bulk density is a promising material for the cleanup of oil spills from the surface of sea water with respect to its high sorption capacity for different oils.

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