Engineering Chemistry
ISSN: 2813-6535, Vol. 8, pp 23-29
doi:10.4028/p-r32WGe

Submitted: 2024-04-22
Revised: 2024-09-01
Accepted: 2024-09-04
Online: 2024-12-13

Recyclability and Carbonization Regeneration of Oil Adsorbing Materials Based on Commercial Expandable Graphite

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Keywords: Expanded graphite, oil adsorbing material, adsorption capacity, recyclability, carbonization regeneration

Abstract: This study focused on the oil absorption and carbonization regeneration properties of expanded graphite (EG) prepared from commercial expandable graphite as an oil absorbing material for different oils. The specific surface area of the prepared EG sample was 37.15 m^2/g, and the oil absorption was as high as 76 g/g. More importantly, the prepared expanded graphite had excellent recyclability and good carbonization regeneration performance. Even after 5 cycles, the adsorption capacity remained above 80%. The regenerated EG sample regained a high oil absorption capacity of 44.64g/g. This article has important guiding significance for promoting the large-scale practical application of expanded graphite oil absorbing materials.

Introduction

In recent years, with the development of the petroleum industry, there has been an increase in offshore oil spills and the discharge of oily wastewater worldwide, leading to increasingly serious environmental oil pollution. The oil spill has caused serious environmental damage to marine water resources, posing a significant threat to human survival and ecosystems [1]. Adsorption method is the use of adsorbents to adsorb organic matter, inorganic salts, and oils in wastewater, achieving the goal of cleaning up pollution[2]. It is one of the effective methods for treating polluted wastewater and marine oil spills. Commonly used adsorbents include natural waste such as carbon-based materials, diatomaceous earth, fly ash, and sawdust. But the oil absorption capacity of most natural waste is relatively low. The oil adsorption capacity of the natural adsorbent for corn cob (Zea mays L.) powder is only 0.0124 g/g [3], the absorption capacity of discarded durian peel is 1.301 g/g [4], the maximum oil absorption capacity of sawdust particles is 2.216 g/g [5], the maximum oil absorption capacity of fly ash achieves at 0.6494 g/g [6], and the oil adsorption capacity of activated carbon is 1.6 g/g [7]. Although delignified wood [8], electrospun cellulose fiber three-dimensional aerogel [9] and super hydrophobic cotton [10] have high oil absorption capacity of 20~50 g/g, the process of these absorbents is complex, which is not conducive to large-scale practical application. As one of carbon-based material, expanded graphite (EG) is a worm like porous material obtained from natural graphite flakes after intercalation, water washing, drying, and high-temperature heat treatment [11]. EG has a worm like structure and developed pore structure. Compared with commonly used activated carbon adsorption material, the oil adsorption capacity of EG is about ten times that of activated carbon, making it an ideal material for treating oil pollution[12-14]. The present reports mainly focus on the preparation and the oil absorption property of EG prepared from expandable graphite in the laboratory [12-18]. However, there have been no reports on the oil absorption and regeneration performance of EG oil absorbing materials based on commercial expandable graphite, which is not conducive to the large-scale practical application of EG oil absorbing materials. Herein, EG based on commercial expandable graphite was used as the absorbing materials of different oil, and its oil absorption performance and carbonization regeneration performance were focused on. This paper has important guiding significance for promoting the large-scale practical application and development of expanded graphite oil absorbing materials.

Experimental Method

Commercial expandable graphite was purchased from Qingdao Chenyang Graphite Co., Ltd of China. Commercial expandable graphite was heat-treated at 800 ºC for 60 seconds in a muffle furnace to form EG sample. The oil adsorption performance of EG was tested by adsorption experiment according to the reported method [17,18]. The oil adsorption performance of EG was tested by adsorption experiment. All tests were performed at 25 ºC. Simply put 50 ml of oil materials in a beaker, and then about 0.1 g of EG is weighed and poured into the oil and stirred to stand. At the end of the experiment, the EG was filtered out of the oil to drip the residual liquid on the surface for 2 min, and finally weighed. Then the oil absorption capacity (m) was calculated with the following equation (Eq.1) to evaluate the oil absorption capacity of the EG sample,

$$m = \frac{m_2 - m_1}{m_1}, \qquad (1)$$

where, m is the adsorption capacity of EG at a certain time (3 min), g/g; m_2 is the weight of EG after oil absorption, g; m_1 is the initial weight of EG, g.

Heating and evaporative condensation processes under vacuum was utilized to recover EG and oil [17]. The EG sample after oil adsorption was heated to the boiling point of oil sample under 0.01 MPa pressure to evaporate, and the condensation recovery device was used to collect the oil (the weight was recorded). After heating, the remaining part of the tube was the recycled EG ((the weight was recorded)). The recycled EG was further used to adsorb oil and repeated 5~10 times to determine the recyclability. The carbonization regeneration of the EG sample after adsorption and recovery of oil (after 10 times recycle) was carried out in a vacuum tube furnace at 600 ºC for 1 h under different atmosphere (vacuum or nitrogen). The recyclability of the regenerated EG sample was also tested.

The phase composition of all the expanded graphite samples were tested by X-ray diffraction (XRD) on a Philips X'pert diffraction instrument with Cu-Kα incident radiation (40 kV, 40 mA), the morphology and the microstructures were analyzed by scanning electron microscope (SEM, Hitachi 8010), the chemical groups were characterized by Fourier transform infrared spectrometer (FTIR, TENSOR27, Bruker, Germany), and the Brunauer-Emmet-Teller (BET) specific surface area was detected by Nitrogen sorption (Quantachrome Corporation, USA). The pore size distribution was plotted based on the Barrett–Joyner–Halenda (BJH) method.

Results and Discussion

Fig. 1 illustrated SEM images of the initially prepared EG sample and the regenerated EG samples. It could be seen that all the three EG samples was composed of many adhered and stacked graphite flakes. The graphite flakes were interwoven with each other, and a large number of interconnected micro-scaled pores were formed. The layered structure and a large number of pores are conducive to improving the adsorption capacity of EG. More importantly, the EG samples had high specific surface area and large pore volume which is very important for the adsorption performance of adsorption material[16-18], and the graphite flakes possessed mesoporous structure, as shown in Fig. 2. The initially prepared EG sample from commercial expandable graphite by heat-treating at 800 ºC had a specific surface area of 37.15 m^2/g and a pore volume of 0.2182 cm^3/g with a pore diameter of 30.7 nm. The specific surface area of the regenerated EG sample carbonized at 600 ºC under nitrogen condition and that under vacuum condition decreased to 32.32 m^2/g and 29.89 m^2/g, respectively, but the pore diameter of the two samples increased to around 49 nm.

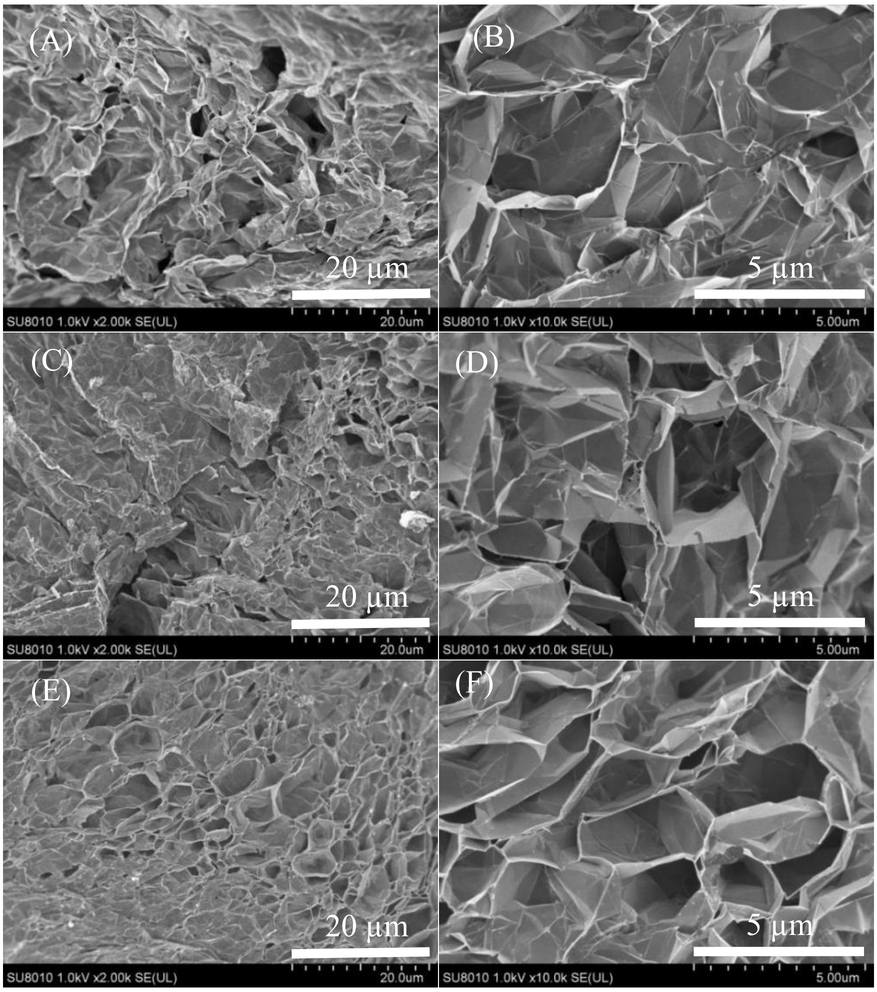

Fig. 1 SEM images of (A) and (B) the initially prepared EG and the regenerated EG samples: (C) and (D) at nitrogen atmosphere, (E) and (F) at vacuum atmosphere

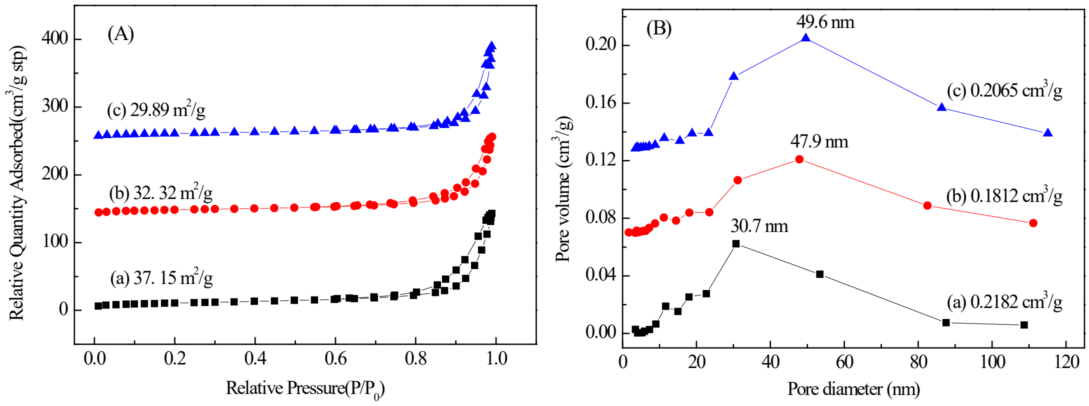

Fig. 2 (A) nitrogen adsorption desorption isotherms and (B) BJH pore size distribution curves of different EG samples: (a) the initially prepared EG, (b) EG regenerated at nitrogen atmosphere, and (c) EG regenerated at vacuum atmosphere

It was precisely because of its unique loose porous structure that the EG samples had good adsorption performance for macromolecular compounds. The initially prepared EG sample from commercial expandable graphite by heat-treating at 800 ºC demonstrated an adsorption capacity of dimethyl silicone oil as high as 76 g/g and over 50 g/g for other kind oil (see Table 1). And also the initially prepared EG sample had excellent recyclability, after 5 times recycle the adsorption capacity still kept over 80% (as shown in Fig. 3A). After 10 times recycle, the adsorption capacity decreased to 27.38% (20.82g/g). Interestingly, after carbonization regeneration, the EG sample of 10 times recycle reacquired a high oil adsorption capacity of 44.64 g/g, as shown in Fig. 3B. And 3 times recycle the adsorption capacity still kept over 80%. Table 2 gives the comparison of oil adsorption capacities of the reported absorbents [4, 5-10, 18]. The oil absorption capacity of the EG sample prepared in this study is much higher than that of most natural adsorbents. By the way, the recovery rates of dimethyl silicone oil, soybean oil, lubricating oil, liquid paraffin, and circulating pump oil are 98.0%, 96.8%, 94.5%, 96.0%, and 93.7%, respectively, which decrease as the boiling point decreases. The ratio of m_1 after the recycling process to m_1 before the first cycle is approximately 0.985. This means that the EG absorbent lost 1.5% after a single recovery process. Fig. 4 is the FTIR image of the prepared EG sample.

Table 1 The adsorption capacity of the initially prepared EG sample for different oil

Oil type	Dimethyl silicone oil	Soybean oil	Lubricating oil	Liquid paraffin	Recycle pump oil
Oil boiling point	~220ºC	~260ºC	~290ºC	~270ºC	~300ºC
m_1 (g)	0.1035±0.02	0.104±0.02	0.1035±0.01	0.1045±0.03	0.1005±0.04
m_2-m_1 (g)	7.8690±0.04	6.8485±0.02	6.1155±0.03	6.1245±0.04	5.0800±0.06
Adsorption capacity (g/g)	76.03±0.04	65.85±0.02	59.09±0.03	58.61±0.04	50.28±0.06

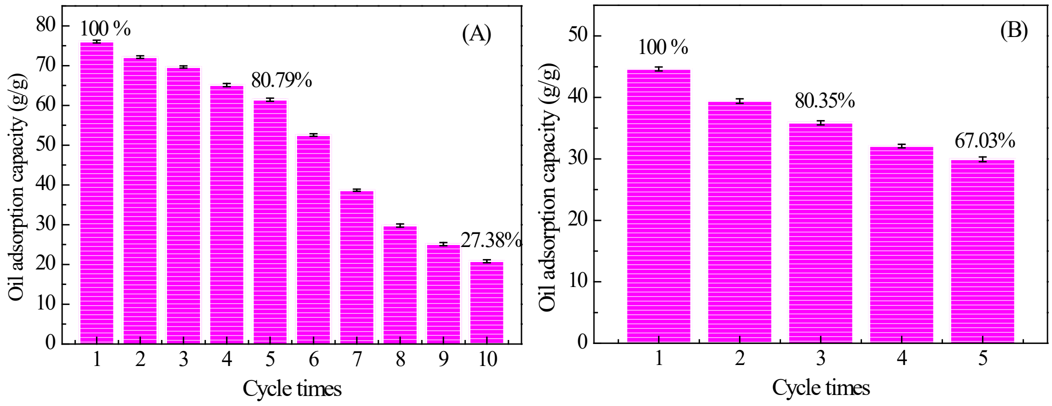

Fig. 3 (A) the adsorption recyclability of the initially prepared EG sample for dimethyl silicone oil over 10 cycles and (B) the adsorption recyclability of the EG sample regenerated at nitrogen atmosphere for dimethyl silicone oil over 5 cycles

Table 2 Comparison of oil adsorption capacities of the reported absorbents

Absorbents	Oil type	Absorption capacity (g/g)	Reference
EG	Dimethyl silicone oil	76	this work
EG	Pump oil	50.28	this work
EG	Soybean Oil	65.85	this work
Discarded durian peel	Cooking oil	1.301	[4]
Sawdust particles	Engine oil, Soybean oil	2.216, 1.9	[5]
Activated carbon	vegetable oil, crude oil	1.4, 1.6	[7]
Delignified wood	Silicone oil	37	[8]
Three dimensional cellulose fiber aerogel	Pump oil	27.26	[9]
Super hydrophobic cotton	Pump oil	44	[10]
EG-3 (expanded graphite by microwave irradiation)	Hydraulic oil, vegetable oil	235, 86	[18]

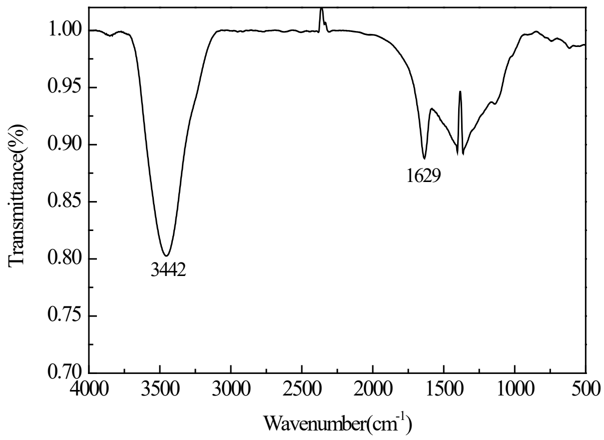

Fig. 4 The FTIR image of the prepared EG sample

The reason why the EG sample has the selective absorption for dimethyl silicone oil is possibly due to the EG sample surfaces possess -C=O and-OH groups as shown in Fig. 4 (the broad absorption peak at 3442 cm^{-1} is caused by the stretching vibration of -OH, while at 1629 cm^{-1} it is caused by the stretching vibration of -C=O). These -C=O and-OH groups can interact with -Si-O group (such hydrogen bonding), leading to the EG sample has the selective absorption for dimethyl silicone oil.

Conclusions

Generally speaking, the prepared expanded graphite sample based commercial expandable graphite possessed a large number of interconnected micro-scaled pores with a specific surface area of 37.15 m^2/g, and demonstrated an adsorption capacity of dimethyl silicone oil as high as 76 g/g. And the prepared expanded graphite had excellent recyclability and good carbonization regeneration performance.

Acknowledgments

This work was supported by Technology Development Project of PipeChina Institute of Science and Technology (Grant No. ZYZL-DTXNY-202204).

References

[1] Carpenter, A., Oil pollution in the North Sea: the impact of governance measures on oil pollution over several decades. *Hydrobiologia 845*, 109-127, (2019).

[2] Bai, Y.R., Dai, L.Y., Sun, J.S., Jiang, G.C., Lv, K.H., R.C., Cheng, Shang, X.S., Plugging performance and mechanism of an oil-absorbing gel for lost circulation control while drilling in fractured formations. *Petroleum Science 19,* 2941-2958, (2022).

[3] Haryanto, B., Nasution, I.T., Polem, A.F., Tambun, R., Alexander, V., Natural adsorbent of corncob (Zea mays L.) powder capability in purification of used cooking oil with shaking operation based on turbidity. *Results in Engineering 19*, 101233, (2023).

[4] Liu, T., A natural armor-protected absorbent from discarded durian peel with rapid and recyclable absorption, high oil retention and self-cleaning ability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects 666,* 131294, (2023).

[5] Lipika, Singh, A.K., Fluorine-free surface coating to prepare hydrophobic and magnetic sawdust particles for oil spill absorption. *Bioresource Technology Reports 25,* 101758, (2024).

[6] Sun, J., Li, R., Wang, X.Y., Zhao, C.H., Song, Q.W., Liu, F., Wang, Z.H., Liu, C.S., Zhang, X.X., Marine oil spill remediation by Candelilla wax modified coal fly ash cenospheres. *Chemosphere 330,* 138619, (2023).

[7] Kyaw, H.H., Myint, M.T.Z., Al-Belushi, M.A., Dobretsov, S., Al-Abri, M., Nanomaterial grafted polymorphous activated carbon cloth surface for antibacterial, capacitive deionization and oil spill cleaning applications. *Chemosphere 350,* 141053, (2024).

[8] Yang, R., Cao, Q.H., Liang, Y.Y., Hong, S., Xia, C.L., Wu, Y.J., Li, J.Z., Cai, L.P., Sonne, C., Le, Q.V., Lam, S.S., High capacity oil absorbent wood prepared through eco-friendly deep eutectic solvent delignification. *Chemical Engineering Journal 401,* 126150, (2020).

[9] Zhang, Y.R., Wang, Y.X., Construction of three-dimensional aerogels from electrospun cellulose fibers as highly efficient and reusable oil absorbents. *Separation and Purification Technology 353,* 128604, (2025).

[10] Wu, D., Wang, T.S., Hu, S.Y., Wu, W.B., Lu, B.B., Huang, X.Y., Yu, W., Wang, M., Wang, G.G., Zhang, J.H., Solvent-free processing of eco-friendly magnetic and superhydrophobic absorbent from all-plant-based materials for efficient oil and organic solvent sorption. *Science of the Total Environment 800,* 149558, (2021).

[11] Bannov, A.G., Timofeeva, A.A., Shinkarev, V.V., Dyukova, K.D., Ukhina, A.V., Maksimovskii, E.A., Yusin, S.I., *Protection of Metals and Physical Chemistry of Surfaces 50(2)*, 183-190, (2014).

[12] Yang, H.W., Bian, S., Hu, J.Q., Li, F.B., Yao, T., Effect of water chemistry on the adsorption of lubricating oil on oxidized graphite. *Journal of Molecular Liquids 219,* 1157-1160, (2016).

[13] Ding, X.H., Wang, R., Zhang, X., Zhang, Y.Z., Deng, S.H., Shen, F., Zhang, X.H., Xiao, H., Wang, L.L., A new magnetic expanded graphite for removal of oil leakage. *Marine Pollution Bulletin 81,* 185-190, (2014).

[14] Tian, Y.Y., Ma, H.Z., Solvent-free green preparation of reusable EG-PVDF foam for efficient oil water separation. *Separation and Purification Technology 253,* 117506, (2020)

[15] Yao, T., Zhang, Y.G., Xiao, Y.P., Zhao, P.C., Guo, L., Yang, H.W., Li, F.B., The effect of environmental factors on the adsorption of lubricating oil onto expanded graphite. *Journal of Molecular Liquids 218*, 611-614 , (2016).

[16] Takeuchi, K., Fujishige, M., Kitazawa, H., Akuzawa, N., Medina, J.O., Morelos-Gomez, A., Cruz-Silva, R., Araki, T., Hayashi, T., Terrones, M., Endo, M., Oil sorption by exfoliated graphite from dilute oil-water emulsion for practical applications in produced water treatments. *Journal of Water Process Engineering 8,* 91-98, (2015).

[17] X u, C.B., Jiao, C.L., Yao, R.H., Lin, A.J., Jiao, W.T., Adsorption and regeneration of expanded graphite modified by CTAB-KBr/H_3PO_4 for marine oil pollution. *Environmental Pollution 233,* 194-200, (2018).

[18] Wei, Q., Xu, L., Tang, Z.M., Xu, Z.B., Xie, C., Guo, L.R., Li, W., High-performance expanded graphite from flake graphite by microwave-assisted chemical intercalation process. *Journal of Industrial and Engineering Chemistry 122,* 562-572, (2023).