Eco-Friendly and Economical Oil Adsorbents Based on PUF and Chitin

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Abstract. Industrialization and modernization have led to a rapid increase in the amount of solid waste around the globe. To reduce the amount of solid waste that is discharged into the environment, it is necessary to select materials that have high reusability and recyclability. This study evaluates the reusability of the grafted oil adsorbent PPU10M based on polyurethane foam (PUF) and chitin. The result shows that the sorbent PPU10M can reuse up to 20 cycles after sorbent regeneration by the mechanochemical method. The amount of adsorbed oil is recovered up to 91.5%. The use of waste sorbents as the filler into the process synthesis of the oil sorbent containing waste is studied in this work. The results present that the sorbents containing 5% mass of the waste have the oil capacity equivalent to the sorbent without waste. At the same time, the water adsorption of this material reaches lower than in comparison with the non-waste material. This is indicated that the sorbent PPU10M not only has high oil adsorption capacity but also has good reuse and recycling ability. Thus, it is considered that PPU10M is a potential, eco-friendly, and economical sorbent for oil spill removal.

1. Introduction

The distribution of oil petroleum resources is unevenly all over the world, leading to the rapid oil trade between territories due to the increasing demand [1-4]. Currently, oil transport is mainly carried out via waterways. Therefore, it is inevitable the occurrence of oil spills in the water environment [5]. An oil spill accident has very serious consequences such as an effect to aquatic ecosystems, negative impact on the health of humans and living creatures, damage to the seafood industry's economy, damage to the marine tourism industry as well as waterway transportation in the area where the oil spill occurred [4,6,7]. Thus, the oil spill incidents at sea are considered as an urgent problem. Besides, the loss of oil into environmental due to oil spills also is one of the causes of depleting this valuable resource [6]. So, it is necessary and important to develop the methods for the treatment of oil pollution in the water environment and recover thoroughly the lost oil.

Currently, there are various methods for removing oil spills, such as mechanics, chemistry, biology, physics, and use sorbents [8,9]. In particular, the sorbents are considered one of the most effective methods due to its advantages such as high efficiency, hydrophobic properties, reusability, and high buoyancy, … [8,10]. Currently, the combined sorbent between the natural material - chitin and the synthetic polymer - polyurethane foam (PUF) has been developed and designated as a potential absorbent to clean water from oil pollution. This combined material not only has high oil adsorption capacity but also has well buoyancy even in the saturated state. Notably, the economic benefits of the
combined sorbent improve significantly in comparison with the blank material PUF [5]. Therefore, the use of this combined sorbent to clean up oil spills in the water environment will be very wide in the future.

Concerning the rapid development of solid waste in the world in the near years, the use of high reusable and recyclable materials is being encouraged [11]. The reuse of materials is considered one of the methods to significantly reduce the amount of solid waste discharged into the environment. At the same time, it also leads to reducing the cost of the oil spill treatment. However, the amount of final wastes after the adsorption process is inevitable. Therefore, it is important to evaluate the recyclability of sorbent PPU10M after the adsorption process. Currently, there are three main methods for treating waste based on PUF: landfill, burn, and recycling. Due to the low density of PUF-chitin-grafted material, it requires a relatively large area of landfills [12]. The generation of seriously polluted toxic gases is a threat to the atmosphere when using the burn method [12,13]. Therefore, waste treatment by the above two methods is not preferred. Thus, it is important and necessary to develop the sorbent with the high reusability and recyclability to reduce solid waste discharged into the environment. For recycling sorbent PPU10M, the use of the spent sorbent as a filler comeback the synthesis process sorbent is significant potential, simple and economic.

This study evaluates the reusability and oil recovery ability of the combined sorbent PPU10M. Besides, the development of the sorbent containing the spent sorbent (the waste sorbent) also is studied. The parameters of the foam synthesis process and the sorption capacity of the sorbents containing various degrees of filler also are surveyed and compared in this paper.

2. Materials and methods

2.1. Materials
Chitin is purchased from the Chitosan Vietnam company, Ho Chi Minh City, Vietnam. Chitin is cut to the small flake with size 1-3 mm and storage in the nylon bags. Components isocyanate and polyol are purchased from the Dau Izoland, Vladimir City, Russia. The other chemicals are used in this study such as NaCl, MgCl₂, Na₂SO₄, CaCl₂, KCl, NaHCO₃, KBr, H₃BO₃, SrCl₂, NaF, and toluene.

2.2. Synthesis sorbents
For synthesis sorbent PPU10M: the sorbent is prepared according to the method described in the study [14].

For synthesis the sorbents containing waste (the spent sorbent): The synthesis process is carried out as same as the synthesis process PPU10M. However, in addition to 10% by mass of the chitin, the amount of waste sorbent also is added into the PUF. Three degrees addition of the waste is studied 5, 10, and 15% by mass, respectively. The waste sorbent has a size of 1-3 mm. The schema of the synthesis process is described in the fig.1.

![Figure 1. The schema of the synthesis sorbent containing waste.](image-url)

2.3. Some properties and oil capacity of the sorbents
The time parameters of the synthesis process are determined by the method described in the previous study [15]. The density of sorbents is measured according to method GOCT-409-77 [16]. The oil and water capacity in the system containing only oil or water is carried out according to the weight method [15].
For the oil-water system, the adsorption is carried out in the system of the artificial seawater containing oil [17]. Also, the oil capacity is determined by using the improved method ASTM F726-06 [19]. The principle of the method is to use toluene to dissolve the residual oil after adsorption. Oil adsorption capacity is calculated by the difference between the amount of oil before and after adsorption [5].

2.4. Sorbent regeneration
The sorbent is regenerated by the mechanochemical method. To do this, the sorbent after the adsorption process is squeezed mechanic to recover adsorbed oil (the mechanic regeneration). Next, it is used to the next adsorption and this regeneration is repeated 15 cycles adsorption. Then, the solvent toluene is used to washing the sorbent at the next 5 cycles after the sorbent is squeezed. The wash with toluene is carried out 3 times until the oil containing in the sorbent is removed. After washing, the sorbent is squeezed to remove the solvent and dried at the temperature 70–80°C during 30-45 minutes. The dried sorbent is used for the next cycle.

3. Results and discussion
3.1. Sorbent regeneration
Currently, mechanic and chemical regeneration are the two most common methods regeneration of the sorbent for purpose reuse sorbent. The sorbent regeneration by the mechanic method is one of the simple, cheap, and safe methods. However, this method does not completely recover adsorbed oil. The amount of the remaining oil after squeezing reduces the oil capacity of the sorbent in the next cycle [19], the reduction of the oil capacity ranges about 5% (Fig.2). At the same time, the residual oil in the cube sorbents leads to the difficulty of the waste treatment. Therefore, the chemical regeneration of the sorbent is used in the last 5 cycles of the process adsorption. Due to the solvent toluene can dissolve the remaining oil in the cube sorbent after squeezing, thus, the pores in the sorbent are free. Leading to the easily entering of the oil in the next cycle. This explains the increase of the oil capacity when using chemical regeneration. However, using a large number of chemical solvents for washing adsorbents is expensive and not environmentally friendly. Besides, due to the chemical interaction of toluene with the residual isocyanate and polyol functional groups in the adsorbent, it reduces the durability of the adsorbents [20]. Therefore, the adsorbent cleaning by the toluene is considered only in the last 5 cycles adsorption in this study.

Figure 2. The reusability of the sorbents.

The result from fig.2 shows that the sorbent PPU10M not only has a high oil adsorption capacity but also has high reusability. After 20 regeneration cycles, the average oil capacity reaches 12.4 g/g and it can recover up to 91.5% adsorbed oil (Table 1). In comparison with the blank adsorbent PUF, it
is found that the addition of chitin into the component PUF does not affect the durability of the adsorbent. Thus, the number of reuses as well as the oil recovery efficiency of the sorbent PPU10M is equivalent to the PUF without chitin.

Table 1. The reusability of the sorbents PUF and PPU10M.

|                  | PUF         | PPU10M     |
|------------------|-------------|------------|
| The number of reuses, cycles | 20          | 20         |
| Average oil capacity, g/g     | 14.97       | 12.38      |
| The degree of oil recovery, % | 90.2        | 91.5       |

The adsorbent regeneration is both significant for the reduction of material costs significantly, and there is great significance for environmental protection. The adsorbed oil recovery contributes to reducing the amount of oil lost to the environment. This may limit the negative impact of the oil on the environment, on the other hand, it will help recover the oil so that it can be used for different purposes, avoiding wasting of depleting resources. Besides, the reuse of adsorbents also contributes to reducing the amount of initial raw materials that are used for the adsorbent synthesis. Besides, materials with high reusable reduce the amount of solid waste released into the environment. Thus, it is clear that the material PPU10M presents to be an efficient, economical, and environmentally friendly adsorbent.

3.2. Recycling waste after the sorption process

The use of highly recyclable materials is also one of the popular and desirable options for reducing the amount of solid waste into the environment. Similar to reuse material, recycling waste not only reduces the cost of the product but also reduces the amount of the raw material used for material synthesis. Besides, recycling waste helps to reduce landfill costs as well as reduce the release of toxic waste gases into the environment during the burning process [12].

In this paper, the recycling of spent sorbents is studied by using it as fillers in the synthesis of oil sorbents containing waste. Previously, the author Wang and et al reported that it was possible to use wastes from PUF as the filler up to 20% mass but the properties of obtained materials did not change [21]. Therefore, this study evaluates three additional levels of waste adsorbents, respectively 5, 10, and 15% by mass. The time parameters and the density as well as the adsorption capacity of sorbents containing waste are investigated and compared with the non-waste materials PPU10M. Table 2.

Table 2. Some properties and the sorption capacity of adsorbents.

|                  | The non-waste sorbent PPU10M [15] | The sorbents containing waste 5% mass. | 10% mass. | 15% mass. |
|------------------|----------------------------------|--------------------------------------|------------|------------|
| Start time, s    | 33                               | 50                                   | 61         | 67         |
| Rise time, s     | 112                              | 241                                  | 275        | 316        |
| Density, kg/m³   | 69.91                            | 103.4                                | 107.09     | 111.37     |
| Oil capacity, g/g | 12.72                            | 12.48                                | 9.17       | 7.27       |
| Water capacity, g/g | 5.79                             | 3.44                                | 3.40       | 3.29       |
| Coefficient “a”  | 0.45                             | 0.30                                | 0.37       | 0.45       |

For the foaming process, the adsorbents containing waste have higher time parameters compared to the sorbent without waste. This can be explained that due to the number of impurities (such as oil, toluene, salts, etc.) presents in the composition of spent adsorbents; it leads to more difficult interactions between components in the synthesis process. On the other hand, similar to the synthesis
process of the non-waste adsorbent, the more the degree of fillers increases, the more the time parameters of the synthesis process increase [14].

The density of the adsorbents is the main factor that affects the buoyancy of the adsorbent at the saturation state, so it is necessary to investigate the density of the adsorbents. Because the waste after the adsorption process contains some impurities, these "heavy" components increase the density of the sorbents containing the waste in comparison to the adsorbent without waste. It is obvious that the larger the amount of filler, the higher the density of the obtained adsorbents.

The adsorption capacity is an important factor to evaluate the sorbent for oil spill removal. The results from table 1 show that the adsorbents containing waste have a lower oil adsorption capacity than the sorbent PPU10M. The adsorbent containing 5% waste has higher oil and water capacity than adsorbents containing 10% and 15% waste, its oil capacity reaches 12.48 g/g.

The selective adsorption between oil and water is evaluated by the coefficient "a", shows that the sorbents containing waste prioritize oil adsorption than water adsorption. This coefficient is significantly improved in comparison with the sorbent without waste PPU10M. Because of the waste sorbent after the washing, its composition presents the amount of residual oil and toluene. These are hydrophobic components that lead to a decrease in the water sorption of adsorbents containing waste in comparison to the sorbent PPU10M.

So, the usage for filler from the waste sorbent to create the new oil sorbent is a potential method. This method of the waste treatment not only creates the adsorbent with oil sorption capacity, which is equivalent to the non-waste adsorbent but also significantly improves the water adsorption of the original adsorbent. Also, this recycling method contributes to reducing the cost of sorbents in general and the cost of cleaning up oil spills in particular. So, once again it is confirmed that the sorbent PPU10M is an economical, simple, and environmentally friendly material for the cleanup oil spills.

4. Conclusions
The reusability of the sorbent PPU10M is studied in this paper. The result presents that the combined sorbent PPU10M is high reusable up to 20 cycles adsorption after using mechanochemical regeneration. The amount of oil recovery reaches up to 91.5% and the oil capacity reaches 12.4 g/g. The waste sorbent is recycled by using the spent sorbent as the filler for the synthesis process of the oil sorbent containing waste. The additional degrees of waste adsorbents are 5, 10, and 15% mass, respectively. The results indicate that the oil sorbent containing 5% mass waste sorbent has a higher oil capacity than the degrees 10 and 15% of the waste. Besides, in comparison with the non-waste sorbent PPU10M, the sorbent containing waste has the commensurate oil capacity, and its water capacity is improved. The use of waste sorbent as the filler for the synthesis of oil sorbent containing waste contributes to reducing significantly to solid waste into the environment. The study presents that the combined sorbent PPU10M is a friendly environmental, economic, and potential sorbent for treatment oil spills in the water environment.

5. References
[1] Chen J, Zhang W, Wan Z, Li S, Huang T and Fei Y 2019 J. of Cleaner Prod. 227 p 20
[2] Arslan O and Turan O 2009 Marit. Pol. Manag. 36(2) p 131
[3] International Tanker Owners Pollution Federation Ltd (ITOPF) 2019 London 16
[4] Jafarinejad S 2017 Petroleum waste treatment and pollution control 2017 p19
[5] Tran Y D T and Zenitova L A 2020 Current Applied Sci. and Tech. 20(2) p 321
[6] Hua L, Lifen L and Fenglin Y 2013 Procedia Envir. Sci. 18 p528
[7] Nance E, King D, Wright B and Bullard R D 2015 J. of the air and waste manag. Association 66(2) p 224
[8] Lidia B, Agnieszka W, Dorota K and Wojciech F 2017 Minerals 7(3) 37
[9] Broje V, Keller A A 2006 Environ. Sci. Technol. 40 p 7914
[10] Dong X, Chen J, Ma Y, Wang J, Chan-Park M B, Liu X and Chen P 2012 Chem. Communications 48 p 10660
[11] Samiha B 2013 Mediterranean J. of social Sci. 4(3) p 129
[12] Wenqing Y, Qingyin D, Shili L, Henghua X, Lili L and Jinhui L 2012 The 7th Int. conf. on Waste Manag. and Tech. p 167
[13] Liu J P, Wang Y F, Zheng X X and et al 2010 New Chem. Materials 38(12) p 21
[14] Tran Y D T and Zenitova L A 2019 IOP Conf. Series: Earth and Envir. Sci. 337 doi:10.1088/1755-1315/337/1/012008
[15] Chang I D Ch and Zenitova L A 2019 Bulletin of PNRPU. Chemical technology and biotechnology 52(2) p 33
[16] GOST 409-77 Official publication, and IC Publishing Standards (Moscow)
[17] ASTM D1141-98 2013 West Conshohocken: ASTM International (USA)
[18] ASTM D95-13 2018 West Conshohocken: ASTM international (USA)
[19] Keshavarz A, Zilouei H, Abdolmaleki A, Asadinezhad A and Nikkhah A A 2016 Int. J. Enciron. Sci. Technol. 13 p 699
[20] Amir A N, Hamid Z, Ahmad A and Alireza K 2015 Chem. Eng. J. 62 p 278
[21] Wang J R and Chen D J 2013 China Elastomerics 13(6) p 61