Int. J. New. Chem., 2021, Vol. 8, Issue 3, pp 240-251.

International Journal of New Chemistry

Published online 2021 in http://www.ijnc.ir/.

Open Access

Print ISSN: 2645-7236

Online ISSN: 2383-188x

Original Research Article

Removal of Oil from water Surfaces via Recyclable $NiFe_2O_4$/Polyurethane Sponge

Azita Seyed Shariatdoost[1], Pirouz Derakhshi[2], Kambiz Larijani[1], Aliakbar Safekordi[1], Mohammad Yousefi[3]*

[1]Department of chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

[2] Department of chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

[3] Department of chemistry, Yadegar-e Imam Khomeini (RAH) Shahr-e Rey Branch, Islamic Azad University, Tehran, Iran

Received: 2019-10-12 *Accepted: 2021-03-02* *Published: 2021-07-01*

ABSTRACT

In an attempt to develop the methodologies used for oil spill clean-up, polyurethane sponge was modified by deposition of $NiFe_2O_4$ nanoparticles on the surface of the original polyurethane sponge under ultrasonic treatment. The fabrication process was facile and low-cost. The as-prepared magnetic sponge exhibited remarkable features including great porosity, high oil adsorption capacity, hydrophobicity, and reusability. In addition, the magnetic property of the modified sponge facilitated the process of oil-water separation. Indeed, the hydrophobicity of the modified sponge contributed to the adsorption of different types of oil and organic solvent on the sponge surface. The modified sponge exhibited the same characteristic peaks as those of the $NiFe_2O_4$ magnetic nanoparticles, ascertaining the formation of the crystalline nickel ferrite nanoparticles. The XRD and FTIR results proved the formation of the composite. FESEM images of the nanocomposite showed a highly porous mulberry-like structure with a rough skeleton. More importantly, the oil and water contact angle measurements proved the hydrophobicity of the modified sponge.

Keywords: Polyurethane, oil adsorption, sponge, reusability, magnetic separation, $NiFe_2O_4$nanoparticles, oil removal

***Corresponding Author: Tel.: +98(912)5252435E-mail: myousefi50@hotmail.com**

Introduction

Adverse effects of water pollution on human and aquatic ecosystems represent a major concern. As a workaround, water purification techniques have been widely studied [1,2]. Oil removal represents an important stage of water treatment in industrial countries, by which many recent scientific investigations have been inspired given the growing demand for novel methods to efficiently separate oil from water [3].

Previous oil-water separation methods have been focused on silica aerogels [4], nanowire membranes[5], mesh films [6], carbon nanotubes [7–10], sawdust [11], and sponges [12–15]. Meanwhile, porous-surface [16–18] and high-hydrophobicity materials have been largely regarded for oil removal applications [12,19–21]. Various techniques have been reported for fabricating superhydrophobic adsorbents, such as chemical vapor deposition (CVD) [22] , emulsion polymerization[23-24], sol-gel processes [25-27] , and solution immersion[28-32]. In recent years, magnetic nanocomposites have been paid much attention thanks to their facile separation capabilities. In order to achieve an efficient and fast separation procedure, it is essential to combine the hydrophobicity with the magnetic property. Sponges have been widely studied in different fields of research because of their three-dimensional porous structure. However, previous reports on oil-water separation have relied on expensive materials and severe preparation conditions. Thus, a major challenge to address is develop adsorbents with high oil adsorption capacity, remarkable selectivity, low-cost fabrication process, and environmental friendliness.

In this study, a magnetic nanocompostie was fabricated through modification of commercially available polyurethane sponge, which is a common oil adsorbent thanks to its high porosity. Spectacular advantages of the as-produced magnetic nanocomposite, including facile preparation, high chemical stability, excellent performance, and reusability, provides new prospects in the water purification industry.

Experimental

Materials

All chemicals were of analytical grade and used without further purification. Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, purity = 98%), iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, purity = 98%), citric acid ($C_6H_8O_7$, purity = 99%), ammonium hydroxide (NH_4OH, purity = 99%) and vinyltriethoxysilane (purity = 98%, Merck) were supplied from Merck. The commercially available polyurethane was directly purchased from a local store in Tehran.

Synthesis of NiFe2O4 nanoparticles

Nickel ferrite nanoparticles were synthesized through a sol-gel auto combustion method. Appropriate initial amounts of $Ni(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ and citric acid were dissolved into 50 mL of deionized water under vigorous stirring for 1 h. Then the temperature was raised to 80℃ for 2 h while adding the ammonium hydroxide to adjust the pH value of the solution to 7. At this step, the solution had its color changed to green. The greenish solution was then heated at 120℃till it was gradually changed into a gel. The heating process was continued to form a dried gel. The dried gel eventually started to ignite and nanoparticles effused. Finally, the nanoparticles were collected and calcinated at 1000℃ for 5 h.

Fabrication of magnetic sponge

The purchased polyurethane sponge was cut into pieces of 4 ×4 × 2 mm in dimensions. The pieces were rinsed with deionized water and then submerged into a solution of deionized water and ethanol at 50:50 for 48 h followed by dehydrating at room temperature. The prepared pieces of sponge were then immersed into a mixture containing 100 mg of $NiFe_2O_4$nanoparticles, 80mL of ethanol and 2 mL of vinlytriethoxysilane under ultrasonication for 6 h. The obtained sponge was then rinsed with deionized water and dried at room temperature.

Oil-water separation test

In order to investigate the oil adsorption efficiency of the magnetic sponge, weight measurements were performed. In this study, five types of oil and organic solvent were considered; these included the turbine oil, n-hexane, toluene, lubricating oil, and engine oil. The oil adsorption capacity (Q) of $NiFe_2O_4$/polyurethane sponge was evaluated for different oil types by measuring the weights of the as-produced sponge before (m_1) and after(m_2) adsorbing the oil. Oil adsorption capacity of the modified sponge was calculated as follows:(m_2-m_1/m_1). The pieces of modified $NiFe_2O_4$/PU sponge were placed into a mixture of oil and water to undertake the separation tests for different periods of time. For each oil separation test, measurements were performed in triplicates and average values were reported. Recyclability of the manufactured nanocomposite was also investigated by removing the oil from the magnetic sponge under vigorous stirring in ethanol solution for 30 min. The modified sponge could be reused after drying at 100℃ for 10 h.

Characterization

The morphology of the modified sponge was observed by field emission scanning electron microscopy (FESEM, TESCAN MIRA). The composition of the magnetic sponge was analyzed by X-ray diffraction analysis (XRD, PW1730 PHILIPS) and Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27). Oil and water contact angles were measured by a contact angle meter (CA, CA-EF20, FARS EOR TECH). Magnetic behavior of the treated sponge was also investigated by a vibrating-sample magnetometer at room temperature (VSM, LBKFB, MEGNATIS DAGHIGH KAVIR Co).

Results and discussion

Contact angle study

In this project, water and oil contact angles were measured to examine the hydrophobicity and lipophilicity of the as-prepared sponge. As shown in Figure 1, the water droplet retained its spherical shape when placed on the surface of the modified sponge. The measured water contact angle (145°) indicated the hydrophobicity of the sponge after modification.

Figure 1. Optical image of a water droplet on $NiFe_2O_4$/PU sponge

The oil contact angle was further studied (Figure 2), with the oil droplet being able to penetrate into the sponge. The oil contact angle (31°) demonstrated the lipophilicity of the $NiFe_2O_4$/PU sponge particles. The hydrophobicity and lipophilicityof the nanocomposite suggest its large potentials for removing the oil from water.

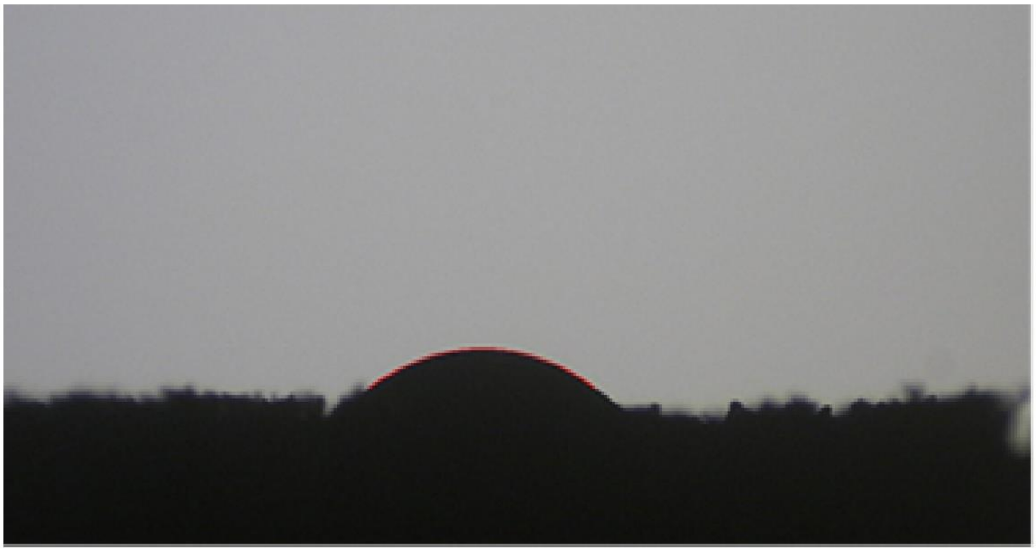

Figure 2. Optical image of an oil droplet on $NiFe_2O_4$/PU sponge

XRD Study

To study surface chemical composition of the modified polyurethane sponge, X-ray diffraction (XRD) analyses were carried out. The XRD pattern is presented in Figure3. According to this pattern, significant peaks were absent in the range of 2ɵ=0° to 2ɵ=24°, due to the presence of the amorphous phase (PU sponge). Moreover, the reflection peaks at 2ɵ =30.10°,36.17°, 43.61°, 54.16°, 54.16°, 57.76°, and 63.16°confirm the crystalline structure of the specimen. This XRD pattern is in accordance with the standard card JCPDS NO 01-087-2336, suggesting the loading of nickel ferrite magnetic nanoparticles on this composite.

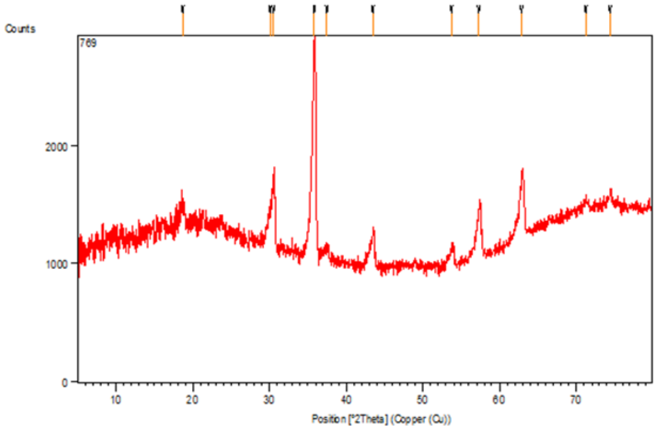

Figure 3. XRD pattern of $NiFe_2O_4$/PU nanocomposite

FTIR study

The FTIR spectra recorded from the $NiFe_2O_4$ polyurethane sponge are presented in Figure 4. The absorption bands around 3301.96 and 1541.30 cm^{-1} are related to stretching vibration of N-H and bending vibration of N-H, respectively. The stretching vibration of the C=O bond and asymmetric stretching vibration of the c-o correspond to the absorption bands around 1648cm^{-1} and 1223.89 cm^{-1}, respectively. The weak band around 924.73cm^{-1} is caused by N-CO-O symmetric stretching vibration. The asymmetric stretching vibration of Si-O is marked by the broad bands at 1097.09 and 1286.68cm^{-1}. The strong absorption at 591.24 cm^{-1} is ascribed to stretching vibration of Fe-O. The characteristic bands at 1601.45, 2869.54, 2972, 1097.09 and 1298.68 cm^{-1} were attributed to typical absorption bands of vinlytriethxysilane. The stretching vibrations of C=C in $CH=CH_2$ and CH_2 in $CH=CH_2$ were assigned to the absorption bands at 1601.45 and 2869.54 cm^{-1}, respectively[33-35].

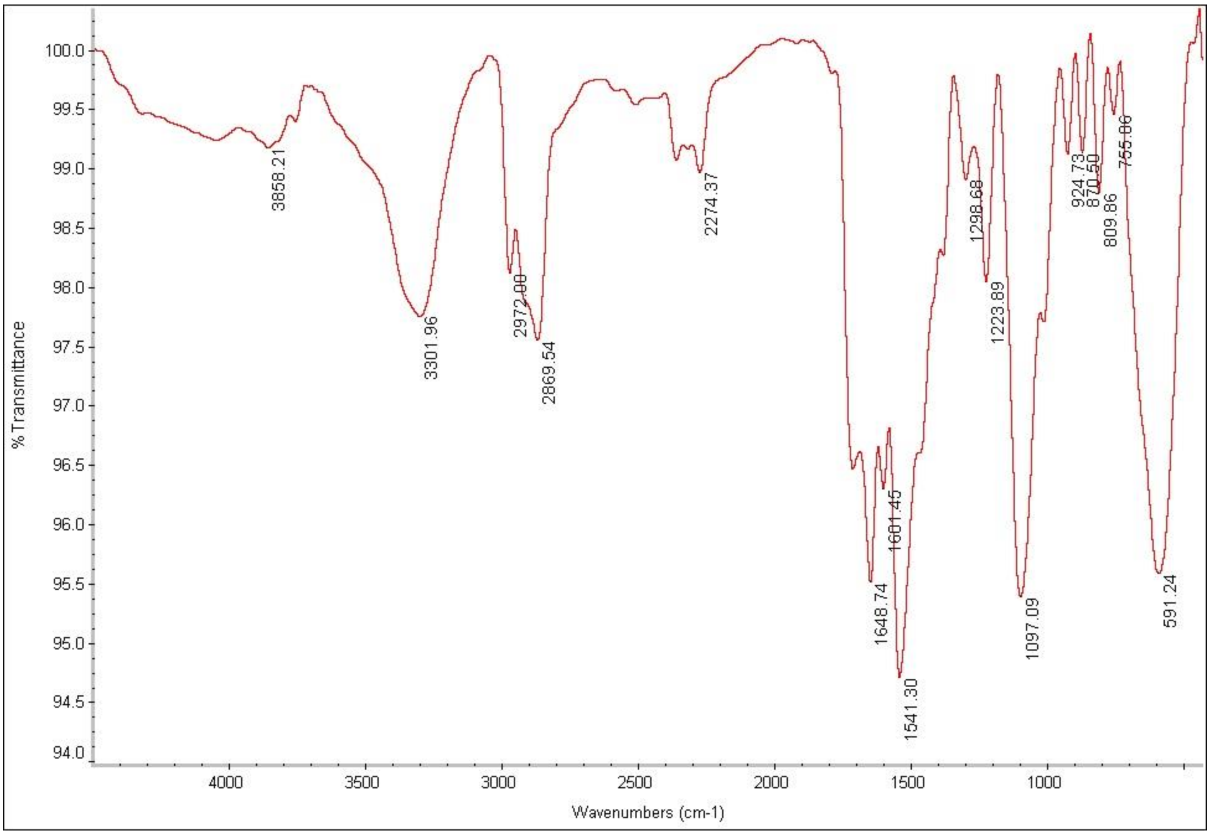

Figure 4. FTIR spectrum of NiFe2O4/PU sponge

FESEM Study

The morphology of the polyurethane sponge was studied by FESEM images both before and after such modifications. As shown in Figure5a, the original polyurethane sponge had a three-dimensional porous structure. Figure 5b illustrates that, upon the modification process, aggregation of $NiFe_2O_4$nanoparticles formed a mulberry-like hierarchical structure. The three-dimensional interconnected structure and rough skeleton of this adsorbent attributed to its high performance in oil-water separation test.

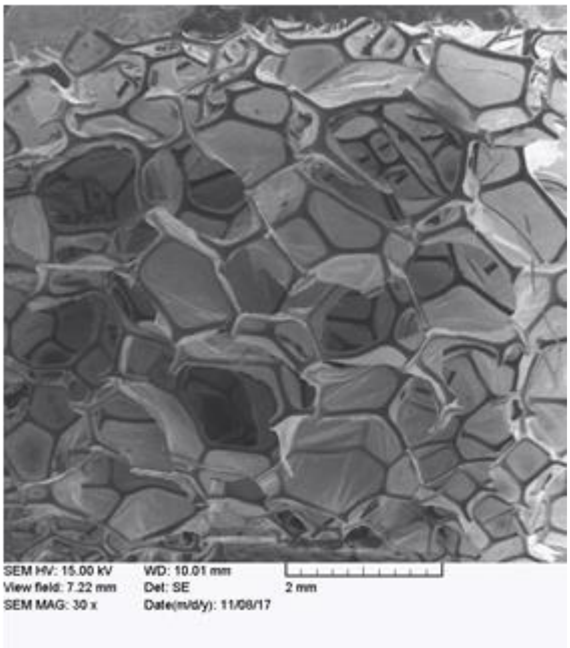

Figure 5a..FESEM image of polyurethane sponge

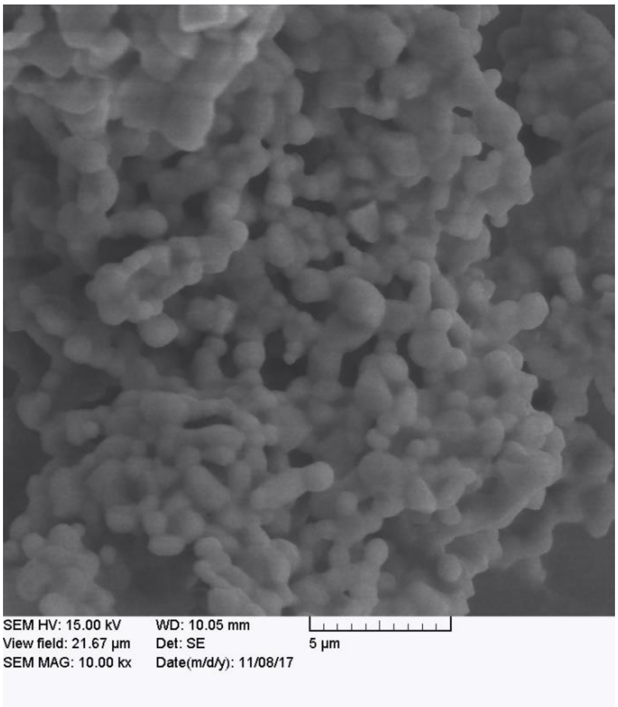

Figure 5b. FESEM image of $NiFe_2O_4$/polyurethane sponge

VSM Study

The hysteretic curve of the $NiFe_2O_4$ nanoparticles was developed by using a vibrating-sample magnetometer at room temperature. The hysteresis curve signifies a room-temperature saturation magnetization (M_s) and coercivity (H_c) of 64.92 and 350.19 emu/g, respectively(Fig.6.). According to this curve, the as-prepared nanoparticles could be categorized under soft magnetic material.

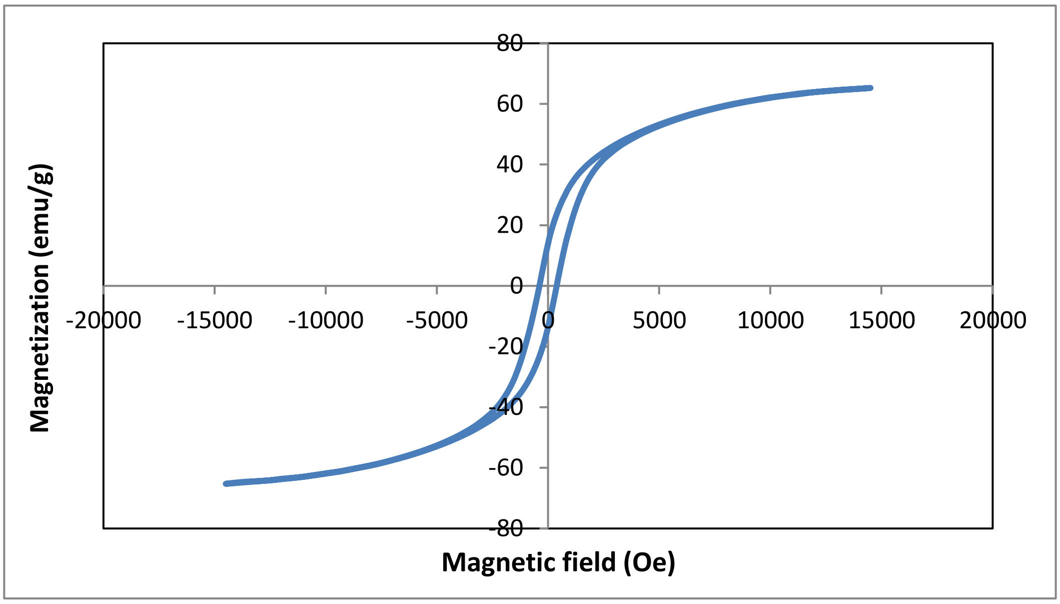

Figure 6. Hysteresis curve of $NiFe_2O_4$ nanoparticles at room temperature.

Oil adsorption study

The results of the oil-water separation tests implied remarkable separation efficiency of the as-prepared sponge. In these tests, the magnetic sponge could quickly adsorb the oil (by up to 28 times as the original weight of the sponge) while completely repelling water (Figure 7). In addition, upon adsorbing the oil, the sponge, thanks to its magnetic property, could be easily separated from the water surface by using an external magnet. Furthermore, according to results, the $NiFe_2O_4$/polyurethane sponge could be reused for 10 cycles (Figure 8).

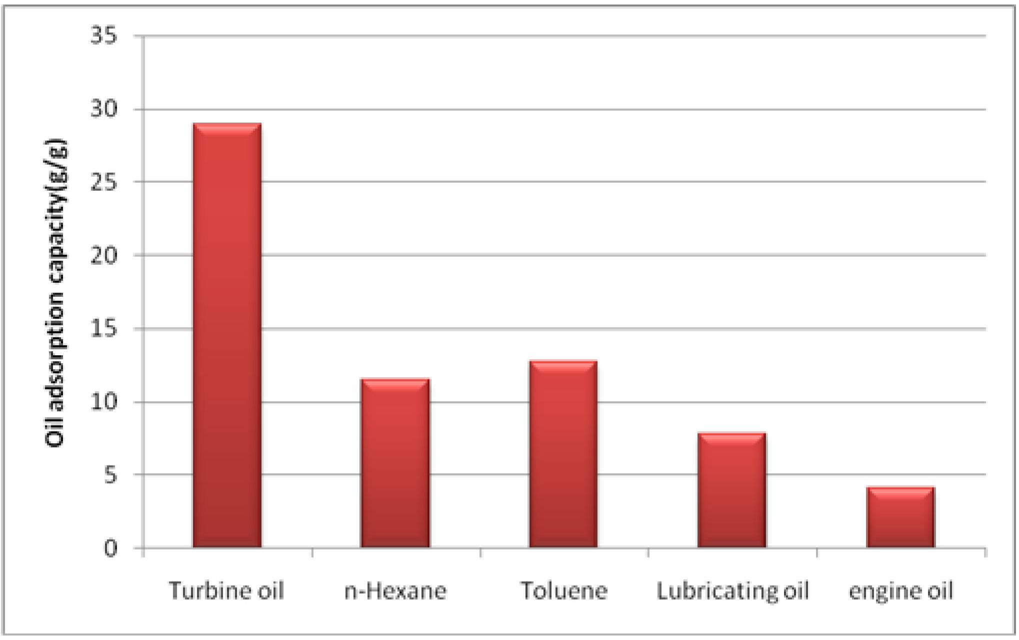

Figure 7. Oil adsorption capacity of $NiFe_2O_4$/PU sponge for different types of oils and organic solvents

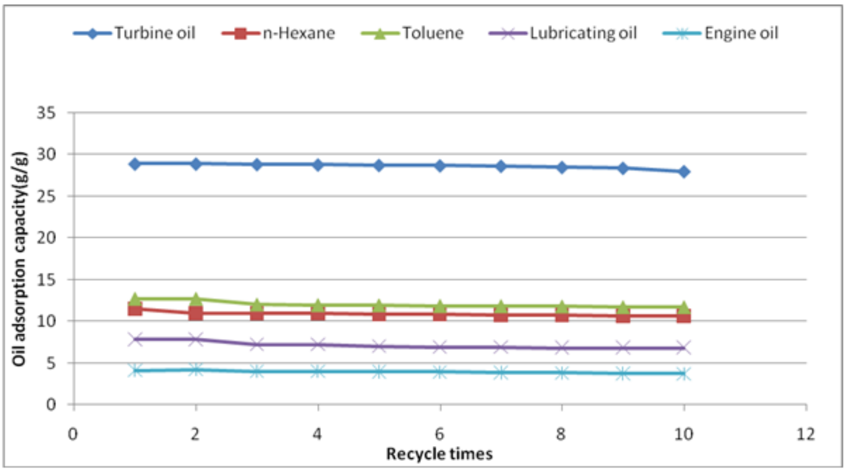

Figure 8. Oil adsorption capacity of $NiFe_2O_4$/PU sponge for after 10 oil removal cycles

Conclusion

$NiFe_2O_4$/polyurethane magnetic sponge was fabricated via ultrasonic-assisted dipping treatment of polyurethane sponge in a solution containing $NiFe_2O_4$ nanoparticles and vinlyltriethoxysilane. As a highly effective adsorbent for oil, the modified magnetic sponge can be used to remove oil from water in oil-polluted bodies of water. The as-produced nanocomposite indicated large potentials for adsorbing different types of oil and organic solvent. In addition, given that the adsorbed oil on the modified magnetic sponge could be easily removed, the sponge could be used for several cycles of oil removal. As an important finding, the selective oil adsorption behavior of the obtained composite was seen to attenuate only slightly even after 10 cycles of oil-water separation thanks to its high chemical stability and porous structure. This research showed that the $NiFe_2O_4$/polyurethane sponge provides a promising alternative for developing practical methods for the removal of contaminants from water.

Acknowledgment

Financial supports from science and research branch, Islamic Azad University is gratefully acknowledged.

References

[1] S. Bruni, F. Cariati, M. Casu, A. Lai, A. Musinu, G. Piccaluga, and S. Solinas, Nanostructured Mater.,11, 573 (1999).
[2] X. Chen, J. A. Weibel, and S. V. Garimella, Ind. Eng. Chem. Res., 55, 3596 (2016).
[3] U. H. Yim, M. Kim, S. Y. Ha, S. Kim, and W. J. Shim, Environ. Sci. Technol., 46, 6431 (2012).
[4] E. Worch, Adsorption Technology in Water Treatment (2012).
[5] J. Yuan, X. Liu, O. Akbulut, J. Hu, S. L. Suib, J. Kong, and F. Stellacci, Nat. Nanotechnol.,3,332 (2008).
[6] B. Wang and Z. Guo, Appl. Phys. Lett.,103,63704 (2013).
[7] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, and C. Galiotis, Carbon N. Y.,46,833 (2008).
[8] J. G. Yu, X. H. Zhao, H. Yang, X. H. Chen, Q. Yang, L. Y. Yu, J. H. Jiang, and X. Q. Chen, Sci. Total Environ.,482,241 (2014).
[9] X. Gui, J. Wei, K. Wang, A. Cao, H. Zhu, Y. Jia, Q. Shu, and D. Wu, Adv. Mater.,22,617 (2010).
[10] X. Ren, C. Chen, M. Nagatsu, and X. Wang, Chem. Eng. J.,170,395 (2011).
[11] W. Gan, L. Gao, W. Zhang, J. Li, L. Cai, and X. Zhan, Mater. Des.,98,194 (2016).
[12] Q. Ke, Y. Jin, P. Jiang, and J. Yu, Langmuir.,30,13137 (2014).
[13] G. Wang, Y. He, H. Wang, L. Zhang, Q. Yu, S. Peng, X. Wu, T. Ren, Z. Zeng, and Q. Xue, Green Chem.,17,3093 (2015).
[14] H. Peng, H. Wang, J. Wu, G. Meng, Y. Wang, Y. Shi, Z. Liu, and X. Guo, Ind. Eng. Chem. Res.,55,832 (2016).
[15] M. Khosravi and S. Azizian, ACS Appl. Mater. Interfaces., **7**, 25326 (2015).
[16] L. Jiang and Z. Fan, Nanoscale (2014).
[17] J. Pinto, A. Athanassiou, and D. Fragouli, J. Phys. D. Appl. Phys.49,145601 (2016).
[18] S. Yu, H. Tan, J. Wang, X. Liu, and K. Zhou, ACS Appl. Mater. Interfaces,7,6745

(2015).
[19] X. Zhou, Z. Zhang, X. Xu, X. Men, and X. Zhu, Ind. Eng. Chem. Res.,52,9411 (2013).
[20] N. Cao, B. Yang, A. Barras, S. Szunerits, and R. Boukherroub, Chem. Eng. J.,307,319 (2017).
[21] Z. Chu, Y. Feng, and S. Seeger, Angew. Chemie - Int. Ed.,54,2328 (2015).
[22] L. Shi, K. Chen, R. Du, A. Bachmatiuk, M. H. Rümmeli, K. Xie, Y. Huang, Y. Zhang, and Z. Liu, J. Am. Chem. Soc.,138,6360 (2016).
[23] N. Anton and T. F. Vandamme, in Handb. Nanoparticles (2015).
[24] R. Zolfaghari, A. Fakhru'l-Razi, L. C. Abdullah, S. S. E. H. Elnashaie, and A. Pendashteh, Sep. Purif. Technol.,170,377 (2016).
[25] R. A. Caruso and M. Antonietti, Chem. Mater.,13, 3272(2001).
[26] A. K. Mishra, Sol-Gel Based Nanoceramic Materials: Preparation, Properties and Applications (2016).
[27] S. Rondinini, S. Ardizzone, G. Cappelletti, A. Minguzzi, and A. Vertova, in Encycl. Electrochem. Power Sources (2009).
[28] T.Elshaddai Harris, R. Jai shalini, A. L. Subrmanian , Int .J. New. Chem.,5,181 (2018).
[29] G. Mahmoudzadeh, S. A Khorrami, Int .J. New. Chem.,5,172 (2018).
[30] A. Mohasseb, Int .J. New. Chem.,6,215 (2019).
[31] M.Noormohammadi, M.Barmala, Int .J. New. Chem.,6,289 (2019).
[32] A. Beiraghi, A.R.Shirkhani, A.Z.Halimehjani, Int .J. New. Chem.,6,163 (2019).
[33] S. Sindhu, S. Jegadesan, A. Parthiban, and S. Valiyaveettil, J. Magn. Magn. Mater.,296,104 (2006).
[34] H. Madra, S. B. Tantekin-Ersolmaz, and F. S. Guner, Polym. Test.,28,773 (2009).
[35] G. Trovati, E. A. Sanches, S. C. Neto, Y. P. Mascarenhas, and G. O. Chierice, J. Appl. Polym. Sci.,115,263 (2010).

How to Cite This Article

Azita Seyed Shariatdoost, Pirouz Derakhshi, Kambiz Larijani, Aliakbar Safekordi, Mohammad Yousefi, **"Removal of Oil from water Surfaces via Recyclable $NiFe_2O_4$/Polyurethane Sponge"** International Journal of New Chemistry., 2021; DOI: 10.22034/ijnc.2021.115674.1059.