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Study on the Use of Natural Adsorbents for Oil Spill Removal

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Abstract

Today, the removal of crude oil by using low-cost adsorbent is one of the most important challenges in the world. In this research, Expanded perlite and Natural zeolite have been used as a low cost adsorbent for the treatment of water pollution by petroleum compounds.The adsorption capacity of two different types of natural adsorbents was examined.Expanded perlite is a glassy volcanic rock of rhyolitic composition,usually contains between 2 % and 6%water,and Natural zeolite which is widely used due to its abundance and low cost for the environment remediation.The maximum capacity removal of water pollutions by natural adsorbents at room temperature were found to be3.50 g/g and2.21 g/g for expanded perlite and natural zeolite ,respectively.The characteristics of the expanded perlite and natural zeolite were investigated by FT-IR and BET analyses.

Keywords: Oil Pollution, Expanded Perlite, Natural Zeolite and Sorption Capacity.

Introduction

Today, one of the important tasks and challenges worldwide is oil spill pollution, because oil is considered as one of the most dangerous pollutants, due to its toxicity to many life forms. Oil spill also has a great negative impact on the ecosystem by putting the marine lives at high risk (Sulyman, Mohamed et al., 2018). Human dependence on oil has led to catastrophic effects in the past, and in the future, these injuries will probably continue. Because oil and water do not mix,the oil eventually forms a thin and often large layer on the surface of the water.The impact of oil spills is not exclusively confined to the water-oil can wash up on shores,damaging ecosystems for years. For example,due to the oil contamination in the Gulf of Mexico,fisherman can no longer earn aliving by fishing (Cai, Jenny et al., 2010).The physical-chemical properties of crude oil are summarized in Table 1. Petroleum (crude oil) is not a uniform substance since its physical and chemical properties vary from oilfield to oilfield and can even vary within wells at the same oilfield. At one extreme, it is a light, mobile, straw colored liquid. At the other extreme, it is a highly viscous, semi-solid, black substance from which little can be distilled at atmospheric pressure before thermal decomposition occurs (Screening-level Hazard Characterization Crude Oil Category, 2011).

Oil waste is estimated at about 900 million barrels in Persian Gulf (Inagaki et al., 2001). It has also been reported that around 39000 barrels of oil has leaked from oil reservoirs (Page, Cheryl et al., 2002). Other oil spill incidents that could be mentioned, For example, in 1978, 227,000 tons of crude oil was spilled during the amoco cadiez incident at Lyme Bay, Great Britain due to harsh weather conditions and more recently in 2010, the Deepwater Horizon incident in the Gulf of Mexico resulted in a spill of 780,000 tonnes of crude oil. These incidents are not isolated and there have been numerous other incidents between and after them (Jain, Akshay, 2017). The marine or ocean Environment is a complex system controlled by a variety of physical,chemical and biological process.The understanding of

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these processes is essential in determining the fate of substances introduced into this environment.Oil pollution of the oceans could be due to many sources.Both crude and refined oil could be introduced by:i)Tanker accidents,ii)Deballasting operations,iii)Tank washing,iv)Refinery effluents,v)Municiple &Industrial discharges,vi)Losses from pipelines,vii)Off-shore production,viii)Natural seepages.The input of petroleum into the marine environment from all sources is thought to range from 2-20 million tons per year.Recent estimates reveal the figure to be around 6 milion tons of which 1/10th is probably from the atmosphere (International Conference on the Impact of Oil Spill in the Persian Gulf, 1985).

Table 1. Physical-Chemical Properties of Petroleum (Screening-level Hazard Characterization Crude Oil Category, 2011)

Property	Petroleum (Crude Oil)
CASRN	8002-05-9
Molecular Weight	Complex Mixture
Physical State	Light, mobile, straw-colored liquid to highly viscous, semi-solid, black substance
Melting Point	-30 to 30 °C (measured pour points)
Boling Point	-1 to 565 °C (measured distillation range)
Dissociation Constant (pK_a)	Not applicable
Water Solubility	30 mg/L (measured at 5 °C; Norman Wells crude oil)[1,4];
	29-33 mg/L (measured at 20 °C; Norman Wells crude oil)[1,4];
	31.8-33.5 mg/L (measured at 22 °C; Norman Wells crude oil)[1,4];
	33 mg/L (measured at 20 °C; Norman Wells crude oil)[1,4];
	25.02 mg/L (measured at 22 °C; Alberta crude oil)[1,4];
	35.1 mg/L (measured at 22 °C; Swan Hills)[1,4];
	29.01 mg/L (measured at 22 °C; Prudhoe Bay crude oil)[1,4];
	23.66-25.5 mg/L (measured at 22 °C; Lago Medio crude oil)[1,4];
	10.42 mg/L (measured at 22 °C; Kopanoar crude oil)[1,4];
	28.62 mg/L (measured at 22 °C; Murban crude oil)[1,4];
	29.6 mg/L (measured at 22 °C; Mobil A crude oil)[1,4];
	58 mg/L (measured at 22 °C; Mobil B crude oil)[1,4]
	Aliphatic Fraction[2,3]
	36 mg/L (estimated >C5-C6);
	5.4 mg/L (estimated >C6-C8);
	0.43 mg/L (estimated >C8-C10);
	0.034 mg/L (estimated >C10-C12);
	7.6 × 10-4 mg/L (estimated >C12-C16);
	Aromatic Fraction [2,3]
	1,800 mg/L (estimated >C5-C7);
	520 mg/L (estimated >C7-C8);
	65 mg/L (estimated >C8-C10);
	25 mg/L (estimated >C10-C12);
	5.8 mg/L (estimated >C12-C16);
	0.65 mg/L (estimated >C16-C21);
	6.6 × 10-3 mg/L (estimated >C21-C35)
Log K_{ow}	2 to > 6 (estimated)

[1]American Petroleum Institute Petroleum HPV Testing Group. Test Plan and Robust Summary for Crude Oil.November 15, 2003.

Available online at http://www.epa.gov/oppt/chemrtk/pubs/summaries/crdoilct/c14858tc.htm as of December 7, 2010.
[2]Total Petroleum Hydrocarbon Criteria Working Group; Human Health Risk- Based Evaluation of Petroleum Release Sites: Implementing the Working Group Approach Volume 5. June 1999.
[3]The Total Petroleum Hydrocarbon Working Group subdivided aromatics and aliphatic hydrocarbons of crude oilinto 13 aliphatic and aromatic fractions and provided representative physical-chemical properties for these fractions.
[4]Results based on the water soluble fraction of total benzene, toluene, ethyl benzene + xylenes (combined concentration) and naphthalenes. The lower molecular weight components may dissolve in water while other fractions may float and spread out on water where they may form emulsions.

It should be stressed that the Environmental pollution caused by petroleum substances can be divided into four groups,according to location:i) atmospheric pollution caused by the evaporation of volatile components of petroleum products;ii) pollution of soils;iii) pollution of aquatic systems;vi) environmental pollution caused by land-based spills of petroleum products.For each of these groups, it is important to choose appropriate methods for the removal of undesirable substances in the most efficient way (Bandura et al., 2017). Awide range of materials for oil remediation have actually been employed such as dispersants,adsorbents,solidifiers,booms and skimmers.Dispersants simply disperse the oil to accelerate the oil and separate if from the water by absorption.Booms and skimmers physically corral the oil for collection (Adebajo, Moses et al., 2003). Among these methods ,adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design,easy of operation and insensitivity to toxic substances (Wang, Shaobin, and Yuelian Peng, 2010). Literature reports some methods for the removal of pollutants from water.

For example, In 2004, Mehmet Doĝan et al,used perlite for the removal of methylene blue from aqueous solution at different concentration, pH, and temperature. Adsorption measurements showed that the process is very fast and physical in nature. The extent of the dye removal increased with increase in the initial concentration of the dye and the initial pH and temperature of solution (Doğan et al., 2004).

S.A. Sayed and A.M. Zayed studied the adsorption capacity of three different types of materials: a sludge which is mainly composed of calcium aluminum silicate ,garlic and onion peel as agricultural wastes. Results showed that the adsorption capacities of the chemically treated sludge with 30 μg/mL dodecyl benzene sulphonic acid, untreated sludge and the thermally treated sludge at 1200 °C are 2, 1.388 and 0.8 g/g respectively, while, garlic and onion peelshave adsorption capacities of 0.385 and 0.455 g/g respectively (Sayed and Zayed, 2006).

In 2016,Wang-Yu Cheng et al studied the effectiveness of modified zeolite for the adsorption of Rhodamine B in water.According to the results of investigations,Modified zeolite were found to be superior to raw zeolite in adsorption of Rhodamine B. Also,the experimental results indicated that as the dosage of adsorbent increased the removal percentage of Rhodamine in water increased (Cheng et al., 2016). Heman A .Smail et al investigated the adsorption of lead ion on different types of synthesized zeolite.The results showed that the different synthesized zeolites were efficient ion exchanges for removing heavy metal,in particular ,the modified zeolite from shale clay by oxalic acid (Smail et al., 2017). In another research,the removal of arsenate and arsenite by Fe-modified activated carbon supported nano-TiO_2 have been investigated by F.X.Qin et al. The removal rates of arsenic were evaluated using batch tests under several simulated conditions, including pH, ionic strength, material dosage, and initial arsenic concentration. The results indicated that arsenic removal was effective in weak alkaline conditions, and the maximum adsorption for arsenic was observed at pH = 8.Also,the arsenic removal rate was improved by increasing the ionic strength and the adsorbent dosage (Qin et al., 2018).

Mineral compounds such as an Expanded perlite and natural zeolite,due to their abundance,low cost, ecofriendly as well as to the molecular sieve properties have been used as adsorbents in separation and purification processes in water and wastewater treatment in the past decades (Wang, Shaobin, and Yuelian Peng, 2010).

In the present work ,two types of adsorbents (expanded perlite and Natural zeolite) with different physical properties,were used to adsorbe oil speard on water surface.The experiments were carried out in dynamic method.

Characteristic of Materials

Expanded Perlite used in this study has been purchased from tabande toos mashhad company and the natural zeolite obtained from semnan mines.Table 2 gives the bulk density ,porosity and BET surface area of all types of expanded perlite and natural zeolite used in this work. As seen in table2, expanded perlite due to its lower density ,higher porosity and surface area makes it more applicable than natural zeolite in oil spill clean up. Surface area of natural oil sorbents from previous studies are listed in Table 3.

Table 2: The Results of BET analyses for two types of different adsorbents

Sample	Bulk density(gr cm^{-3})	Porosity	BET surface area(m^2g^{-1})
Expanded perlite Natural Zeolite	<0.12 1	>90 <65	139.5 32.46

Table 3: The surface area of some natural Sorbent oil obtained from previous studies (Wahi et al., 2013)

Sorbent	**Surface area (m^2/g)**	**Sorption capacity (g oil/g sorbent)**
Salvinia cucullata Roxb.	218	Vaseline: 3.6–7.3
		Nujol: 4.7–8.6
		Marlin oil: 4.8–11.6
Walnut Shell	0.1713	Mineral oil: 0.6
		Canola oil: 0.6
		Cutting oil: 0.8
Rice husk (carbonised)	240	Gasoline: 3.7
		Diesel oil: 5.5
		Light crude oil: 6.0
Expannded Perlite with Porosity less than 65	120	Iranian oil light:3.2 (D.Bastani et al,2006)

Also, Infrared spectra of each adsorbent was recorded on a FTIR spectrometer (NexusFTIR-870). Fig 1.and 2 shows infra red spectra of Expanded perlite and Natural zeolite respectively. In Fig. 1. shows the band in 3612/54cm^{-1}, which is attributed to surface –OH groups of –Si-OH and water molecules adsorbed on the surface (Kabra et al., 2013).The band in the spectrum at 2357cm^{-1} is assigned mainly to SiO_2,Al_2O_3 (Liu, 2013). A peak at 1632cm^{-1} in the spectrum of perlite is attributed to bending mode (δO-H) of water molecule. The band near 1030 cm^{-1} corresponds to Si-O-Si asymmetric stretching vibration.Also,the region around 805cm^{-1} is characteristic of Si-O-Si symmetric stretching modes. As can be seen in figure,Amorphous silica exhibited a relatively strong peak at about 800 cm $^{-1}$ indicating the Expanded perlite is composed of crystalline silicate (Kabra et al., 2013). The band close to 450 cm^{-1} are related to T-O-T bending vibration (T = Si or Al) (Meesuk and Saowanee, 2010).

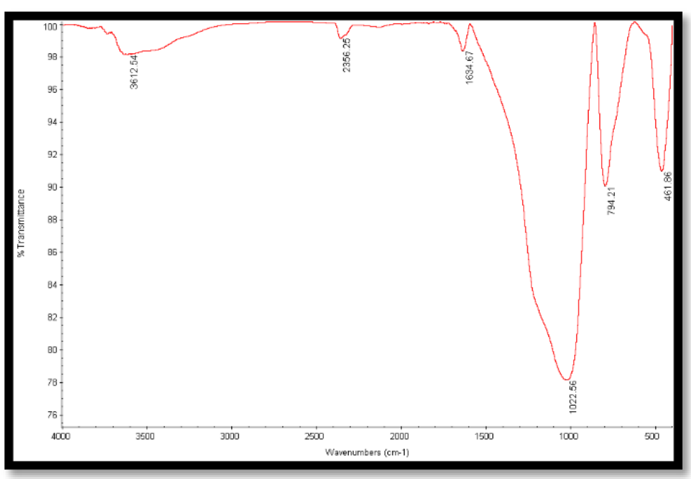

Fig. 1. FT-IR spectra of Expanded perlite

FTIR results demonstrate (Fig.2) that zeolites are significantly hydrated which is illustrated by a discrete water absorption bands in the 3500 and 1640 cm^{-1} region (Mansouri et al., 2013). The bond near 3448cm^{-1}corresponds to H-bonding between SiO-H at surface (Meesuk and Saowanee, 2010). The band in the spectrum close to 2357cm^{-1} is related to SiO_2,Al_2O_3 (Liu, 2013). It should be noted that Vibrations of the frameworks of zeolites give rise to typical bands in the mid and far infrared. A distinction is made between external and internal vibrations of the TO_4 tetrahedra. The peaks around 920-1250cm^{-1}, are assigned to asymmetrical stretch of internal tetrahedral(TO_4,T=Si or Al) ,The Peaks appearing in the FTIR region 500-650 cm^{-1} are also considered to be associated with characteristic double ring vibrations (Karge, Hellmut, 2001). The bands near 796 and 469 cm^{-1} are assigned to the stretching vibration modes of O–T–O groups and the bending vibrations of T–O bonds,respectively (Mansouri et al., 2013).

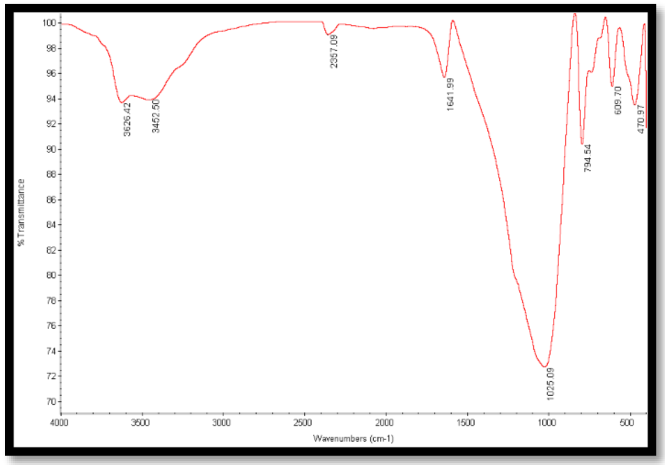

Fig. 2. FT-IR spectra of Natural Zeolite

Experimental Section

Materials & Instruments

As previously mentioned,Expanded Perlite was purchased from tabande toos mashhad company and the natural zeolite obtained from semnan mines.Oil samples were provided form hengam oil field in south of Iran.

Procedure

In this work we used dynamic method to perform the experiments.In the dynamic method a 100 ml sample of sea water,taken from Persian gulf in south of iran,was placed in abeaker and the desired amount of oil (10-40 g)was added,then,the desired amount of adsorbents (1g)was added to the oil-water mixture. Dynamic environment was created using an orbital shaker table which was set at 75 rpm (Jain, Akshay, 2017). These tests were performed at different periods of time from 1-60 min.The each adsorbent was then collected from the mixture surface and wetted adsorbent material was weighted after being drained for 2 min ,the weight of oil and water sorbed on to the adsorbent was measured (Bastani et al., 2006). Also the weight of the absorbed water in each sample was measured using Karl Fischer technique (Standard, 2004). The sorption capacity of the samples was calculated using equation 1 (Jain, Akshay, 2017).

(1) Oil sorption capacity= $(S_{st} - S_w - S_o)/ S_o = S_s/S_o$

So =the initial dry sorbent weight

S_{st} =the weight of sorbent with oil and water at the end of the sorption test,

$S_{s,,}$(Sst -So)=the net oil sorbed.(All weighted are measured in grams)

Result and Discussion

The effect of contact time

The effect of the contact time, expressed in minutes, the adsorption of oil spill was studied by placing 10 g crude oil on a 100 ml sea water at 25˚c with 1 g of each adsorbent for different contact times.Fig. 3 shows the effect of sorption times (1–60min) on crude oil sorption capacity. As shown in Fig. 3, there are at least three distinct zones in each curve. The first region is the initial phase of adsorption which occurs during the first minutes .The rate of sorption is very high during this period. The second, or transition zone, occurs from 10 and 15 min for EP and NZ respectively. Over this period, the rate of sorption is reduced. The third zone represents the steady-state period. During this period, the sorbent tends to begin a descent toward a steady state. In this zone, the extra time will not release a significant amount of crude oil. However, although the sorption capacity curves for both adsorbents show similar trends,It should be noted that Expanded perlite exhibits higher efficiency of removal of crude oil in comparison with Natural zeolite.

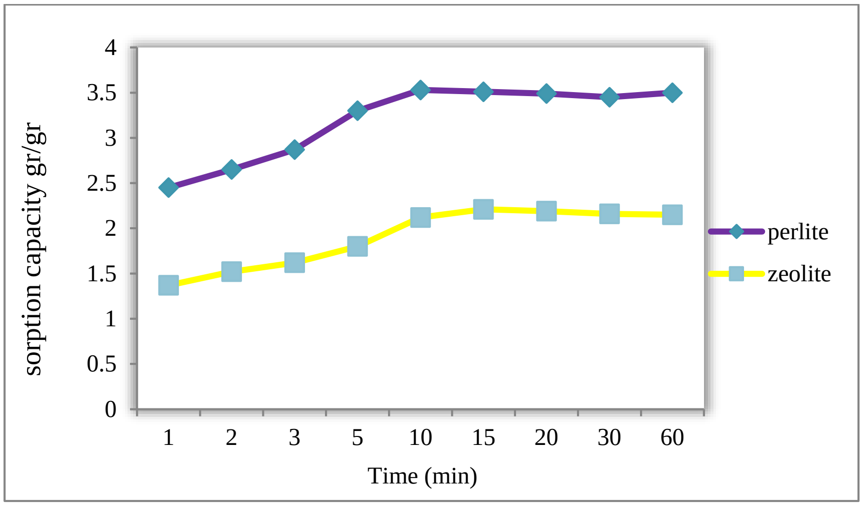

Fig. 3: Effect of contact time on sorption capacity of Exapanded perlite and Natural zeolite at 10 g crude oil, 25°c and 1g of each adsorbent.

Effect of Initial concentration of adsorbate

Initial concentration of crude oil is an important factor in sorpion capacity.In this stage the effect of amount of crude oil on adsorption obtained with placing 1g of each adsorbent and desired amount of oil from 10 g to 40 g in 100 ml sea water at 25˚c. The results shown in Fig. 4 reveal the effect of initial amount of cude oilof varied from 10 to 40 g of adsorbate. The figure shows the effect of sorbate dosage on oil sorption capacity, to find the maximum dosage for the maximum crude oil removal.In fact ,Oil sorption capacity increased with amounts of crude oils increases, until saturation of the Natural adsorbents with crude oil almost achieved.

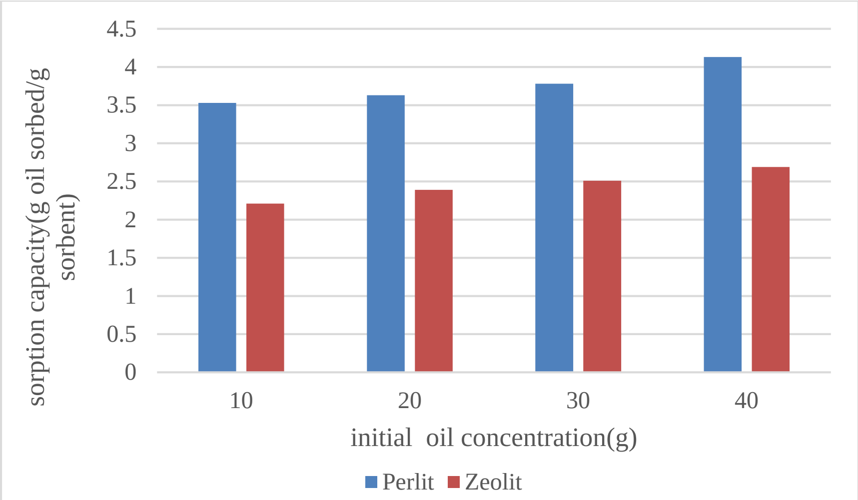

Fig. 4: The effect of initial oil concentration on sorption capacity of Expanded perlite and Natural zeolite at 10,20,30 and 40 g crude oil,25°c and 1g of each adsorbent .

Conclusions

The present study concerns the utilization of Expanded perlite and Natural zeolite, for the removal of Crude oil which belongs to Hengam oilfield from the sea water.It worth to mention that the experiments were carried out under small scale conditions using the dynamic system.The results showed that the adsorption capacities of Expanded perlite with high surface area and high porosity shows good results when compared with Natural zeolite,In fact, increase in active surface area increases sorption capacity.It is important to note that in oil spill clean up treatment, select of the best technology is based on costeffectiveness,eco-friendly and space availability.so expanded perlite because of their inexpensiveness and free availability could have wide range of applications to remove different types of pollutants , that’s why it’s recommended to use the EP in oil spill clean up.

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