

Expanded Polystyrene (EPS) Waste as Sorbent for Crude Oil Spill Cleanup: From Laboratory Experiments to Field Application

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Abstract

EPS is a major constituent of plastic waste. Reuse of waste EPS which is non-biodegradable, to useful products is a way of effective waste management. Oil is one of the most important energy sources but oil spill accidents often take place during the oil utilization process, resulting in threats to the environment. We reported the use of EPS waste to obtain an adsorbent material to cleanup crude oil spill from water. The effects of major factors such as sorption time, adsorbent surface areas, kind of surface (smooth or rough) and thermo-modification and mechanical modification (punching holes) were investigated on laboratory experiments and presented at ADIPEC 2014(Abu Dhabi International Petroleum Exhibition & Conference, 10-13 Nov., 2014, Session 52 Environment, SPE 172000-MS). The laboratory experiments carried out with about 0.9 g EPS sorbent for oil sorption times of 5 to 120 min at 350 g oil only and at 100 g oil over 500 mL water. The sorbent were punched with holes of 1.65 mm diameter. To verify the above laboratory experiments a field study for oil spill cleanup at crude oil pond from a rupture pipeline in Basrah was conducted. About 40 g EPS waste of small pieces (0.100-0.200 g) packed in 40x30 cm mesh net plastic bags. More than 40 bags were placed on the surface of a pond containing the spill crude oil over water. The pond was of about 6 meter diameter with oil layer of about 1.0 cm thickness. The bags were agitated manually after placing it on the oil surface to increase oil distribution to all EPS pieces. Oil sorption Capacity (OSC) of EPS in the field application increased with the increasing of the sorption times. The oil sorption was measured after 30 min sorption time and then every 15 min till 150 min. OSC of 43- 53 g oil/ g EPS sorbent for a sorption time of 30- 150 min respectively, were determined. The OSC are about 4 times the maximum OSC of the laboratory tests. The increasing in OSC of field application over laboratory tests due to utilization of all EPS 6 surfaces in place of one surface in laboratory tests, using lower density EPS and high density crude oil. The use of EPS waste in oil spill cleanup will reduce pollution in two ways, remediation of oil spill and reduce the landfill area due EPS waste.

Keywords: E PS Waste; crude oil, Sorbent; Oil Spill Cleanup; OSC

Introduction

Oil is a high energy density abundant fuel, which is relatively easy to transport and store, and is extremely versatile in its end uses. The movement of petroleum from the oil fields to the consumer involves as many as 10 to 15 transfers between many different modes of transportation including tankers, pipelines, railcars, and tank trucks. Transportation of oil results in regular oil spills throughout the world. During land-based transport, oils and other oil-based products are spilled with adverse impact on the transport infrastructure as well as affecting the environment and the community [1-2]. Oil spills have been considered as one of the most serious disasters that are threatening the ecosystem and human health [3-4]. Various processes have been developed to control oil spill, such as the use of dispersants, skimmers, bioremediation, in situ burning or sorbent materials. Among these methods, sorption with sorbent has been considered to be one of the most effective ways for oil spill cleaning due to its ability of collection and the complete removal of oil from oil spill sites [5-8]. Large amounts of waste are generated from various industries and activities of human being specially packaging of consumer products mainly EPS. Much of them are disposed of in the limited disposal sites available which will be exhausted in the near future. The hierarchy in waste management is waste minimization, proper treatment, reuse/recycling and energy recovery [9]. EPS waste are reused/recycled as construction or thermal reduction in building materials, energy recycling, where wastes are incinerated and chemical treatment for converting it into valuable products [10-12].

EPS is a rigid and tough, closed-cell foam. It is usually white and made of pre-expanded polystyrene beads. It is hydrophobic that is not bio-degradable. Since polystyrene (including EPS) is hydrophobic / oleophilic, it will have attraction force toward oil and oil products. So, it can be utilized in remediation of oil and organic contaminates [13]. Bajdur and Sułkowski [14] have use modified EPS waste in sewage treatment processes. Siyal et. al. [15] used chemical modified EPS waste for the treatment of phenol contaminated industrial wastewater. [Bajdur](#) et al. [16] obtained effective polyelectrolytes by synthesis of sulphonated derivatives of expanded polystyrene wastes. The synthesized polyelectrolytes were used in treatment of coal mine water. While Lin et al. [17] developed nonporous polystyrene (PS) fibers prepared via a

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one-step electrospinning process used as oil sorbents for oil spill cleanup. In general all the processes above used EPS or PS after chemical modification.

In our previous work [18], EPS waste, originally used as packaging materials, were evaluated as sorbent materials for crude oil spills in laboratory experiments. The EPS were used as its and after simple mechanical modification (cutting and punching holes with nails) to improve their performance as sorbents of oil in aqueous conditions. Crude oil sorption uptake experiments at different conditions (sorption period, with holes of different sizes) and without, smooth surface and rough, one to eight pieces) were evaluated and discussed. The process is simple and very cheap as the EPS is a waste material going to garbage, turning it to be used in oil spill cleanup. The process is turning waste materials to a value added useful products in environmental remediation and reducing the garbage that will save landfill space.

To implement the laboratory experiments we selected pond oil spill from a rupture oil pipeline in Basrah, south Iraq as field application of our experiments. The oil spill layer about 1 cm thickness floated over water collected from rains or from ground water. The spilled oil was weathered as it happened many months before field application take place. As a result it gets thicker because of the evaporation and other weathering factor. So the purpose of this work is to apply the laboratory experiments into field for finding sustainable sources for oil spill remediation and turning waste material to useful product which lead to landfill reduction.

Materials and Methods

Crude oil spill originally was exporting oil having the specification shows in Table 1(S. # 1, 2 & 3 are exporting oil samples). The spilled is weathered oil turned to thick oil having high specific gravity (S. # 4).

**Table (1). Specifications of the crude oil (before weathering 1, 2, 3 & after weathering 4)
Using the standard methods mentioned below***

S. #	Sp. Gr. (60 ° F)	API (60 ° F)	Salt Content (ppm)	Water Content (%)	Viscosity Cst. @	
					21.1° C	60.0 ° C
1	0.8773	29.83	10.0	0.025	Not determined	
2	0.8924	27.10	27.70	0.025	28.24	8.21
3	0.8822	28.90	15.5	0.05	28.52	8.70
4	0.9731	13.9	29.60	19.56	Not determined	

* Specific Gravity & API Gravity; ASTM D-1298, salt content; IP-77
Kinematic Viscosity; ASTM D-445, water content; ASTM D-4006

The EPS waste used in this work are packaging and building materials. The density are 13.1-14.0 Kg/ m³. It have been cut to small pieces (0.100- 0.200 gm.) with a serrated knife . The holes in the EPS were made with lab made holes puncher with nails of 1.65mm diameter as shows in Fig. 1. About 40 g EPS waste of small pieces (0.100-0.200 g) packed in 40x30 cm mesh net plastic bags shows in Figure(2) More than 40 bags were placed on the surface of the pond containing the spill crude oil over water. The pond was of about 6 meter diameter with oil layer of about 1.0 cm thickness. The bags were agitated manually after placing it on the oil surface to increase oil distribution to all EPS pieces. The oil sorption was measured after 30 min sorption time gravimetrically and then every 15 min till 150 min. Three bags were taken each time. The mesh net bags containing wet sorbent was left to drain by hanging in air for about 40-50 sec. then transfer into plastic bags for weighing. The weight of plastic bags were determined and recorded and the net of mesh net bags as well as oil adsorbed were calculated. Some of these bags were taken to the laboratory for farther oil analysis.



Fig(1). Photograph of holes puncher with nails of 1.65 mm (diameter) and 3 nails in 10 mm (9 nails in 100 mm²), and about 15 mm hole depth.



Fig(2). Photograph of mesh net plastic bags (40x 30 cm) containing 40 gm small pieces of EPS waste before putting it on the spill oil surface.

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The oil sorption capacity (OSC) of the sorbent was obtained with the formula:

$$\text{OSC} = \frac{\text{New weight gain (g)}}{\text{Initial weight of Sorbent (g)}}$$

Where the,

New weight gain = weight of sorbent containing oil - Initial weight of Sorbent



Fig(3). Photograph of the set for separation of water and sediment from oil and determined the ratio of each, after removing it from mesh plastic bags.

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To determine if the crude oil spill containing water or sediment, we used process Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (ASTM D-4007). About 50 mL of the crude oil was placed into a cone-shaped centrifuge tube 100 mL. Then a 50 mL of toluene was added to the same tube. After centrifugation, the volume of high gravity water and sediment layer at the bottom of the tube can be read and recorded as shown in Figure (3).

Gas Chromatography analysis of crude oil

Crude oil samples were analyzed using an Agilent 6890 GC (Agilent Technologies, Inc., USA) equipped with a split/splitless injector, autosampler and flame ionization detector (FID). Helium was used as carrier gas at a constant flow (1.8 mL/min) and injected sample size, 1 μ L. A Db-petro capillary column (100 m, 252 μ m(ID), 0.50- μ m film thickness) a 100% methyl polysiloxane was used for the separation of compounds in the analyzed samples. Peak area was used to calculate the percentage ratio of the components. The sample was injected in split mode with a split ratio of 50:1. The GC oven was programmed from 50 °C to 114°C at rate 1.7 °C/min and then to 280 °C rate 1.7 °C/min. The injector temperature was maintained at 280° C with the FID temperature set at 300 °C. The GC FID signal was sampled at 50 Hz. And data was processed with GC Chemstation software. GC analysis were done for three samples namely, crude oil passing the pipeline, spill crude oil in the pond and spill oil adsorbed by sorbent. The high peak around 6 min retention times in Figure (5) (sample 1 & 3) is for hexane solvent to make the injection of high density oil easy.

Results and Discussion

Expanded polystyrene (EPS) is a rigid and tough, closed-cell foam. It is usually white and made of pre-expanded polystyrene beads. The EPS used in this work has a density about 13.1-14.0 Kg/m³. So, it is very light weight and will float over all liquid including oil. This is a good characteristic of a sorbent. It is usual in oil spill case for floating or stranded oil that was not recoverable by vacuum truck to be recovered by hand crews working with sorbents [19].

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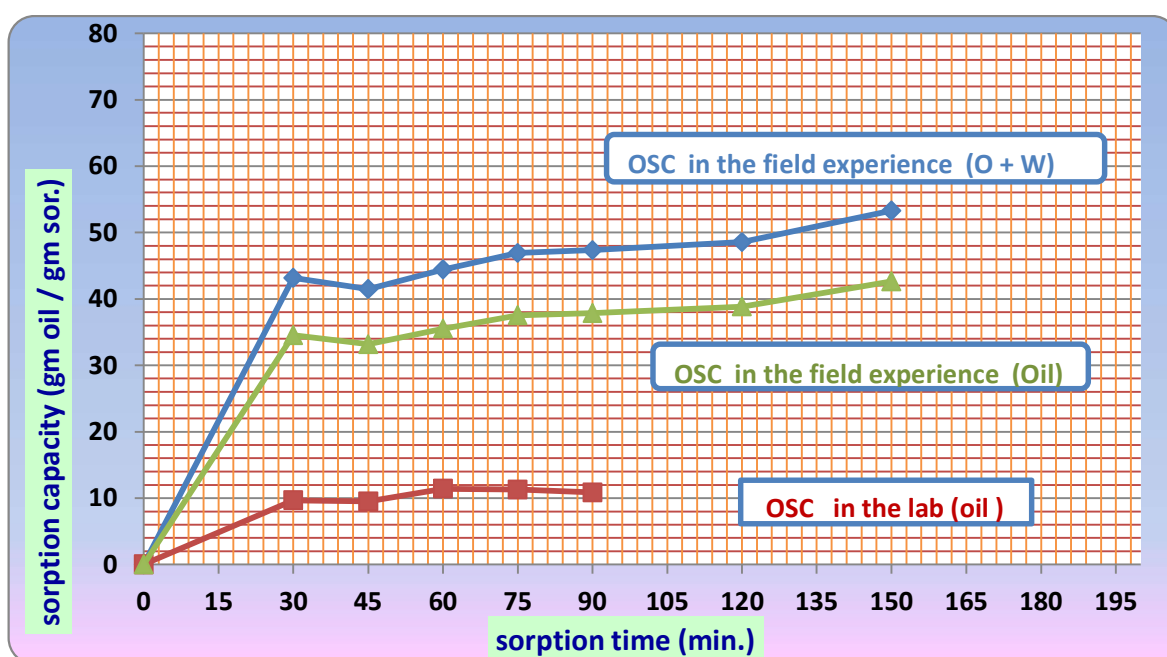
From our previous work [18], we take small pieces sorbent to increase surface area in contact with spill oil. We took pieces about 0.100- 0.200 gm or even smaller than that. The EPS pieces were put in mesh net plastic bags so that it will be easy to collect the wetted sorbent and to allow the oil to penetrate into the sorbent.

The values of oil sorption capacity (OSC) via sorption times for laboratory and field works are presented in Fig. 4. There is increase of sorption value as the sorption times increase from 30 to 150 min. in field work, although the increase was not very sharp after the 30 min. The trends of sorption are very similar in both laboratory and the field application as show in Fig. 4. This indicated that the sorption mechanism of oil into EPS is adsorption first which is very fast and then capillary action which is very slow. Since the adsorption process of oil into EPS is governs by oleophilic-hydrophobic, so it is very fast. It takes place once the contact between oil and EPS [18]. The OSC of the field application are having higher values than that of the laboratory. The tope one of the fields is for crude oil with water and sediment while the one below is for net oil after reduction of water and sediment. Higher OSC in the field probably due to utilization of all ESP 6 surfaces (one surface utilized in laboratory experiment), high viscosity of the crude oil compare to that use in laboratory tests as showed in Table 1, and lighter EPS waste (13.1 Kg/m^3) compare to 18 Kg/m^3 used in laboratory.

Utilizing 6 surfaces mean increasing the surface area and that contributed to increase the OSC in the field application [20-21]. Surface area is very important here because the sorption meanly adsorption and that happen in the out surface of the sorbent. The high viscosity oil happened as result of evaporation of light components of oil. An estimated 10 to 16 percent of the oil released may have evaporated in the first 24 hours after the spill [19]. Since our spill happened for many months (more than 6 months) so more than that evaporated. Table (2) and Figure (5) (samples 1& 3) show that from C_2 - C_{12} components have evaporated. Comparing the GC analysis of spilled oil and non-spilled (Table not shown), it estimated that more than 39.90 % of the oil was evaporated during weathering time (more than 6 months). This was behind the high viscosity of crude oil. As oil get viscose it intends to stick strongly to the sorbent surface as well as to each other's. That why high OSC was observed as in Figure (4). Regarding the lighter EPS waste sorbent it will contribute to higher sorption in two ways.

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Lighter EPS mean the beads have not pressed strongly and give more interstitial gaps and vacuum between the beads that form an open network of channels between the bonded beads. That mean more space will be available for oil to penetrate into EPS pieces. Secondly light EPS mean larger surface area per unit weight. In addition, the drainage times in the field work are little less than that of the laboratory



Fig(4). Oil sorption capacity via sorption times of crude oil into EPS punched holes with large nails (1.65 mm diameter, 9 nails in 100 mm²) at oil over water situation in lab and field.

Experiments e.g. about 10-20 Sec. less, that may contribute to the high OSC. Overall the field application of using EPS waste as sorbent in oil spill showed its high effectiveness as observed in Figures (6 & 7). Where in Figure (7) show clear water area after removing the spill oil by sorbent compare with Figure (6).

Conclusion

Discarded polystyrene does not biodegrade for hundreds of years and is demonstrated that waste EPS are promising sorbent for oil spill cleanup. Its hydrophobicity towards oil made it

more selective to oil than water. Mechanical modification with holes puncher especially of 1.65 mm diameter will enhance oil sorption capacity. The oil sorption capacity value we got consider to be very good if we looking to waste material we used. In addition OSC will increase with increasing in the oil density.

Table (2). Components of Spilled Oil before absorption by EPS waste as analyzed by GC (Sample 3 in Figure 5).

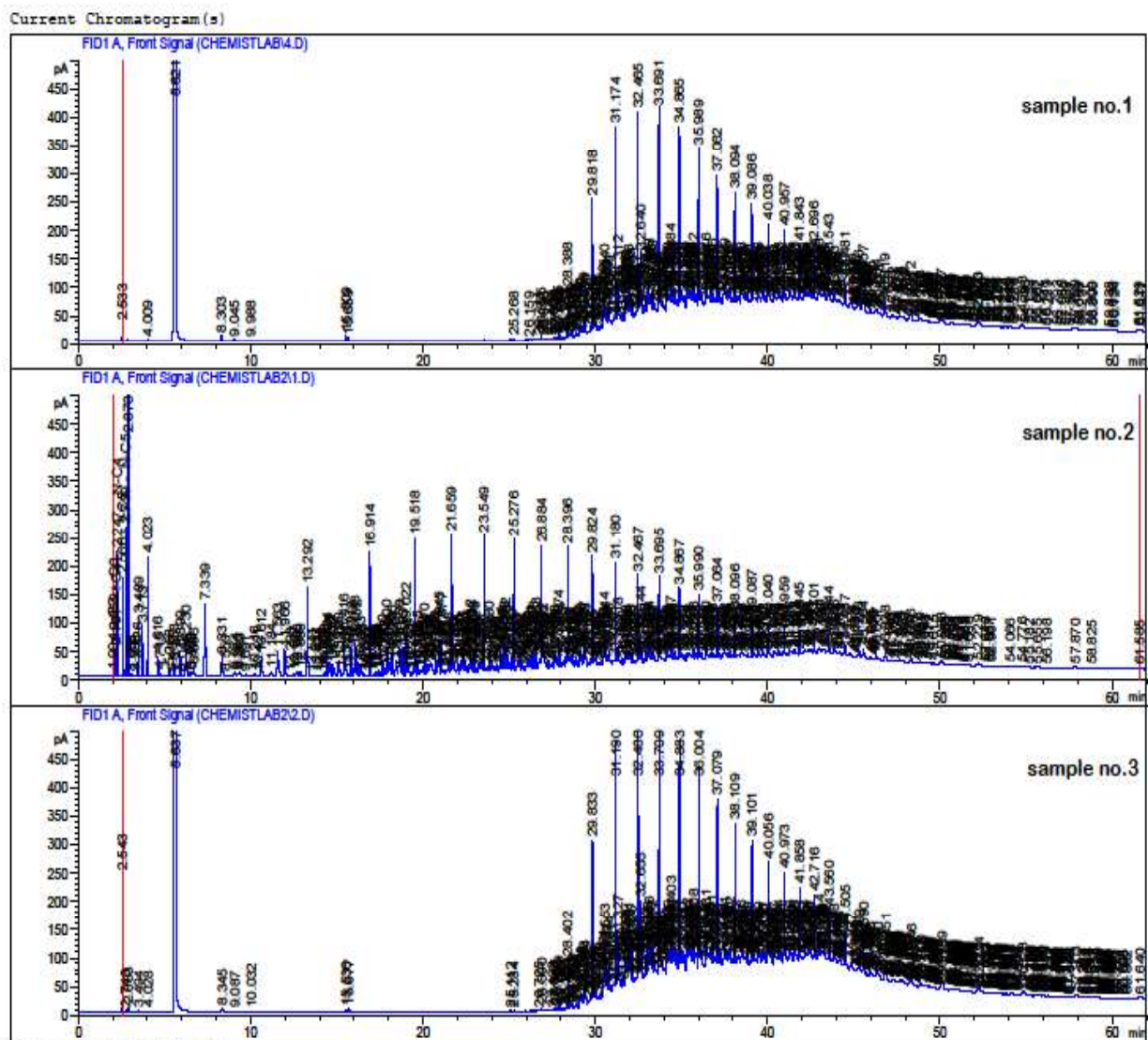
Component	Ratio % (area)
C ₁₃	0.006
C ₁₄	0.020
C ₁₅	0.367
C ₁₆	1.953
C ₁₇	4.160
C ₁₈	5.827
C ₁₉	7.161
C ₂₀	6.761
C ₂₁	6.804
C ₂₂	6.333
C ₂₃	5.825
C ₂₄	5.499
C ₂₅	5.245
C ₂₆	4.861
C ₂₇	4.868
C ₂₈	4.749
C ₂₉	4.637
C ₃₀	4.725
C ₃₁	3.705
C ₃₂	3.800
C ₃₃	3.378
C ₃₄	3.067
C ₃₅	2.597
C ₃₆	1.964
C ₃₇	1.270
C ₃₈	0.306
C ₃₉	0.112
Total	100.00

EPS will have higher OSC value when it used with heavy oil. Moreover, the use of waste EPS in oil spill cleanup will reduce the garbage volume and so reduce the landfill area. In addition,

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waste EPS after use in spill cleanup it can be used as fuel as it contains high burning energy [23]. The drawback of waste EPS as sorbent for oil spill cleanup are two.

Print of window 38: Current Chromatogram(s)



GC 1 3/19/2015 8:35:08 AM SYSTEM

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Fig(5). Gas chromatograms of samples of crude oil. Sample no. 1 of spilled crude oil sorbed by EPS. Sample no. 2 of crude oil in pipeline (non-spill). Sample no. 3 of spilled crude oil before sorption process.

First, we cannot reuse the sorbent again and oil sorbed into EPS cannot be collected or is not economic to collect it. Overall, the process is turning a waste to a value added useful products in a two ways environmental remediation. In addition, the holes puncher can be fixed to

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mechanical handle or automatic machine to make punching hole easier. In addition the oily EPS waste can be utilized in Steel and Bricks industries [23].



Fig(6). Photograph of the pond containing spill crude oil before starting the application of remediation of oil spill.



Fig(7). Photograph of the pond containing spill crude oil after taking the mesh bags with wet SPE. It shows the oil have cleared from some portion of the pond.

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