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Utilizing Attapulgite as Anti-Spill Liners of Crude Oil

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Abstract:

The efficiency of attapulgite liners as anti-seepage for crude oil is examined. Consideration is given to the potential use of raw attapulgite and mixture attapulgite with prairie hay and coconut husk as liners to prevent crude oil seepage. Attapulgite clay used in this study was brought from Injana formation /Western Desert of Iraq. Two types of Crude oil brought from Iraqi oil fields were used in experiments; heavy crude oil from East-Baghdad oil field and light crude oil from Nassiriya oil field. Initially the basic properties of attapulgite and crude oils were determined. The attapulgite clay was subjected to mineralogical, chemical and scanning electron microscope analyses. Raw Attapulgite 150µm, 75µm, and 53µm were tested as anti-seepage liners for heavy and light crude oil. Experiments showed that raw attapulgite liners 53µm and 75µm are good in terms of retention and prevention of seepage so they can be used as the main layer to impede the flow of heavy crude oil. Raw attapulgite150µm could not be used as a liner to impede the flow of crude oil. This type of liner is totally inefficient for heavy and light crude oil. Adding prairie hay to attapulgite 150µm gives a good barrier medium that retains heavy crude oil and prevents it from seepage as long as possible. Raw attapulgite liners failed to prevent light crude oil seepage whereas the partial substitution of attapulgite by prairie hay or coconut enhanced the performance of the liner. Moreover, the addition of prairie hay with coconut to attapulgite enhanced the performance of the liner to a greater extent compared to raw attapulgite liners and mixture liner attapulgite with prairie hay.

Keywords: Attapulgite, Biomaterials, Clay liner, Crude oil, Pollution, Sorption process

Introduction:

Even though petroleum is among the main necessities of modern society, it has become one of the most important types of organic pollutant substances for the environment[1]. Petroleum pollution is usually due to accidental spills, well blow out and ruptures of pipelines resulting in the release of crude and refined oil into terrestrial and aquatic environments. Soil and groundwater contamination with petroleum components can result from small leaks to large seepage [2, 3], therefore surface of waste disposal sites usually coat with layers of materials prevent leakage called liner [4]. Liner should have hydraulic conductivity less than 10^{-7} cm/sec and a minimum thickness 600mm [5].

Clay liner is the most widely used and preferred due to the relatively low cost and wide versatility of reactive barriers [6]. A simple clay liner consists of either compacted clay liner (CCL) or geosynthetic clay liners (GLs) in conjunction with compacted clay liner or as alternative to compacted clay liner [7,8].

Clay minerals play an important role in the effectiveness of clay liners as a hydraulic barrier. Usually, Bentonite clay employed as a liner to prevent the migration of pollutants due to low permeability to liquids and gases [9]. Many researchers studied bentonite liners as anti-seepage [10-13]. Gitipour et al. studied hydraulic and sorption behavior of geosynthetic clay liners (GCLs) with ordinary and modified bentonite. Modified bentonite showed much lower permeability values compared to ordinary bentonites when exposed to crude oil, hence denoting the viability of modified clays as GCLs materials at petroleum contaminated sites [14]. AL-Bidry et al. also studied Na-bentonite and Ca-bentonite with different grain sizes as compacted liners. Results showed that Na-bentonite was better than Ca-bentonite as an anti-spill of crude oil, and the efficiency of Na-bentonite increased with decreased grain size and increased API gravity of crude oil [15].

Attapulgite clay mineral has a high specific surface area and high absorption capacity due to the presence of micropores and parallel channels in the structure [16]. Despite the high absorption properties of attapulgite, it did not receive much attention from researchers as a new type of material in the anti-seepage liner. Some research has indicated the use of attapulgite as a substitute for bentonite in vertical cutoff walls as well as in compacted clay liners [17]. Broderick and Daniel evaluated the mechanical and chemical methods of stabilizing four different types of compacted clay against chemical attack. They found that attapulgite to be relatively unaffected by concentrated organic chemicals [18]. AL-Rawasi et al. investigated the potential use of sand–attapulgite mixtures as a landfill liner. The geotechnical study showed that sand mixture and 30% attapulgite can be considered to satisfy the requirements for landfill liners and that adding attapulgite to sand has improved shear strength [19]. Also, Zhang et al. applied sand-attapulgite backfills to cut-off walls, and the results showed that the compression and swell indexes of the backfills increased with increasing attapulgite content. They conclude that sand-attapulgite backfills can be used as a substitute for soil-bentonite backfills in cut-off walls [20]. However, previous findings are limited and the literature survey showed that most of the published work focuses on the use of bentonite liner, so systematic studies about attapulgite as anti-seepage of crude oil are required.

Moreover, natural fibers (organic materials) such as straw, milkweed, grain crops hull, sawdust, and cotton can be used in oil sorption applications as sorbents and often used to clean up marine oil spills [21]. Partial or complete replacement of synthetic sorbents by natural sorbents could be modified sorption process and provide other benefits such as biodegradability [22,23]. Organic materials are renewable sources, non- toxic, and low cost, and must utilization of biomaterials to prevent crude oil seepage. To the best of the author's knowledge, there are no research using prairie hay, coconut husk in anti-seepage clay liners.

In this paper, we described a detailed experimental study for raw attapulgite and natural fibers as liner which may provide a basis for the application of attapulgite and organic materials as anti-seepage liners for crude oil. The objectives of this study are: 1) to explore the effect of attapulgite grain size on the saturation rate of crude oil and seal of attapulgite liner, 2) to study the effect of crude oil type on the saturation rate and seal of attapulgite liner, and 3) to study the effect of using prairie hay and coconut husk on attapulgite liner.

Materials and Methods:

Iraqi Attapulgite

Raw attapulgite clay from Injana formation (Western Desert of Iraq) was acquired from Iraqi Geological Survey Company. Attapulgite was treated using rolling grinded and passed throw a 53µm sieve, 75µm sieve, and 150µm sieve. All samples were dried at 110^{o} C for 4 hours to remove moisture before experiments. The samples were denoted as 53µm, 75µm, and 150µm according to their grain sizes. XRF analysis was performed on spectrometer for X-ray fluorescence to investigate mineral composition for Iraqi attapulgite clay. X-Ray Diffraction (XRD) was performed on equipment XRD 7000, with Cu (λ = 1.5406 Å), voltage: 40.0 kV and current: 30.0 mA. Chemical composition was determined with atomic absorption spectrometer. The surface morphology and surface roughness of the attapulgite were characterized by scanning electron microscope SEM (SEM-EDS brand Instrument JEOL JSM 6510L A).

Sucker-up (coconut husk)

Sucker-up (coconut husk) organic absorbent is 100% organic and contains no chemical residues. It is manufactured from coconut husk and has excellent absorbent characteristics with hydrocarbon and water-based liquids. The reason it being an effective absorbent is that each particle consists of tiny capillaries working together as thousands of micro sponges that absorb and hold up to 5 times its weight in liquids. Sucker-up organic is an annually renewable resource that is safe for the workplace and the environment. Coconut husk was dried at 110^{o} C for 6 hours then grinding to 150µm. This organic material was used as an additive to design a low-cost and high-efficiency clay liner with no impact on the environment.

Prairie Hay

Prairie Hay is grass plants that have been cut, dried, and stored for use as animal fodder. We used plants for hay including mixtures of barley and wheat. Hay was dried at 110^{o} C for 2 hours then ground to 75µm and 150µm. Prairie Hay was used as an additive organic material to design a low-cost and high-efficiency clay liner with no impact on the environment.

Physical properties of crude oils

Crude's oil classification as either light or heavy depends on the oil relative density, based on the American Petroleum Institute (API) Gravity. In this research, we used two types of crude oil from Iraqi oil fields to examine its effect on attapulgite liner, heavy crude oil from East Baghdad oil field (EBF) and light crude from Nassiriya oil field (NF). The physical properties of crude oil have been tested in basic crude oil laboratory/department of petroleum technology /University of Technology as shown in Table 1.

Table 1. Physical properties of crude oils.

Crude oil property	East Baghdad oil field	Nassiriya oil field
API	20	29.72
Viscosity	3.09CP AT(100 RPM) and (17.3C)	0.05CP AT(100 RPM) and (17.3 C)
Density	0.935	0.8777
Specific gravity	0.935	0.8777
Sulfur content %	0.72 %	0.39 %
Sediment content%	2%	1.4%

Methods and Procedure:

This part includes the experiments to detect the ability of attapulgite clay liners to retain crude oil as follows:

Preparation of open ended tubes, fixing them using stands and putting beakers under the tubes. Fixing a mish sieve at the lower open end which represents the ground under tank, pipe, etc. Putting attapulgite clay inside the tube and compact it with a compaction tool. Then, crude oil is being poured over the clay.

Recording of crude oil drain with time and calculation of sorbent percent of crude oil in clay with time for each liner. Oil retention test is a laboratory method that was used to determine the amount of crude oil remaining in a sorbent material. Oil retention was measured as the ratio of oil adsorbed to dry sorbent weight according to the following equation (1):

Oil retention %=(Os – On)/Os ----- (1)

where: Os: total oil adsorbed, On: net oil remaining (after oil retention test) [15].

Oil retention was measured for four liners with heavy crude oil and six liners with light crude oil, and then the relative effectiveness for each liner was evaluated.

Test procedure with heavy crude oil includes: (1) 40 gm of raw attapulgite 53µm, 75µm and 150µm tested with 100 ml crude oil. (2) 32gm of attapulgite 150µm mixed with 8gm prairie hay 150µm and 2ml water to decrease the hydraulic conductivity, and then tested with 100 ml crude oil.

Test procedure of liners with light crude oil includes: (1) 40 gm of attapulgite 53µm, 75µm and 150µm tested with 100 ml crude oil. (2) 32gm of attapulgite 75µm mixed with 8gm prairie hay 75µm and 2 ml water, and then liner was tested with 100ml crude oil. (3) 32gm of attapulgite 150µm mixed with 8gm prairie hay 150µm and 2ml water, and then tested with 100ml crude oil. (4) 32gm of attapulgite 150µm mixed with 3gm prairie hay 150µm, 5gm coconut husk 150µm and 2ml water, and then liner was tested with 100ml crude oil. Liners were left for two months after the test to verify their suitability as a sealant

Results:

Attapulgite characterization

The X- ray analysis of raw Iraqi attapulgite clay is shown in Fig.1, of which the main indication of the presence of attapulgite clay occurs by the appearance of peak at 21°, 23.2° and 26.9°. Besides the attapulgite there is also the presence of quartz, evidenced by the peak around 29.8°, 36° and 39.8°.

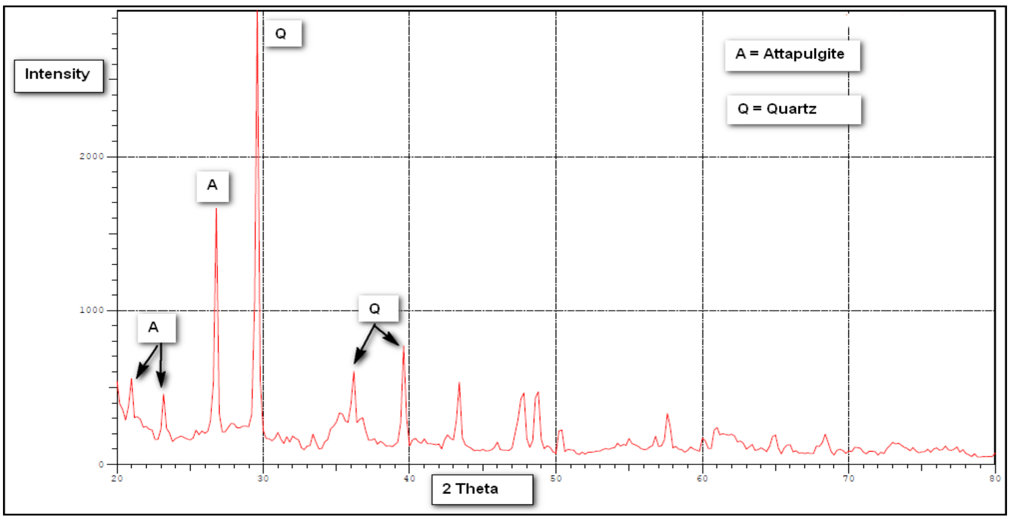

Figure 1. X-ray analysis of raw attapulgite clay.

The results of XRF shows that chemical composition for attapulgite, where it is observed that 50.8% SiO_2, 13.2% Al_2O_3, 5.3% Fe_2O_3, 4.6% CaO, 1.3% Na_2O, 8.0% MgO, 2.8 K_2O.

SEM images show the surface morphology and surface roughness of the attapulgite, it was observed that the attapulgite exhibits fibrous forms, forming clusters of ribbons as shown in Fig. 2.

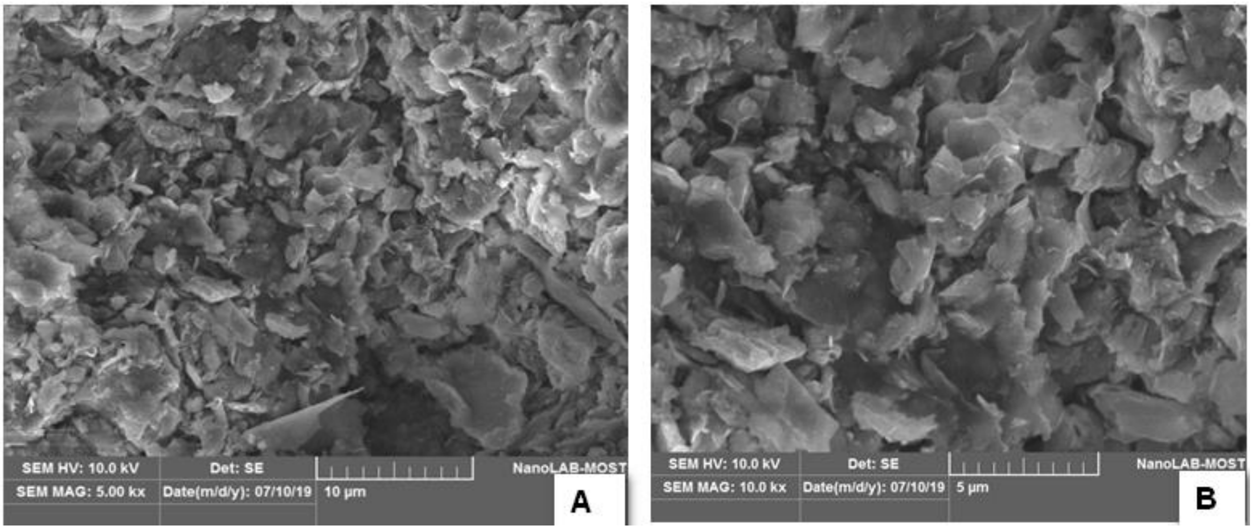

Figure 2. SEM images of raw attapulgite clay; A: 10 µm, B: 5 µm

Attapulgite liners tested with heavy crude oil

Raw attapulgite liners

According to grain size, three attapulgite liners were tested using heavy crude oil to investigate the effect of grain size on liner ability to retain heavy crude oil. Table 2 shows oil saturation rate of attapulgite liners with different grain size over time. Liner 150µm failed to impede and retain oil where 4 ml of oil spilled out after 104 hours, thus liner 150µm is totally inefficient. Liner 75µm and liner 53µm are suitable for use as an engineered barrier system because they prevent oil seepage, as the maximum saturation rate of 75µm and 53µm liners was 28.8% and 22.8% respectively after 531 hours. In general, attapulgite 53µm and 75µm liners gave a good seal that impedes and prevents movement of pollutants Fig. 3. Furthermore, grinding attapulgite to 53µm made efficient more than grain sizes 150µm and 75µm in terms of retention and prevention of seepage. In addition, it was an effect on increasing the unsaturated part of liner, where height of the unsaturated liner for 53µm 3.5cm after 531 hours, 75µm 2.5cm after 531 hours and 150µm zero cm after 96 hours.

Liner attapulgite 150µm + Prairie Hay 150µm

Liner of raw attapulgite 150µm failed to prevent heavy crude oil seepage; therefore, prairie hay was added to modify it. Table 2 and Fig. 4 illustrate that adding 25% prairie hay (by weight of attapulgite) with 2ml water to attapulgite makes liner stronger and more coherent. The maximum saturation 49.1% after 215 hours with unsaturated height zone about 1.7cm, while liner raw attapulgite150µm by 78.9% after 96 hours.

Table 2. Results of attapulgite liners with heavy crude oil.

150µm attapulgite			75µm attapulgite		53µm attapulgite		150µm attapulgite and 150µm prairie hay	
Time (hr)	Height of Saturated liner (cm)	Saturation rate %	Height of Saturated liner (cm)	Saturation rate %	Height of Saturated liner (cm)	Saturation rate %	Height of Saturated liner (cm)	Saturation rate %
0	0	0	0	0	0	0	0	0
1	0.4	7.017	0.3	5.26	0.2	3.5	0.3	5.26
2	0.8	14.03	0.5	7.88	0.4	7.01	0.4	7.01
3	1.1	19.29	0.6	10.52	0.5	8.77	0.5	8.77
5.	1.2	21.05	0.8	14.03	0.7	12.28	0.6	10.52
24	2.2	38.59	1.4	24.56	1.2	21.05	1.4	24.56
28	2.5	43.85	1.4	24.56	1.2	21.05	1.5	26.31
48	3.7	64.91	1.6	28.07	1.3	22.80	2.4	42.10
53	3.8	66.66	1.6	28.07	1.3	22.80	2.4	42.10
72	4.2	73.68	1.6	28.07	1.3	22.80	2.6	45.61
77	4.3	75.43	1.6	28.07	1.3	22.80	2.6	45.61
96	4.5	78.94	1.6	28.07	1.3	22.80	2.7	47.36
120	C.S.	78.94	1.6	28.07	1.3	22.80	2.7	47.36
216	C.S.	78.94	1.6	28.07	1.3	22.80	2.7	47.36
312	C.S	78.94	1.6	28.07	1.3	22.80	2.7	47.36
531	C.S	78.94	1.6	28.07	1.3	22.80	2.7	47.36

C.S. completely saturated

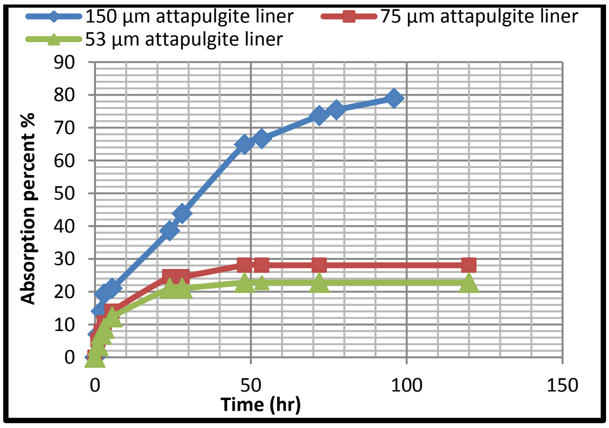

Figure 3. Liners 53µm, 75µm and 150µm with heavy crude oil.

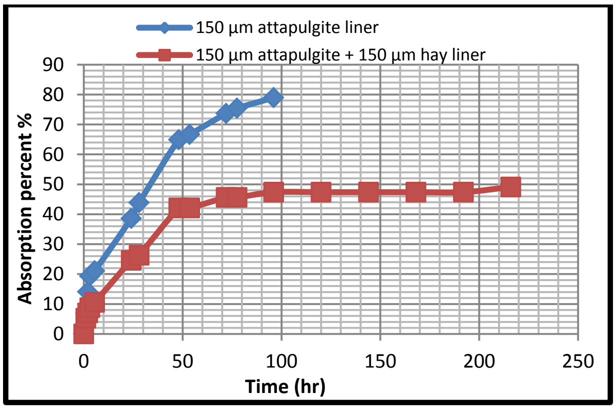

Figure 4. Liner attapulgite 150µm and liner attapulgite 150µm with prairie hay 150µm tested with heavy crude oil.

Attapulgite liners tested with light crude oil

Raw attapulgite liners

These experimental tests aim to evaluate the efficacy of attapulgite clay with different grain sizes 53µm, 75µm and 150µm as an anti-seepage liner for light crude oil. Table 3 and Fig. 5 illustrate the following: (1) Liner 150µm failed to retain oil and spilled out after 56 hours about 12 ml. (2) Liner 75µm retained by 52.6 % after 528 hours and spilled out after one month. (3) Liner 53µm retained by 43.8 % after 528 hours. Light crude oil diffusion was irregular through liners, thus calculating the height of the unsaturated area was approximate. The height of unsaturated area for liner 150µm was zero cm after 48 hours, while liners 75µm and 53µm about 1.5 cm and 2cm respectively after 528 hours. Depending on saturated rate and unsaturated height attapulgite 53µm liner is better than liners 75µm and 150µm.

Table 3. Results of attapulgite liner tested with light crude oil.

Time (hr)	150µm		75µm		53µm	
	Height of Saturated liner (cm)	saturation rate %	Height of Saturated liner (cm)	saturation rate %	Height of Saturated liner (cm)	saturation rate %
0	0	0	0	0	0	0
1	0.8	14.03	0.6	10.52	0.4	7.01
2	1.5	26.31	1.1	19.29	0.8	14.03
3	2	35.08	1.4	24.56	1.1	19.29
5	2.5	43.85	1.7	29.82	1.4	24.56
24	4.2	73.68	2.4	42.10	2.1	36.84
30	4.3	75.43	2.8	45.61	2.2	38.59
38	4.4	77.19	2.9	50.87	2.2	38.59
48	4.5	78.94	2.9	50.87	2.4	42.10
72	4.5	78.94	2.9	50.87	2.4	42.10
96	4.5	78.94	3	52.63	2.4	42.10
120	4.5	78.94	3	52.63	2.4	42.10
216	4.5	78.94	3	52.63	2.5	43.85
240	C.S.□	78.94	3	52.63	2.5	43.85
348	C.S.□	78.94	3	52.63	2.5	43.85
408	C.S.□	78.94	3	52.63	2.5	43.85
528	C.S.□ irregular	78.94	3 irregular	52.63	2.5 irregular	43.85

C.S.□ completely saturated

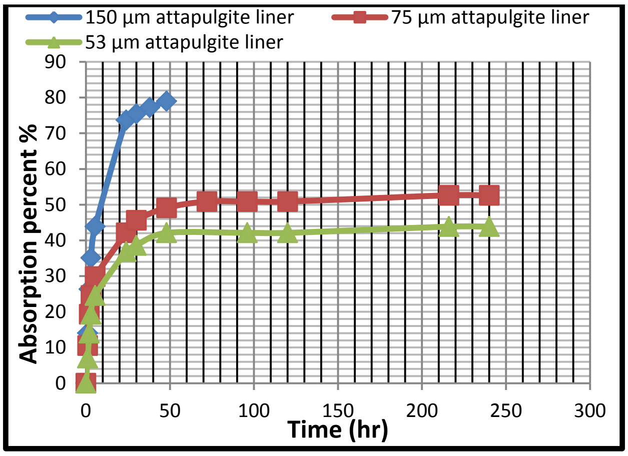

Figure 5. Attapulgite liners 53µm, 75µm, 150µm tested with light crude oil.

Liner attapulgite + Prairie Hay

Two liners were developed by substituting part of attapulgite with prairie hay, thus creating a liner could retention light crude oil and prevent seepage as shown in Table 4.

First liner consists of 32 gm of attapulgite 150µm with 8 gm of prairie hay 150µm and 2ml of water. Figure 6 illustrates that adding 25% of prairie hay makes the liner more coherent in comparison to liner consisting only attapulgite 150µm. Maximum saturation rate for the mixture liner by 57.89% after 408 hours whereas raw attapulgite 150µm by 78.94% after 48 hour.

In the second liner Fig. 7, the size of materials was reduced to 75µm then mixed in the same amounts as the first liner. Reducing grain sizes resulted in a reduction in the saturation rate of liner by 35.08% after 408 hours, compared to raw attapulgite 75µm by 52.63% after 96 hours. Partial substitution of attapulgite by prairie hay enhances the ability of attapulgite clay to impede the flow of heavy crude oil.

Liner attapulgite + Prairie Hay + Coconut Husk

The testing column was designed and packed with the used materials attapulgite 150µm, prairie hay 150µm, coconut husk 150µm and 2ml of water in order to examine the effectiveness of the liner with light crude oil.

Table 4 and Fig. 6 illustrates that liner is the best compared to raw attapulgite liner and mixture attapulgite with prairie hay liner, were adding 9.3% prairie hay with 15.7% coconut husk enhanced the liner to a greater extent. The maximum saturation rate by 15.78% after 528 hours compared with the saturation rate of mixtures attapulgite with prairie hay 150µm 57.89% after 528 hours.

Table 4. Attapulgite mixed with prairie hay and coconut husk tested with light crude oil.

Time (hr)	150µm attapulgite + 150µm prairie hay		150µm attapulgite +150µm prairie hay+150µm coconut husk		75µm attapulgite+ 75µm prairie hay	
	Saturated liner (cm)	saturation rate %	Saturated liner (cm)	saturation rate %	Saturated liner (cm)	saturation rate %
0	0	0	0	0	0	0
1	0.6	10.52	0.5	8.77	0.5	8.77
2	1.1	19.29	0.5	8.77	0.9	15.78
3	1.5	26.31	0.5	8.77	1.2	21.05
5	1.8	31.57	0.5	8.77	1.4	24.56
24	2.5	43.85	0.7	12.28	1.7	29.82
30	2.5	43.85	0.7	12.28	1.7	29.82
38	2.5	43.85	0.7	12.28	1.8	31.57
48	2.7	47.36	0.8	14.03	1.8	31.57
72	2.8	49.12	0.8	14.03	1.8	31.57
96	2.9	50.87	0.8	14.03	1.8	31.57
120	2.9	50.87	0.9	15.78	1.9	33.33
216	3	52.63	0.9	15.78	1.9	33.33
240	3.1	54.38	0.9	15.78	1.9	33.33
348	3.2	56.14	0.9	15.78	1.9	33.33
408	3.3	57.89	0.9	15.78	2	35.08
528	3.3	57.89	0.9	15.78	2	35.08

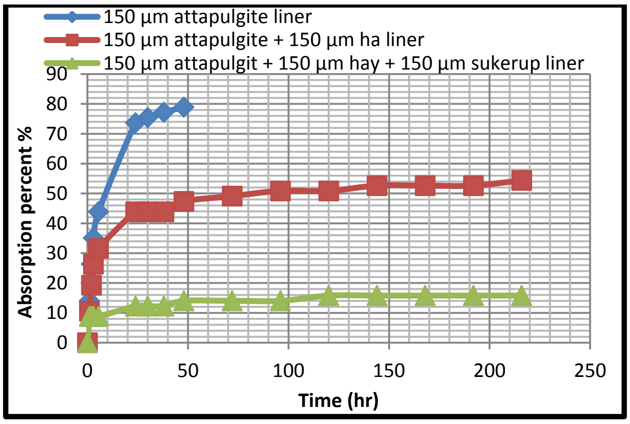

Figure 6. Attapulgite liner mixed with prairie hay and coconut husk tested with light crude oil.

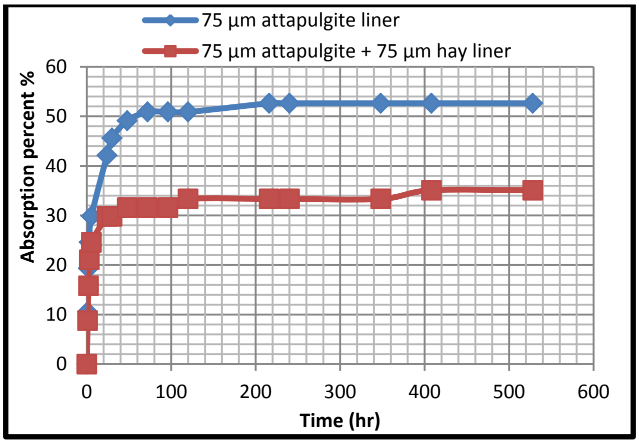

Figure 7. Liner attapulgite 75µm and liner attapulgite75µm mixed with prairie hay 75µm tested with light crude oil.

Discussion:

Effect of attapulgite size

The grain size is an important parameter in the design of the attapulgite liner. Experiments in this study showed an increase in the efficiency of attapulgite liner with a decrease in the grain size, and there is a significant relationship between grain size and saturation rate. Saturation rate of raw attapulgite liners (150, 75, 53) µm increased rapidly for both types of crude oil at the initial five hours. Attapulgite is a complex magnesium aluminum silicate with an open-channel structure and sorption rate of attapulgite include 80% absorption in channels and 20% adsorption on surface area [24, 25], thus at the initial time of sorption process, highly active sorption sites are available resulting in rapid sorption. After that saturation rate of raw attapulgite 75µm and 53µm liners increased very slowly with an extension of time for both types of crude oil until equilibrium after 48 hours. These results are consistent with the reported results by other authors Zhang et al. and Al-Futaisi et al. who studied the adsorption of other attapulgite [24,26]. Moreover, Srivastava et al. mentioned that the sorbent process of attapulgite controlled by film diffusion at a fast rate at the beginning followed by a slower intra-particle diffusion rate through pores [27].

Saturation rate of raw attapulgite 150µm increased more than 75µm and 53µm about twice at first 24 hours. The saturated attapulgite (150µm) was incoherent, flocculate and slightly sticky resulting in failed liner to retain light or heavy crude oil and prevent seepage after 48 hours. Fibers of attapulgite tend to aggregate at high saturation because the level of the negative surface charge is

relatively low and van der waals attraction predominates over electrostatic repulsion [28]. As repulsive forces decreased, clay particles tend to flocculate and form aggregates due to attractive forces among particles, leading to increase flow [29].
Consequently, an increase in size of raw attapulgite grain increases saturation rate and speed, resulting in an increase in fibers aggregated and decrease active sorbent sites [23], which leads to an increase in the diffusion path and oil seepage. Contrarily, decreasing attapulgite size prevented aggregated and formed a coherent part at the liner bottom so it maintained a constant volume and prevented flow. Moreover, reducing attapulgite grains size increases surface area and negative surface charge that reduces clay aggregation thus accumulation crude oil on the clay surface and prevents oil flow through the line, especially crude oil preferentially attracted to the surface of the materials [23]. So, reducing grain size enhances the efficacy of raw attapulgite liner.

Effect of crude oil type

The type of crude oil is an important factor and affects the efficiency of attapulgite liner. Oil is a complex mixture of different chemicals and a mixture of components that range from low viscosity to high viscosity [22]. Heavy crude oil has high viscosity, high density and the cleanup of it is very difficult. Light crude oil has low viscosity and low density that spread rapidly on the solid surface and penetrates porous surface [23].
The results of this research showed that the saturation rate of raw attapulgite was significantly affected by crude oil viscosity compared to the grain size. Increasing oil viscosity (heavy) reduces saturation rate of raw attapulgite by 38.59%, 24.56%, and 21.05% with a maximum saturation rate by 78.94%, 28.07%, and 22.8% for liners 150µm, 75µm and 53µm respectively after 24 hours, then increased very slowly with the extension of time until equilibrium was reached after 48 hours. Teas et al. mentioned that increasing oil viscosity reduces the rate of absorption within clay pores and increases the adherence on the surface of clay [30]. Also, crude oil is preferentially attracted to the surface of the materials [23]. Consequently, decreasing grain size of attapulgite resulting in decreased saturation rate due to increase surface area hence increased adherence on attapulgite surface more than absorption within channels, also heavy crude oil could block the tiny pores [24].

On another hand, low viscosity oil increased saturation rate of attapulgite liners about 40-50% more high viscosity oil, that amount to 73.68%, 42.10%, and 36.84% after 24 hours, with a maximum saturation rate by 78.94%, 52.63% and 43.85% after 528 hours for liners 150µm, 75µm, and 53µm respectively. Light crude oil quickly moves into the fibrous mass as well as on to the surface, also increases the speed of absorption process due to its low viscosity and density, and it adhere to the surface of the adsorbent less effectively than heavy crude oil [22, 23]. Light crude oil was spread irregularly and easily flowed through raw attapulgite liners especially 150µm and 75µm, therefore it is preferable using additives with clay to reduce the saturation rate over time and prevent seepage. So, depending on the type of crude oil, properties of clay liner could be determined in terms of grain size and the type of additives required to raise their efficiency.

Effect of natural materials

The nature of crude oil proved to play an important role in the selection of the proper additives material. Prairie hay and coconut husk were used in this research as new additives in clay liner, given their natural, cheap, friendliness to the environment and their local abundancy. According to the proposed design for the liner in order to check the efficacy of organic additive with attapulgite clay, three mixture liners were tested with light crude oil include 1-prairie hay 150µm + attapulgite 150µm, 2- prairie hay 75µm + attapulgite 75µm and 3-prairie hay 150µm, coconut husk 150µm and attapulgite 150µm.

In general, attapulgite liners improved significantly after adding natural fibers. The maximum saturation rate of light crude oil decreased from 78.94% to 57.89% for attapulgite liner 150µm after adding 25% prairie hay 150µm, whereas it reduced to 15.78%% after adding 9.3% prairie hay 150µm and 15.7% coconut husk 150µm. Also, the maximum saturation rate decreased from 52.63% to 35.08% for attapulgite liner 75µm after adding 25% prairie hay 75µm. Saturation rate of mixture liners increased very slowly over time until equilibrium was reached after 120 hours.
Attapulgite + prairie hay +coconut husk is the best liner that can be used as a sealant for low viscosity crude oil. Liner has prevented the movement and spread of crude oil through it so that crude oil remains accumulated over the liner and the saturated part of the liner was only 0.9 cm. One mixture liner attapulgite 150µm with prairie hay 150µm was tested with heavy crude oil due to the effectiveness of raw attapulgite liners 75µm and 53µm to prevent seepage high viscosity oil. Attapulgite 150µm improved and kept heavy crude oil without seepage after mixing with 25% prairie hay and saturation rate increased very slowly over time until equilibrium after 96 hours, with a

maximum rate of 47.36%. This mixture resulted in increased strength of attapulgite liner and attracted oil onto their surface without penetrating into the material. Partial replacement of attapulgite by natural fibers could increase the adhesion of attapulgite liner surface, also adhesion of crude oil to the sorbent surface. The cohesion of crude oil among the sorbent elements can serve to produce a congealed mass that retards the spreading of the oil, and cohesion is greater for more viscous crude oil [31]. Consequently, it could be said that the decrease sorption process in liners when the organic additives were added is attributed to the changing in the mud liner strength and reduce permeability that accumulated crude oil over the liner.

On the other hand, adding 2 mL of water to the liner mixture also contributed in reducing the saturation of crude oil and increasing the efficiency of liner, because H_2O molecules fill attapulgite needles more quickly than crude oil and thus the relative permeability of the crude oil decreases. As sorption on clay minerals depends on the molecular size, highly polar water molecules that are generally smaller than organic compounds of crude oil covering the clay surface reducing the attraction of organic molecules [20].

Conclusions:

The following conclusions can be drawn from the current study,

-Attapulgite clay, which is locally available, can be efficiently used as a liner to prevent crude oil seepage.

- Coconut husk and prairie hay are renewable resources used as an additive to design a low-cost and high-efficiency clay liner with no impact on the environment.

- Raw attapulgite liners with a grain size 53µm and 75µm are efficient engineered barrier system for heavy crude oil that can be used as a compacted liner under surface storage tanks, underground storage tanks or under pipelines to impede the flow of crude oil.

- Raw attapulgite 150µm is not suitable as a liner to impede the flow of pollutants. This type of liner is totally inefficient for heavy and light crude oil

- Partial substitution of attapulgite by prairie hay or coconut husk enhances the ability of attapulgite liner to impede the flow of crude oil.

-Attapulgite + prairie hay +coconut husk is the best liner that can be used as a sealant for low viscosity crude oil.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Technology.

Authors' contributions statement:

Mayssaa Ali Al-Bidry and Ramzy. S. Hamied contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript

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استخدام الاتبلغايت كبطانه مانعة لتسرب النفط الخام

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الخلاصة :

تم فحص كفاءة بطانات اطيان الأتبلغايت كمانع لتسرب لنفط الخام. حيث تم استخدام للأتبلغايت الخام والأتبلغايت مخلوط مع القش وقشر جوز الهند كبطانات مانعة للتسريب. الأتبلغايت المستخدم في هذه الدراسة من تكوين إنجانة / الصحراء الغربية في العراق. كما تم استخدام نوعين من النفط الخام من حقول النفط العراقية، خام ثقيل من حقل نفط شرق بغداد وخام خفيف من حقل نفط الناصرية. في البداية تم دراسة الخصائص المعدنية للأتبلغايت بواسطة تحليل اشعة اس والمجهر الالكتروني الكاسح، كم تم استخدام جهاز قياس الامتصاص الذري لتحديد التركيب الكيميائي للطين. وكذلك تم قياس المواصفات الفيزيائية للنفط الخام .طحن الأتبلغايت الى ثلاث احجام حبيبية 150 ميكرون و 75 مايكرومتر و 53 ميكرون لتحديد مدى تأثير الحجم الحبيبي على كفاءة الطين كبطانه . أظهرت التجارب أن بطانات المتكونة من طين الأتبلغايت فقط وبحجم حبيبي 53 ميكرون و 75 ميكرون جيدة من حيث الاحتفاظ ومنع التسرب بحيث يمكن استخدامها كطبقة رئيسية لإعاقة تدفق النفط الخام الثقيل. في حين ان بطانة الأتبلغايت بحج حبيبي 150 ميكرون لم تنجح في اعاقة تدفق النفط الخام حيث ان هذا النوع من البطانات غير فعال تمامًا للنفط الخام الثقيل والخفيف على حد سواء. إضافة القش او قشور جوز الهند إلى الاتبلغايت ساهم في زيادة كفاءة الاتبلغايت بالحجم الحبيبي 150 ميكرون حيث عزز كفاءته كحاجزًا جيدًا يحتفظ بالزيت الخام الثقيل ويمنعه من التسرب لأطول فترة ممكنة. كما ان البطانة المكونة من الطين مع القش او قشور جوز الهند كانت ناجحة مع النفط الخفيف حيث ان بطانة الاتبلغايت فقط لم تنجح في منع تسربه. علاوة على ذلك البطانة المكونة من خليط القش وجوز الهند والأتبلغايت عززت أداء البطانة بشكل كبير مقارنة ببطانات الاتبلغايت فقط او الاتبلغايت مع القش.

الكلمات المفتاحية: الاتبلغايت، المواد الحيوية، بطانة الطين، النفط الخام، التلوث، عملية الامتصاص.