

Responding to Oil spill Incidents in the Marine Environment |Using Natural Oil Absorbents

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□ ABSTRACT □

In this study, the optimal absorption time, maximum absorption, equilibrium curve and reusability were determined for four absorbent materials (*Typha domingensis* , *Datura stramonium*, *sorghum vulgare*, *Ammi visnaga*) in the presence of four types of oil with different viscosities. The ability of the absorbent material to remove the spilled oil was related to several factors, the most important of which are the characteristics of the surface of the absorbent material, the viscosity of the oil and the thickness of its layer. The results showed that extending the sorption time had no effect on the sorption capacity of the sorbent materials for both diesel LV and MV While the absorption capacity was increased by extending the absorption time to 30 minutes for HV . *Trichomes* of *Typha* showed a large absorption capacity, followed by *Datura* based on the results obtained, these natural materials can be used to remove oil because they have a high buoyancy, biodegradation, low cost and relatively high absorption capacity.

Keywords: oil, sorption, spill, natural sorbent, capacity.

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الاستجابة لحوادث التسرب النفطي في البيئة البحرية باستخدام مواد ماصة للنفط

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□ ملخص □

في هذه الدراسة ، تم تحديد زمن الامتصاص الأمثل والامتصاص الأعظمي ومنحنى التوازن وقابلية إعادة الاستخدام لأربعة مواد ماصة (*Typha domingensis* , *Datura stramonium*, *sorghum vulgare*, *Ammi visnaga*) بوجود أربعة أنواع من النفط بلزوجات مختلفة. ترتبط قدرة المادة الماصة على تنظيف النفط المتسرب بعدة عوامل أهمها خصائص سطح المادة الماصة ولزوجة النفط وسماكة طبقاته. أظهرت النتائج أن إطالة زمن الامتصاص لم يكن له تأثير على قدرة الامتصاص للمواد الماصة لكل من المازوت والنفط الخفيف للزوجة والمتوسط للزوجة. بينما زادت سعة الامتصاص عن طريق تمديد وقت الامتصاص إلى 30 دقيقة للنفط الثقيل. بناءً على النتائج التي تم الحصول عليها أبدت أوبار التيفا قدرة امتصاص كبيرة ، تلتها الداتورة ، بحيث يمكن استخدام هذه المواد الطبيعية لإزالة النفط لما تتمتع به من قدرة عالية على الطفو والتحلل البيولوجي والتكلفة المنخفضة وقدرة الامتصاص العالية نسبيًا.

الكلمات المفتاحية: نفط، امتصاص، تسرب، مواد ماصة طبيعية، السعة الامتصاصية.

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Introduction:

As crude oil is one of the most important sources of energy and revenue for countries of the world, the urgent need for oil squeegees has begun to be a very important thing. Previously, the oil spill was a very rare accident due to the lack of exploration, transportation and oil refining. However, oil has now become a very important source of income, so the oil spill has become a threat to most countries of the world (Doshi *et al.*, 2018). There are many effective ways to clean up oil spills, in addition to their side effects and the financial burden resulting from them. Therefore, the friendly, effective, and least expensive methods have been taken in our time (Ukotije-ikwut *et al.*, 2016). Several cleaning methods were used: containment, mechanical recovery, in-situ incineration, biological treatment, chemical dispersions, and the use of various absorbent materials. The use of these procedures must be done quickly, taking into account the condition of the sea, the type of oil and environmental considerations during the accident. The most prominent means used: energized booms resulted in burning in situ (Al-Majed *et al.*, 2012). The main obstacle to the use of mechanical and chemical treatment in oil spill accidents lies in its relatively high cost and inefficiency of absorption. The high wind speed and turbulence of the sea waves increase the difficulty of mechanical treatment, but it remains one of the most effective methods adopted. Whereas, chemical treatment, such as dispersal, should be applied after a very short period of time, and it has negative effects on marine organisms of all kinds due to its high toxicity (Liu *et al.*, 2020). Oil-contaminated water is currently dealt by mechanically extracting oil from water using absorbents on a large scale all over the world (Hubbe *et al.*, 2013). Sorbent materials include three main types, including organic industrial products, inorganic mineral products, and organic plant products. The disadvantages of these materials are that they decompose very slowly compared to vegetable or mineral products (Adebajio *et al.*, 2003). The absorption of oil using the absorbent material depends on two main things: the hydrophobic properties of its fibrous structure and the physical properties (Doshi *et al.*, 2018). In general, the absorption capacity of different types of oil from salt water is controlled by several things, the most important of which are the absorption time and system conditions such as the oil layer, its particle size and the amount of absorbent materials used (Abdelwahab *et al.*, 2017). The best oil cleaning technology that has been reached is agricultural waste due to its great buoyancy and biodegradability easily (El-Din *et al.*, 2018). The waxy nature of most agricultural wastes used in this field gives them a great absorbability for petroleum materials, in addition to the light weight after drying, which greatly improves the buoyancy capacity on the surface water (Idris *et al.*, 2014). The degradability of these materials makes them environmentally friendly and very safe compared to other types (Abdelwahab *et al.*, 2017). This method is classified as the most economical and pollution-free as it contributes significantly to oil-water separation techniques with the possibility of its renewal easily without major changes in its efficiency (Gulistan *et al.*, 2016). Despite the fact that polymer products (polyethylene, polypropylene and polyurethane) are the most widely used globally, one of their major disadvantage is their non-biodegradability in system (Deschamps *et al.*, 2003). Thus, sorbents can be a correct choice to be used as an effective alternative to polypropylene in oil-seawater absorbents in terms of biodegradable, low cost and sustainable materials (Sinha *et al.*, 2020). It has been reported that a large number of natural fibers such as kapok, hashish, wool, cotton, etc., are used as oil absorbent materials. Cotton fibers have been studied for oil absorption and reported higher oil absorption than polypropylene (GE *et al.*, 2016). A great deal of research attention has

been devoted in the past two decades to assessing the oil absorption capacity of organic natural products (bio-sorbents) derived from local agricultural waste because of its significant advantages (Pagnucco & Phillies, 2018). Among the local studies that were interested in this field (Krawi & Kara-Ali, 2011), which showed the possibility of replacing the manufactured materials used to remove oil in Syria with natural materials with a relatively high absorptive capacity.

The research aims to investigate the optimal absorption time, determine the maximum absorption capacity of the studied materials using different types of oil, in addition to determining the maximum absorption capacity of materials in the presence of marine water and multiple quantities of oil and study the possibility of reusing the absorbent materials again.

Experimental

Oil sorbent

The absorptive capacity of four natural substances has been reported: (*Trichomes of Typha*, *Datura*, *sorghum*, *Ammi*) It was dried in the open air for two weeks and then used as an oil absorbent material.



Typha domingensis *Datura stramonium* *sorghum vulgare* *Ammi visnaga*

Oil samples

The specifications of the 4 different types of oil used in the experimental procedure showed in (table 1).

Table (1) The specifications of oil types

Oil	Abbreviation of oil	Viscosity (cSt)	Temperature
Diesel	DE	2.9	40
Light oil	LV	2	40
Medium oil	MV	21	40
Heavy oil	HV	92	100

Procedure:

Effect of Absorption Time on Absorption Capacity:

A 250 ml glass beaker was used to determine the optimal absorption time for the studied oil absorbent materials. It was filled with 100 g of each type of oil used separately, then 1 g of the absorbent material was added. Beakers were placed on an automatic shaker with a speed of about 100 rpm. Then, different absorption times were applied (5, 15, 30, 60 min), and the experiments were repeated three times. The oil-soaked absorbent was then taken

out and drained in the beaker for a minute, then weighed. The amount of absorbed oil was determined by the equation (Krawi & Kara-Ali, 2014):

$$S_{\text{oil(g oil/g sorbent)}} = S_T - S_A$$

S_T : total weight (g) S_A : absorbent weight (g)

Absorption from a medium containing sea water/oil:

About (10, 30, 50 g) of oil is added to an 1000 ml beaker containing 500 ml of sea water. The beaker is installed on a shaker. One gram of absorbent material is added to the system. The vibrator operates for 10 minutes at 98 rpm. the absorbents material were drained for a minute, then weighed. The determination of water content in the sorbent material is carried out by the distillation technique described in (ASTM, 2006). A carrier solvent should be used to aid the oil recovery process and separate it from water, which is a mixture of Toluene and Xylene (20\80 v\|v). The amount of absorbed oil is determined by the equation (Teas *et al.*, 2001):

$$\text{The amount of oil which was absorbed} = S_T - S_w - S_a$$

S_T is the total weight (g) of oil, water and absorbent material

S_w is the water weight (g) and S_a is the absorbent material weight (g)

The quantity of oil was recorded as grams per gram of sorbent.

Measurement of the oil release rate of the absorbent material:

The absorbent material is soaked in an oil bath, after which the rate of oil release from the absorbent material is measured by hanging it freely in a vertical manner so that the excess oil is automatically drained over time. The amount of oil spilled is recorded by gradually measuring the weight lost after specific intervals of 0 to 12 minutes. The amount of oil retained is taken by calculating the difference between the initial weight of the soaked absorbent material and its weight after draining for the predetermined period (Sinha *et al.*, 2020).

Reusability:

The main criterion which can be used for judging reusability of the sorbent is the number of cycles it can endure without becoming unusable due to rupture, crushing, or other general impairment. Other influencing factors are the rate of decrease in its oil sorption capacity assemblies for three cycles of sorption/desorption, beyond which the sorption capacity appeared to become constant recovered oil by a simple compressing operation, which could remove oil from the loosely packed sorbent (Husseien *et al.*, 2009).

Absorption from a medium containing sea water/oil:

About (10, 30, 50 g) of oil is added to an 1000 ml beaker containing 500 ml of sea water. The beaker is installed on a shaker. One gram of absorbent material is added to the system. The vibrator operates for 10 minutes at 98 rpm. the absorbents material were drained for a minute, then weighed. The determination of water content in the sorbent material is carried out by the distillation technique described in (ASTM, 2006). A carrier solvent should be used to aid the oil recovery process and separate it from water, which is a mixture of Toluene and Xylene (20\80 v\|v). The amount of absorbed oil is determined by the equation (Teas *et al.*, 2001):

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Results and Discussions:

The effect of absorption time on absorption capacity:

To address the oil spill from all possible aspects, the maximum absorbent capacity of the absorbent materials should be studied to determine the optimal absorption time. These experiments are conducted without involve of water.

Figures (1,2) show the effect of the absorption time of DE, LV on the studied materials. It was noted that the absorption rates of both were very fast. Almost the maximum capacity was reached for most sorbents within 5 min. The extension of the absorption time had no effect on the amount of absorbed oil. The reason for this is due to low viscosity of the oil led to the penetration of oil into the voids of the materials very easily and quickly, especially trichomes of *Typha* and spongy structure of *Datura*.

In the case of MV oil, the results shows in Figure (3). It was found that the absorption of oil gradually increased with increasing absorption time. The saturation was reached within 15 minutes, after which there was no increase in the amount of absorbed oil, except for the trichomes of *Typha*, which showed a longer absorption time of about 30 minutes. With the presence MV oil, the absorbent capacity of both the *Ammi* of the *Sorghum* and the mole increased because the viscosity of the oil contributed to its adhesion to the outer surface layer of the absorbent material.

The sorbents showed a higher ability to absorb high viscosity oil. Figure (4) shows a gradual increase the absorption capacity with extension of absorption time from 30 to 60 minutes. This is due to the very high viscosity, which leads to the occurrence of adhesions on the surfaces of the studied materials. exception of trichomes of *Typha*, it showed a relative decrease in the amount of absorbed oil and only absorbed about 20 grams, due to the increase the oil viscosity, which leads to the occurrence of adhesions that slowed its penetration into the voids of the material. In the case of HV oil, the thorns of *Datura* increased the adsorption of oil on it significantly, as well as the waxy layer of *Sorghum* and *Ammi*. It can be said briefly through this study that trichomes of *Typha* fiber is an important absorbent material for cleaning up the oil spill. While the oil absorption values for the rest of the studied materials were lower than it, In related research conducted using cotton and kapok the adsorption capacity followed the same pattern, so that the adsorption capacity of high viscosity oil was greater than that of low viscosity oil (Wolok *et al.*, 2020).

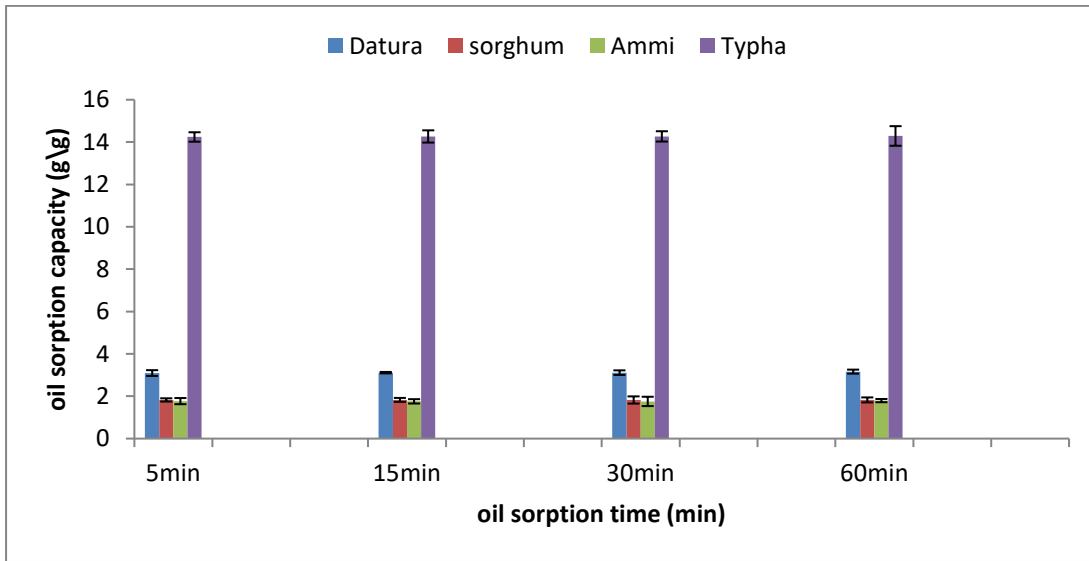


Fig (1): oil sorption times of diesel (DE)

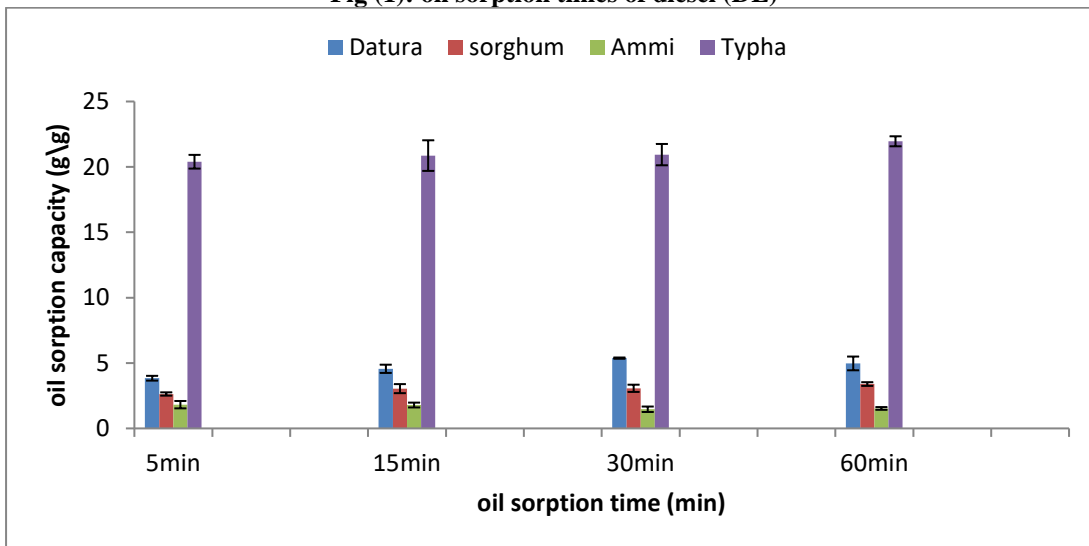


Fig (2): oil sorption Times of light viscosity oil (LV).

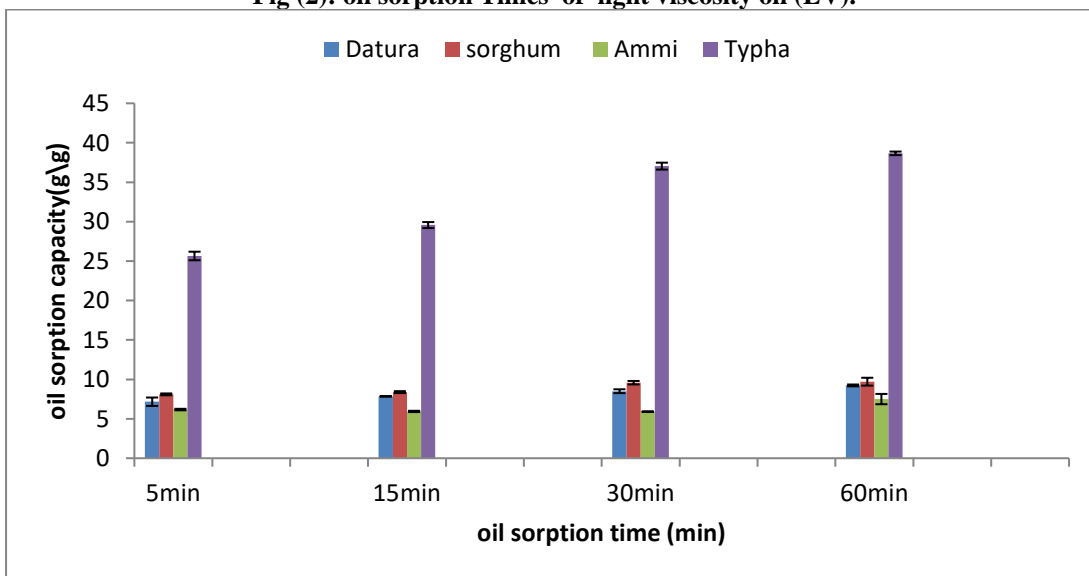


Fig (3): oil sorption times of medium viscosity oil (MV)

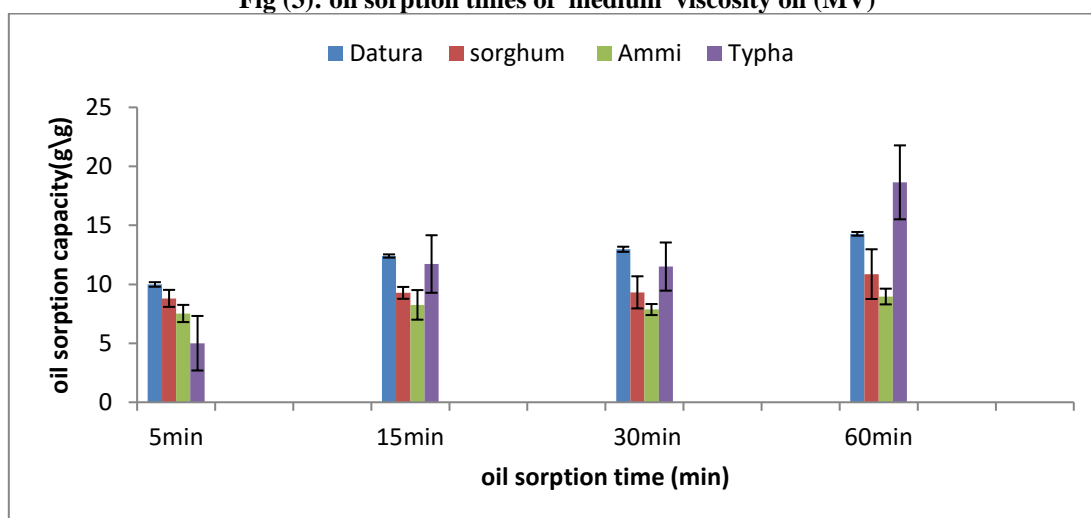


Fig (4): oil sorption times for of heavy viscosity oil (HV)

Absorption from a medium containing oil / sea water:

The absorption of oil from saline water is related to several things, the most important of which are the absorption time, system conditions such as the oil layer, the amount of used sorbent materials and its chemical properties such as hydrophobicity that lead to the absorption of less water, unlike the hydrophilic properties that lead to the absorption of larger quantities (Shojaei *et al.*, 2021)

In this experiment, the adsorption properties were studied and the maximum adsorption capacity of oil absorbent materials was determined in a medium containing sea water/oil in the presence of different quantities of oil.

Figure (5,6) shows the absorbent capacities of the sorbent materials in the presence of DE, LV. The results indicate that trichomes of *Typha* did not leave any oil stain on the surface of the water by 10 g added oil. While the time 10 minutes was not enough for trichomes of *Typha* to reach a maximum absorption capacity at 30 and 50 g added oil. The other materials showed lower absorption values, as their absorbent capacity was less than that of 10 g of floating DE, LV. In general, the absorption capacity of all substances with different amounts of DE, LV was relatively constant.

We note from Figure (7) the absorption capacities of the different absorbent materials studied in the presence of MV oil. The absorption capacity of trichomes of *Typha* was the highest, followed by *Datura*. The absorption of MV oil for trichomes of *Typha* was at a slower rate than DE, LV due to the high viscosity that led to the prolongation of the absorption process. The decrease in the amount of oil absorbed in the case of 10 g is due to the fact that the medium contains a quantity of oil less than the absorption capacity of trichomes of *Typha*, while the other materials maintained a relatively constant absorption capacity at the different amounts of added oil.

In the case of HV oil, *Datura* and *Sorghum* had the highest absorption capacity compared to the other types. Figure (8) shows that the absorption of HV oil by trichomes of *Typha* is less than MV, and the reason for this is that the high viscosity of the oil impeded its penetration into the voids. In general, the amount of absorbed oil increased with increasing the thickness of the added HV layer, as it forms a separating layer between the absorbent materials and the water, which prevents them from contacting the water and thus the

amount of water absorbed decreased compared to previous experiments. It can be noticed that the absorption capacity of all the studied materials in a medium containing only oil is slightly higher than the absorption capacity in the medium of sea water / oil.

It was also found that the absorption of light oil is slightly higher than that of diesel. And trichomes of *Typha* again showed a higher absorption capacity than the rest of the materials because the oil penetrates within its fibers according to the phenomenon capillary action. This result is similar to the observation (Ukotije *et al.*, 2016).

The viscosity of the oil plays the most prominent role in determining the absorption capacity, and this has been reported (Sinha *et al.*, 2020)

It is well-known that the absorption process of oils on absorbents is controlled by the capillary effect, van der Waals forces, hydrophobic interaction between the oils and absorbents, pore morphology, and oil viscosity (Nguyen *et al.*, 2013)

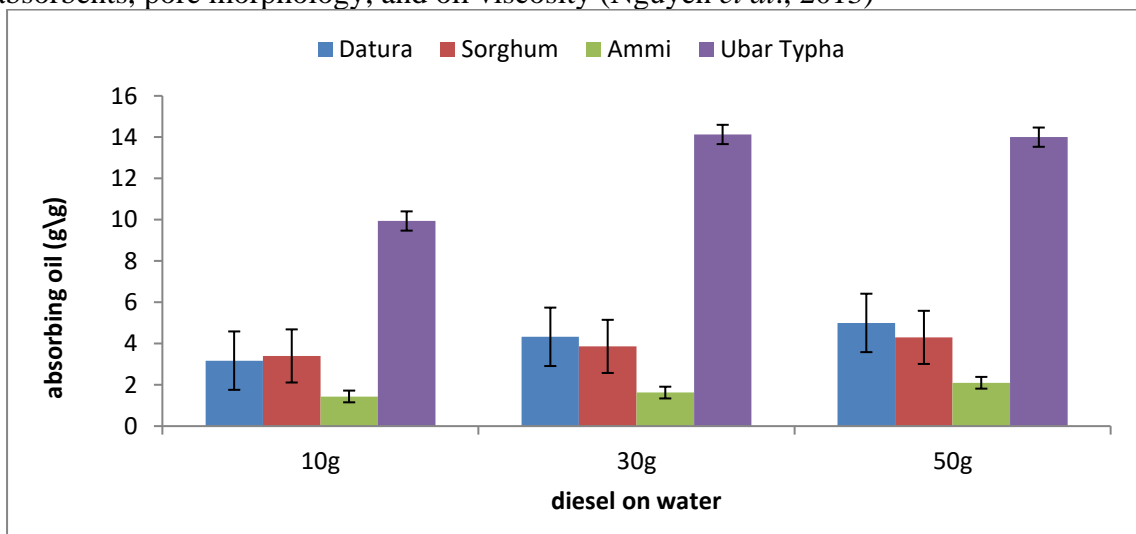


Fig (5): the absorptive capacity of the studied absorbent materials in the presence of sea water and different amounts of diesel.

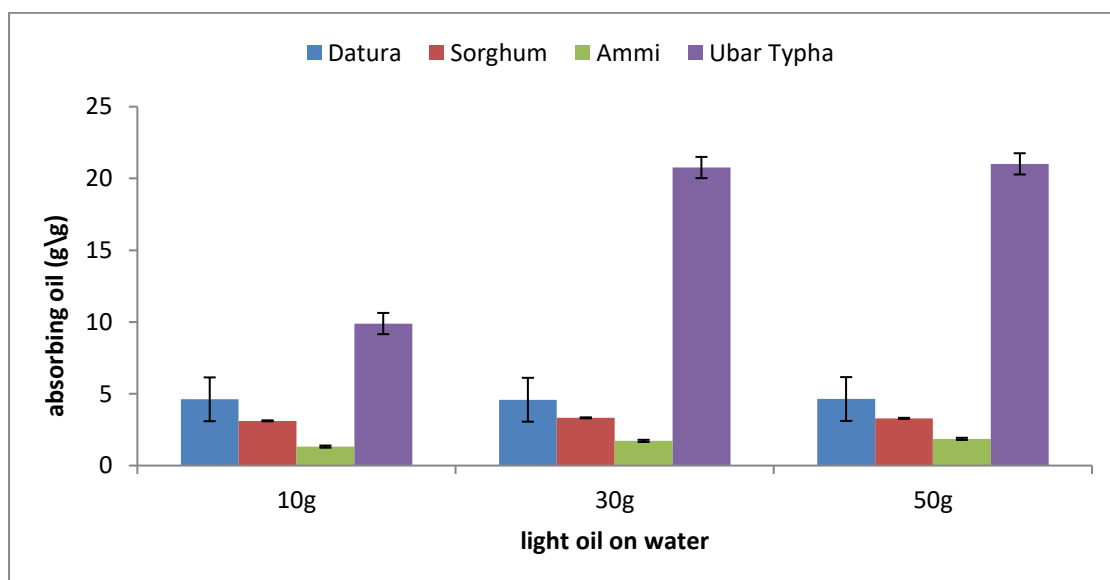


Fig (6): the absorptive capacity of the studied absorbent materials in the presence of sea water and different amounts of light oil.

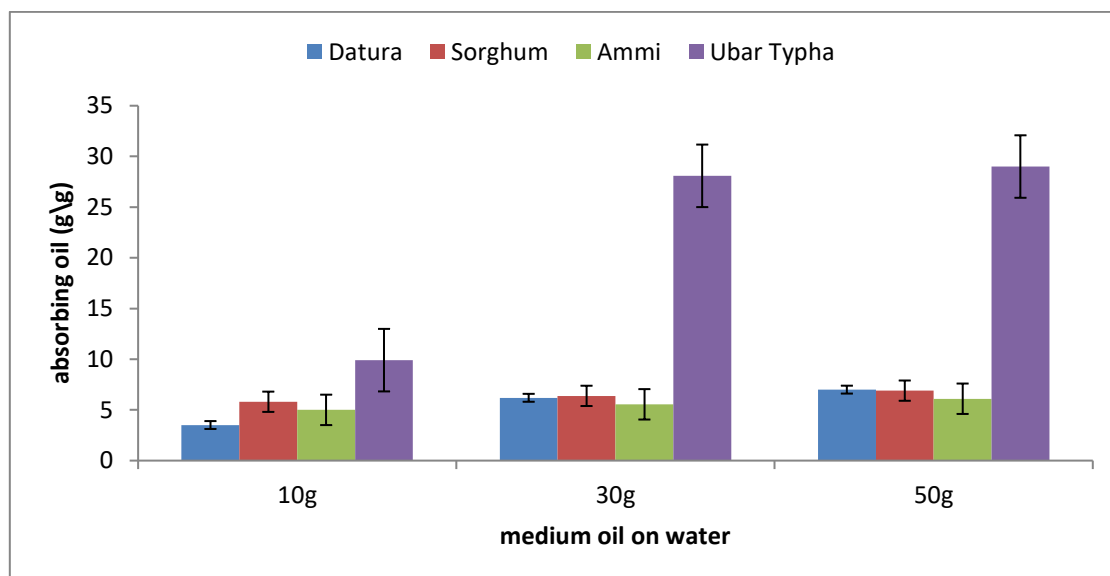


Fig (7): the absorptive capacity of the studied absorbent materials in the presence of sea water and different amounts of medium oil.

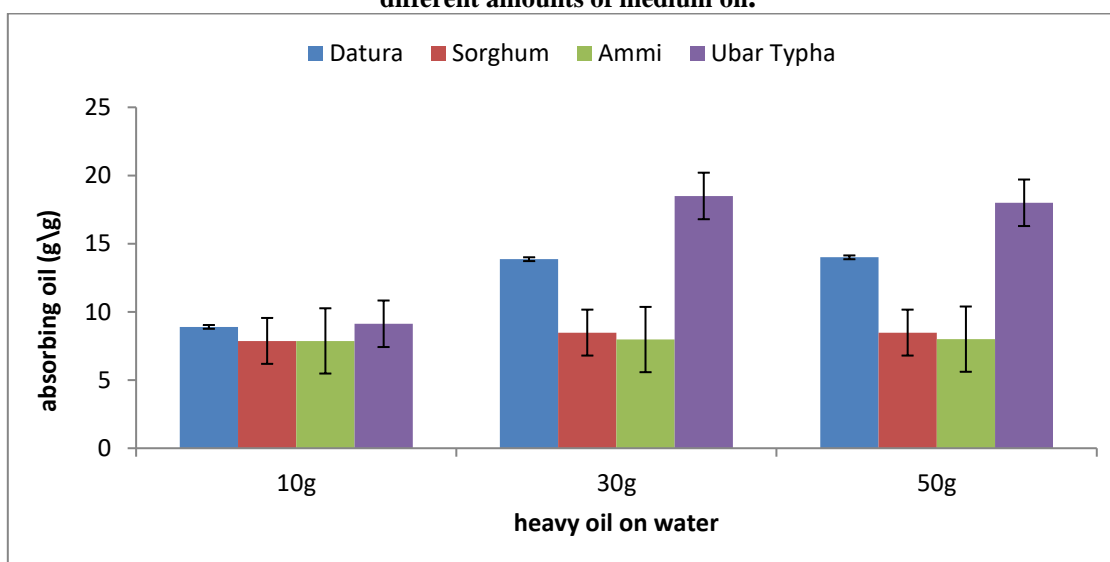


Fig (8): the absorptive capacity of the studied absorbent materials in the presence of sea water and different amounts of heavy oil.

Sorbent oil release rate (equilibrium curve):

The release of the absorbed oil by the free suspension of the sorbent is a phenomenon inverse to the absorption of the oil used in previous experiments.

The average Diesel release for all studied sorbents is shown in Figure (9) and each of these curves includes two distinct phases. The first stage of it includes the initial stage of the launch, which occurs within one minute. It is clear from the graph that the rate of launch in this period is very high. The second period lasts from about 1 to 7 minutes to reach the state of equilibrium. Diesel oil is drained from the absorbent materials very quickly due to the low viscosity that leads to weak surface tension and therefore a weak bond between the oil molecules and the materials and thus the oil drains easily from the material during vertical suspension (Hussein *et al.*, 2011).

From Figure (10) it is observed that the LV discharges very quickly and the stability state is reached quickly within one minute, due to the poor retention of oil within the large voids of the absorbent materials and the ease of draining it as in the previous case (Sinha *et al.*, 2020) .

As for the MV oil, the oil is drained more slowly because of its high viscosity compared to the previous two types, and the stability state was reached within 5 minutes for most of the studied materials, as shown in Figure (11).

In comparison with the above, the high viscosity oil is drained more slowly than other types of oil due to its high viscosity, and the stability state for most absorbent materials was reached after about 9 minutes, as shown in Figure (12). This is due to the high viscosity of the oil, which increases its adhesion to the surface of the materials and within the pore spaces, which hinders the process of oil draining and slows it down due to the formation of a solid cohesive mass. Of the studies whose results are consistent with our study (Cojocaru, 2011).

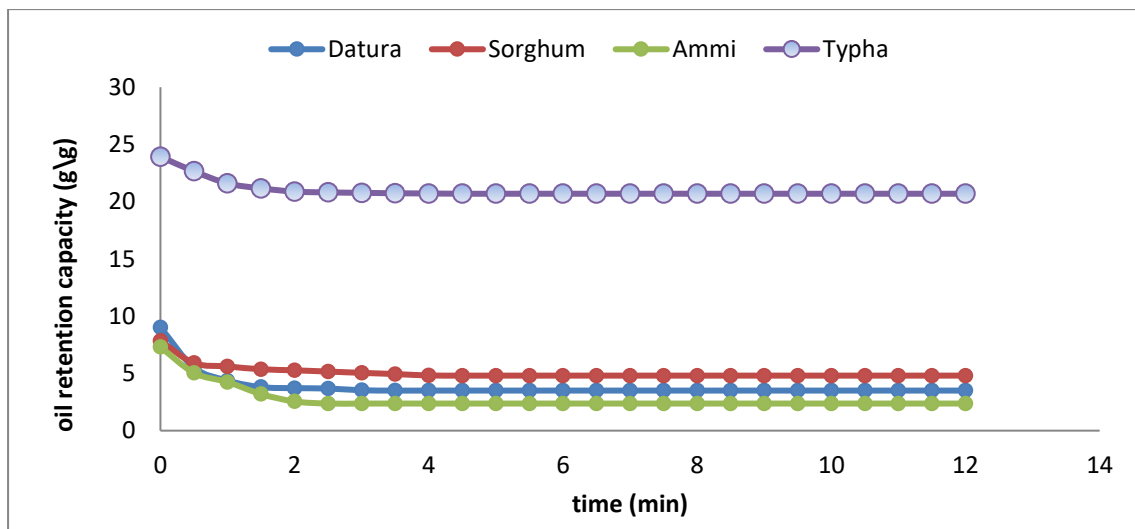


Fig (9): the equilibrium curve for the sorbent materials studied in the presence of diesel.

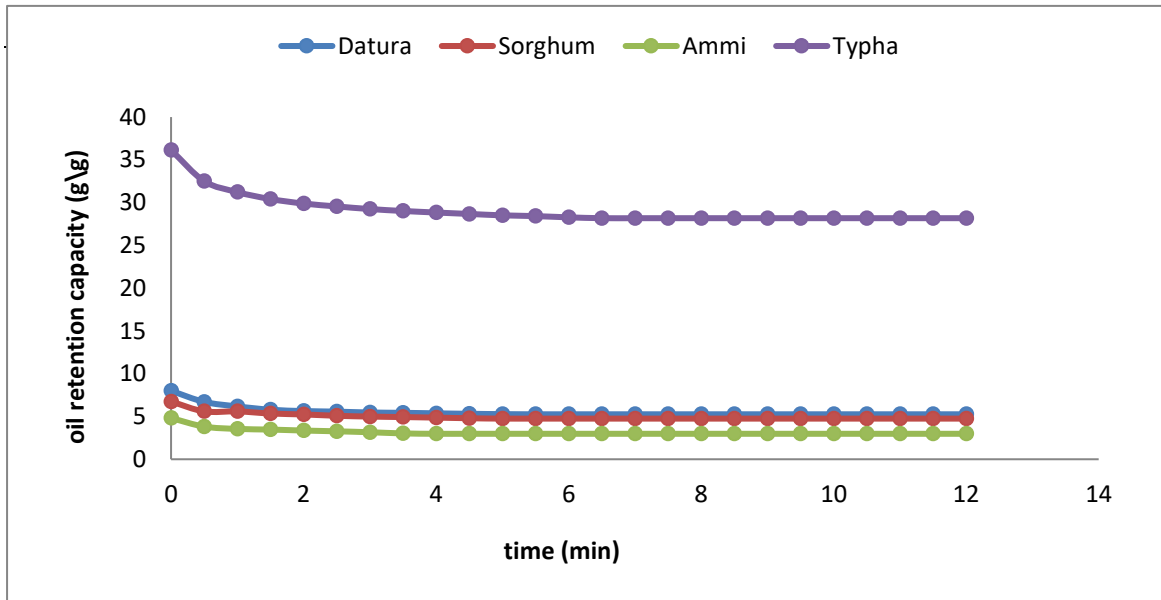
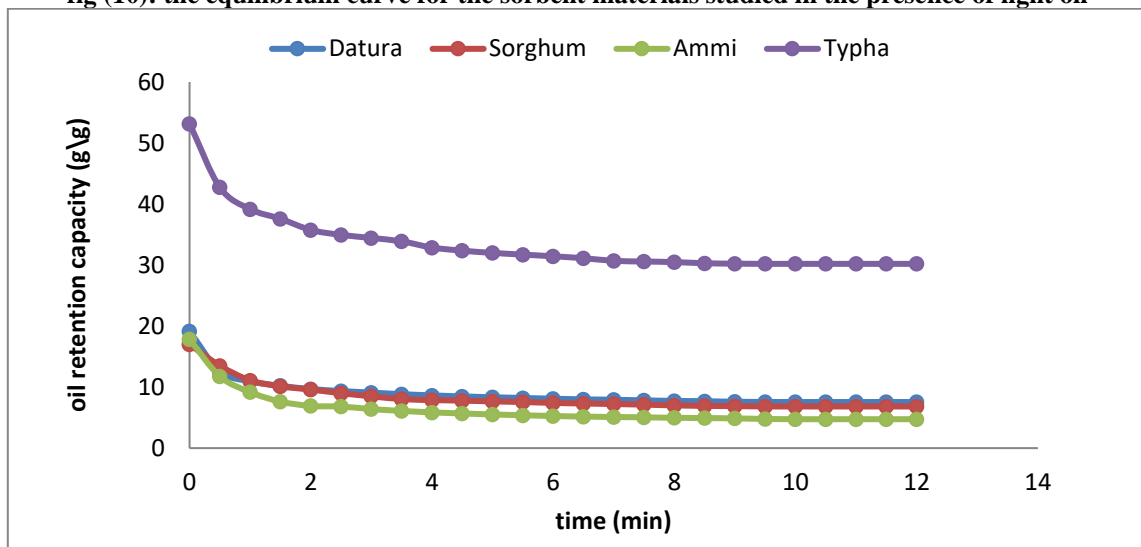


fig (10): the equilibrium curve for the sorbent materials studied in the presence of light oil



Fig(11): the equilibrium curve for the sorbent materials studied in the presence of medium oil.

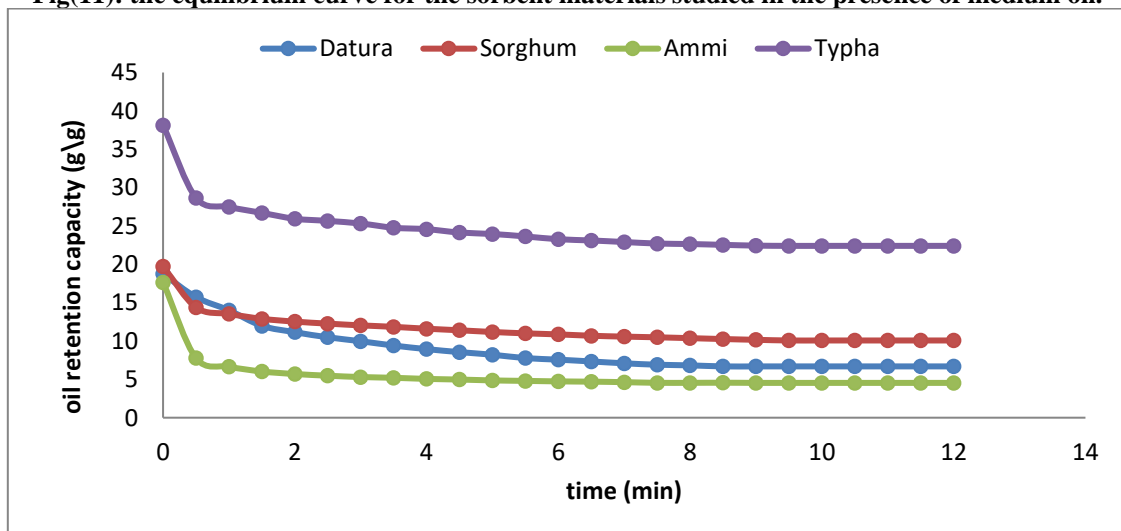


Fig (12): the equilibrium curve for the sorbent materials studied in the presence of heavy oil.

Reuse of absorbent materials:

The oil was recovered from the sorbents by simple pressure with a hand press. It was noticed that the amount of oil absorbed after the second use decreased by half because the size of the voids was not fully recovered again (Hysterical stress - strain relationship or deformation has been observed by Skelton (1975). After that, the adsorption capacity was stable for all absorbent materials up to 10 cycles of sorption/desorption. In addition, the reason for the low absorption of oil by the absorbent materials when re-use is due to our inability to recover all of the oil using a simple pressure method (Lim & Huang, 2007) .

Conclusions:

- The sorbent materials tested in this research showed a great ability to absorb oil floating on the surface of the water, especially trichomes of *Typha* and *Datura*.
- It was observed that the absorbent capacity of oil absorbent materials increased with increasing of its viscosity and the thickness of its layer
- Extension the absorption time of more than 5 minutes did not affect the absorbent capacity of the sorbent materials in the presence of diesel, LV and MV, while it increased significantly in the case of HV oil.
- The sorbents showed a high rate of abandonment of diesel and LV due to their low viscosity, while the abandonment of MV was slower than them and HV was the most slow due to its very high viscosity.
- The absorbent capacity of the absorbent materials decreased by about 50% after the first use, due to the deformation of the structure as a result of the pressure applied to it.

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