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Treatment of Oil Spills and Oily Wastewater by Using some Local Agricultural Wastes.

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Treatment of Oil Spills and Oily Wastewater by Using Some Local Agricultural Wastes.

معالجة البقع الزيتيه والمياه الملوثه الزيتيه باستخدام بعض المخلفات الزراعية المحلية

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ملخص البحث :

يعرض هذا البحث نتائج مجموعة من التجارب على استخدام بعض المخلفات الزراعية المحلية لازالة زيت البترول الخام والكيروسين والزيوت النباتيه المتسربة على الاسطح الصلبة أو على سطح الماء العذب أو المالح. والمواد الماصة التي جربت هي لب مصاصة القصب وقش الارز وقشوره وقد تمت التجارب على الساكن وتحت الظروف الجوية المعتادة. وقد أثبتت التجارب فعالية المواد الماصة المجربة في خلال دقائق معدودة وسهولة جمع المادة المستهلكة وتداولها بعد أداء عملها وأنه يمكن ازالة اكثر من ٩٥٪ من السائل المتسرب باستخدام الكمية المناسبة من المادة الماصة والتي تتوقف على نوع السائل المتسرب ونوع المادة الماصة. وهل التسرب على سطح صلب أو على سطح الماء وعلى درجة ملوحة الماء. هذا ومن مزايا هذه الطريقة المرونة في التشغيل ورخص المواد الماصة ووفرتها محليا وامكانية استخدام مثل هذه المواد لازالة الزيـــــــوت الاخرى وكذلك امكانية استخدام المواد الماصة المستهلكة كمواد وقود كل ذلك يجعل نتائج هذا البحث جذابة ومشجعه للغاية.

ABSTRACT

Set of tests were conducted using bagasse pith, rice straw, and rice hulls as sorbents for the removal of crude oil, cotton-seed oil, and kerosene present as spills or run-off either on solid surfaces or on bodies of waters. Tests were conducted under static conditions at ambient temperature and pressure. These materials were effective within minutes, easily picked up, and easy to handle thereafter. Results indicated that over 95% of the spilled liquid can be removed by using the appropriate mass of the tested material. This mass depends upon type of spilled liquid, type of sorbent used, whether the spilled liquid is on a solid surface or on a body of water, and on the degree of salinity of that water. the operating flexibility inherent to this technique, the local availability and cheapness of the tested materials, the potential use of these materials to remove other oily wastes of various chemical natures and physical forms, and the feasibility of using the exhausted materials as a fuel, makes the obtained results promising and interesting.

INTRODUCTION

The need for oils (petroleum and its distillation products, vegetable oils, and mineral oils) removal either from wastewater or as spills and run-off on solid surfaces is of a growing imprtance for economical and environmental reasons. In the technology of water purification, the traditional method of oil seperation is via the API gravity separator or the tilted-plate separator. In such separators, only free oil will be separated, emulsions are not broken. Dissolved air flotation is normally used for further removal of oil from API separator effluents prior to biological treatment. Chemical flocculating agents are used to aid flotation, they improve the effectiveness of the flotation unit in removing oil emulsions. [1-5] Methods of treatment and removal of oil spills were reviewed in detail in previous articles. [6-8] Sinking the oil is sometimes suggested while dispersents are extensively used in the treatment of oil spills on sea water and on the shore line. [7-10] Generally, oil removal methods are always expensive and a lot of work must be done to search for lessening oil removal expenses. This work is only a trail on that way.

The experiments carried out in the college of Engineering at Al-Mansoura showed that natural rice husks is characterized by a good capability of sorbing petroleum and vegetable oils at ambient temperatures.[11] In view of this study the present work was conducted to explore the possiblity of using rice hulls, rice straw, and bagasse pith to remove oils present as spills or run-off either on solid surfaces or on bodies of water (tap water or sea water).

Rice hulls have a needle shape, rough surface with sharp ends. The grain length is about 0.005 m. Rice straw is the stem of rice plant, about 0.002 m in diameter and from 0.5 to 0.8 m long. Bagasse pith is a waste product from the sugar cane industry in the form of collections of fine fibers with a maximum diameter of 0.001 m and of different lengths (from 0.01 to 0.5 m). The structure of these materials are cellulose based (not less than 50% cellulose).[11-13] These materilas are agricultural wastes available everywhere in Egypt at almost no cost, chemically stable relative to water and oils, and after doing the removal job these materials can be used as a fuel of high calorific value.

Experimental :

The experimental work was divided into three main parts. In the first part the sorption characteristics of water, kerosene,crude oil, and refined cotton-seed oil by the selected sorbents were studied. The second part was a pench scale study for the use of these materials to remove spills of the tested liquids on soild surfaces while the third part was devoted to remove oils from water bodies. Spills either on sea water or on tap water were treated separately. All tests were conducted under static conditions at ambient temperature and pressure.

Rice hulls were tested without crushing while rice straw and bagasse pith were torn into shreds of certain lengths according to the test Conditions. These materials were washed several times with tap water and dried at 110°C for ten hours. They were left to cool in desicators and then stored in clean and well sealed containers ready for subsequent use.

Sorption characteristics of water, kerosene, crude oil, and refined cotton-seed oil by bagasse pith, rice straw and rice hulls :

To get a thorough evaluation for the sorption characteristics of the investigated materials the experimental work encompass the effect of sorbent length, soaking time, and mass of sorbent relative to the mass of liquid present. For rice straw and bagasse pith, the studied lengths were 0.07, 0.05, 0.02 and 0.005m. While the studied soaking time covers the range 5 minutes up to 24 hours.

In each experiment about 250 gm from the tested liquid were placed in a 500-ml beaker. From one up to 5 grams of the sorbent were then added to the beaker contents. After the lapse of a specified soaking time the contents of the beaker were filtered through a 400 μm mesh screen. The investigated material was left on the screen for ten minutes to drain away excess liquid, then weighed to get the amount of liquid sorbed. The collected data were then tabulated and presented.

Table (1) gives the variations in the sorption of water, kerosene, crude oil, and refined cotton-seed oil, by bagasse pith, rice hulls, and rice straw with soaking time. Figure-1 presents the sorption of the tested liquids by bagasse pith versus soaking time while Figure -2 shows the sorption of crude oil by the investigated sorbents versus soaking time. Table -1, and Figures 1 and 2 reveal the following:-

1- Rates of sorption of the tested liquids by the investigated sorbents increases rapidly till reaching a maximum value after the lapse of about 15 minutes then they begin to decrease very slowly till reaching an almost constant value after the lapse of a certain time that depends upon the sorbed liquid and the tested sorbent.

2- Water and kerosene were sorbed by different rates on the three tested materials, while oils were sorbed by almost the same rate on rice hulls and rice straw. This rate is less by about 12% than than detected for the sorption of these oils by bagasse pith.

3- For the same soaking time; a) bagasse pith sorbs more liquids than the other sorbents, and b) for bagasse pith and rice straw, masses of water sorbed exceed those sorbed from oils and kerosene. The reverse is true for rice hulls. This means that sorption on rice hulls appears to happen by a different mechanism than sorption on rice straw and bagasse pith.

Sorption of liquids on rice hulls was discussed in deteils elsewhere. [11] Sorpiton of water, oils, and kerosene on rice straw and bagasse pith appears to happen by the capillary phenomenon where the penetration of liquid molecules into the soild phase involves filling of the fine capillaries of the latter. This suggested mechanism is supported by the following:-

1- The amount sorbed from each liquid depends upon its coefficient of surface tension (σ) as indicated in Figure-3.

2- Negligible changes in material volume were noticed after the sorption process which means that sorption happens along the sorbent capillaries, hence the dimensions of the solid sorbent did not affected.

3- Short time needed for the completion of the sorption process (from 10 to 15 minutes) means very short diffusion paths and strong driving forces (adhesion forces resulting from the differences in molecular fields at the interface between the sorbed liquid and the solid sorbent).

4- The amount sorbed from each liquid decreases as the length of the sorbent fiber decreases as shown in Figure -3. This can be attributed to the fact that penetration of liquids through the sorbent capillaries happen from the both ends of the capillaries. Air present in the capillary will thus enclosed between the two liquid threads forming an air pocket. This air is compressed by the liquid untill reaching an equilibrium state at which the capillary pressure of the tested liquid ($2\sigma / r$)equals to the pressure of the enclosed air, where r denotes the radius of the capillary

Removal of liquid spills and run-off on solid surfaces :

In each one of these experiments from 90 to 300 grams of the tested liquid was placed in a rectangular tray (0.4 x0.25 x0.1m) to get a uniform liquid film of a certain thickness. The trays used were made of galvanized steel (0.0015m thick).

A known mass of the tested material was then spread uniformly over the liquid film in the tray. After the lapse of about 15 minutes, the solid sorbent is skimmed, left on a 400 μm mesh screen for 10 minutes to drain the excess liquid and weighed. The amount of liquid sorbed is calculated as the difference between the masses of the sorbent after and before the sorption process.

In these experiments the lengths of bagasse pith and rice straw fibers were 0.05 m., while rice hulls were used without crushing. As in practical situations oil spills are identified by their thicknesses, the collected data were treated and presented in a convenient manner readily suitable for practical applications in Figure-4. This Figure shows the percentage of liquid removal from 0.001 m^3 of liquid spill (i.e. a spill of $1m^2$ area x 0.001 m thick) versus the mass of sorbent applied to that spill. Table -2 shows pick up ratios accompanying over 95 percent of liquid spill removal. Pick up ratios are given as the mass of spilled liquid sorbed per unit mass of sorbent. Cost of sorbent needed to remove over 95 percent of the spilled liquid is also shown in this table. This cost does not include labor and equipment cost. Figure-4 and Table -2 reveal the following :

1- Over 95 percent of spilled oils or kerosene can be sorbed by using the proper mass of sorbent. This mass is dependent upon the type of the spilled liquid and the type of sorbent used.
2- For the tested sorbents, bagasse pith proved to be the most efficient one.
3- More crude oil is sorbed by the same mass of sorbent followed by cotton-seed oil then comes kerosene. This is compatible with the sequence of values of the coefficients of surface tension for these liquids which supports the previous mentioned mechanism for the sorption of these liquids by the tested sorbents.
4- Table -2 reflects sorbents costs based on the current costs in Egypt and the reported oil sorption capacity of these sorbents. These costs do not reflect the equipment and labor costs associated with their use. Generally, this technique appears to be cost effective as it needs cheap equipment to spread and then collect the sorbent in addition to the local labor availability at low prices.

Removal of oils from the surface water:

Set of tests were conducted using bagasse pith, rice straw, and rice hulls as solid sorbents for removing oils from the surfaces of bodies of water. In these tests both crude oil and refined cotton-seed oil were used with both tap water and sea water. The galvanized steel trays described earlier were used.

The experimental procedure was to half fill the tray with water then a certain mass of the tested oil was added to water to form a film thereon. A known mass of the tested sorbent was spreaded uniformly over the surface of the liquid mixture in the tray without mixing. After 15 minutes the sorbent was collected by skimming, left for 10 minutes over a 400 μm mesh screen to ensure complete drainage of the excess liquid present, and weighed. The sorbent was then dried at 105 ^{o}C for 3 hours and weighed again.

The mass of water sorbed was calculated as the difference between the masses of the sorbent before and after drying, while the mass of oil sorbed was determined as the difference between the masses of the dried sorbent and its initial mass.

All testes were conducted at room temperature while the lengths of bagasse pith and rice straw fibers were 0.05 m. Summing of the treated test data is presented in Table -3. This table reveals the following :

1- Under the same test conditions :

1-1) About 0.32 kilograms of bagasse pith are needed to achieve over 95% oil removal from either one kilogram of oil spill or approximately an oil spill of 1 m^2 areax 0.001 m thick present on a fresh water surface. This mass is almost twice that needed to get the same removal effect if this spill is present on a solid surface as given in Fig. 4.
This can be attributed to the simultaneous penetration of water and oil molecules into the sorbent capillaries. Similar trends were noticed for rice straw and rice hulls.

1-2) Percentages removal of either crude oil or refined cotton-seed oil are nearly equal.

1-3) Negligible differences were noticed between the masses of oil sorbed either by rice straw or rice hulls, thus data for rice straw are only presented here.

1-4) For sorbent to oil mass ratios below 0.32, masses of oil sorbed by those sorbents from spills on sea water exceed those sorbed from spills on tap water by about 11%. This effect decreases with the increase in the sorbent to oil mass ratio.

1-5) The amounts of oils sorbed by bagasse pith exceed those sorbed by the other sorbents by about 10%.

CONCLUSIONS :

Use of bagasse pith, rice straw, and rice hulls for the removal of oils and kerosene either present on solid surfaces or on the surface of bodies of waters was studied in pench-scale experiments. The tested materials are very light agricultural wastes available everywhere in Egypt at very low costs. The sorption abilities of these materials were tested under static conditions at ambient temperature and pressure. Conclusions from tests are as follows :

1) For spills of oils and kerosene on solid surfaces, the maximum sorption values reached per gram of bagasse pith are 5.5 and 3.7 grams respectively. About 50 percent reduction in the mass of oils sorbed is reported when treating oil spills on the surfaces of bodies of fresh water.
2) For rice straw and rice hulls, the maximum sorption values reached are less by about 10 percent than those reported for bagasse pith under the same test conditions.
3) For sorbent to oil mass ratios below 0.32, masses of oils sorbed by these sorbents from spills on sea water exceed those sorbed from spills on tap water by about 11%
4) Bagasse pith proves to be the most efficient sorbent followed by rice straw and rice hulls as indicated in Tables 2 and 3 and Figures 1,2 and 4. These materials proves to have a very rapid sorption rate as the maximum sorption values were reached after the lapse of 15 miunutes only.
5) For bagasse pith and rice straw, the quantity of liquid sorbed is primarily a function of liquid coefficient of surface tension and sorbent length (Fig. 3). Results obtained suggest that sorption of liquids by these materials appears to happen by capillary phenomenon.
6) Over 95 percent of spilled oils and kerosene can be removed by using the appropriate mass of sorbent. This mass is dependent upon the type of spilled liquid, the sorbent to be used, sorbent length, and working temperature as given in Tables 2 and 3.
7) Based on the sorption capacity of the tested materials and the current costs in Egypt, these materials appear to be both efficient and extremely economical. Bagasse pith proves to be the most cost effective for treating spills of oils and kerosene on solid surfaces or oils on the surfaces of bodies of water as given in Table 2.
8) Due to the ability of the tested materials to sorb water and oil simultaneously, oil emulsions can be removed by these materials. They provide promising tools for the removal of other waste substances which occur in practice in the

form of emulsions such as, used motor oils, cutting oils, drilling oils, vegetable and mineral oils, petroleum fractions, as well as machine oils, cylinder oils and lubricating oils. It should be kept in mind that the tested materials are still more efficient for removing any oily liquid or emulsion when present on solid surfaces.

Masses of materials needed to achieve about 95% removal given in Table 2 and 3 must be taken as a guide for use in practical situations. Although greater masses adds to handling and treatment expenses in addition to the lower heating values of the exhausted materials, the use of excess materials is recommended in order to increase the exhausted material handleability.

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Table (1): Effect of soaking time upon the sorption of water, kerosene, crude oil, and refined cotton-seed oil by bagasse pith, rice straw, and rice hulls.

Sorbent	Soaking time (min.)	5	10	15	20	30	45	60	24x60
	Liquid	Grams of liquid sorbed per gram of sorbent							
Bagasse pith*	Water	6.08	6.8	7.4	7.25	7.1	7.0	7.0	6.9
	Kerosene	3.1	3.5	3.75	3.65	3.7	3.65	3.6	3.55
	Crude oil	4.95	5.5	5.6	5.46	5.40	5.42	5.40	5.30
	Cotton-Seed oil	4.9	5.2	5.45	5.25	5.20	5.3	5.30	5.22
Rice Straw*	Water	4.8	5.0	5.4	5.25	5.3	5.25	5.2	5.1
	Kerosene	2.25	2.6	2.95	2.05	2.9	2.8	2.77	2.7
	Crude oil	4.65	4.75	5.1	4.95	4.8	4.9	2.76	4.75
	Cotton-seed oil	4.55	4.65	5.0	4.75	4.7	4.7	4.65	4.6
Rice hulls	Water	2.75	3.35	3.5	3.3	3.2	3.3	3.1	3.0
	Kerosene	2.9	3.4	3.65	3.5	3.4	3.4	3.25	3.1
	Crude oil	4.6	4.8	5.1	4.95	4.85	4.9	4.8	4.8
	Cotton-seed oil	4.5	4.53	4.85	4.7	4.7	4.65	4.65	4.58

* In these tests, lengths of bagasse pith and rice straw fibers were 0.05 m.

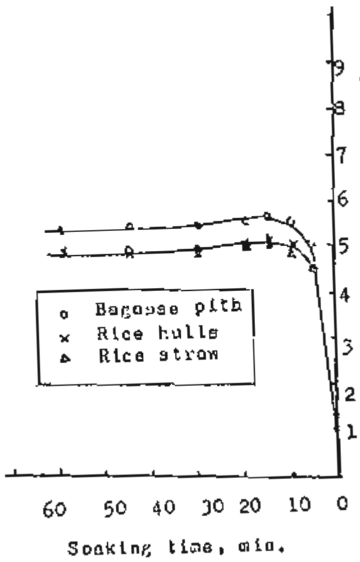

Figure (2) : Sorption of crude oil by he tested sorbents versus soaking time.

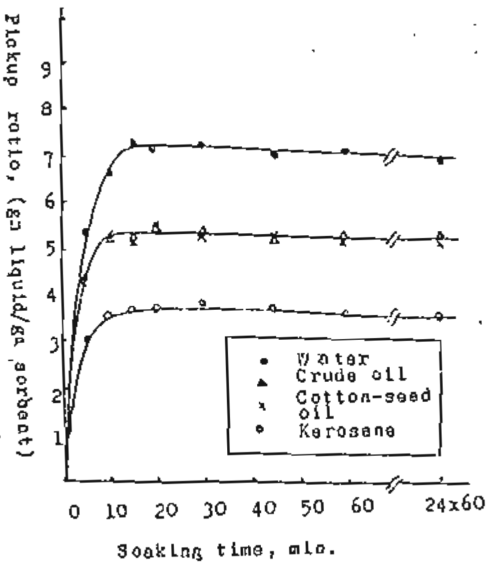

Figure (1): Pickup ratio versus soaking time for bagasse pith.

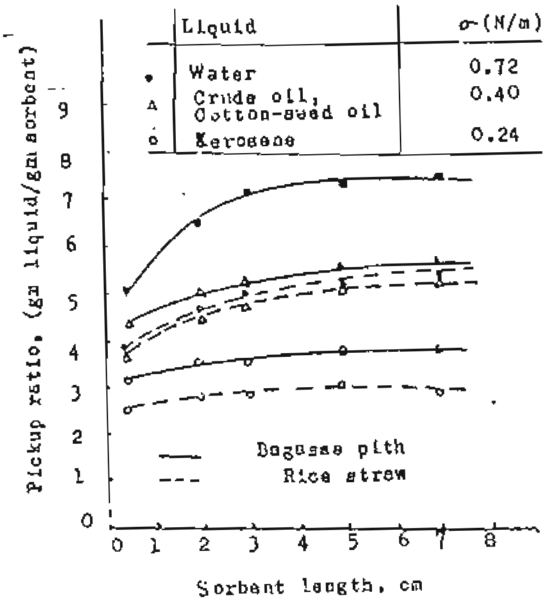

Figure (3): Sorbent length versus pickup ratio for the tested sorbents

Table (2): Pickup ratio and sorbent cost to achieve over 95% removal of spilled liquid.

Sorbent material	Pickup ratio to achieve over 95% spill removal						Unit cost sorbent (LE/ton)	Cost of sorbent for cleanup of 1m3 of spilled liquid		
	A		B		C			A	B	C
	1	2	1	2	1	2				
Bagasse pith	5.8	0.15	5.3	0.162	3.7	0.205	50*	7.5	8.25	10.25
Rice straw	5.2	0.168	4.75	0.17	2.54	0.30	200	33.6	34	60
Rice husks	5.0	0.175	4.6	0.175	2.35	0.32	150	26.25	26.25	48

- A- referrs to crude petroleum, B-referrs to refined cotton-seed oil , and C - referrs to kerosene.

-(1) referrs to pickup ratio as mass of liquid pickup per unit mass of sorbent and (2) referrs to the mass of sorbent(kg)per $1m^2$ areax0.001m

* This represents the cost of collection and transportation of this material as actually this material is available at almost no cost.

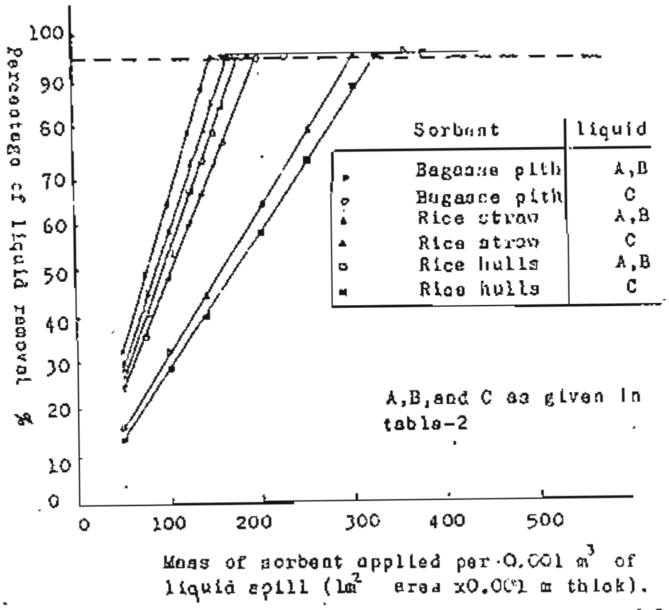

Figure (4): Percetage of oils and kerosene removal from their spills on solid surfaces versus the mass of applied sorbent.

Table (3) : Removal of oils from the surface water by bagasse pith and rice straw

m kg	mo (kg)	0.04					0.06					0.09					0.12				
	Sorbent	I	A		B		I	A		B		I	A		B		I	A		B	
			2	3	2	3		2	3	2	3		2	3	2	3		2	3	2	3
0.28	Rice straw	0.4	43.2	47.9	42	47	0.21	67.5	74.3	64.6	76	0.32	92	95	92.1	95	0.43	95.2	96.2	95.3	95.4
	Bagasse pith		49	52.4	47	52		75	82	71.9	79		95.3	96	95	96.1		96.1	96.2	95.2	95.8
0.4	Rice straw	0.1	33	37	31.2	34.6	0.15	45	51	44.3	51	0.23	73	80	69.7	80.8	0.3	87	93.3	88	97
	Bagasse pith		36.9	41.4	35	38.3		50	55	51	53		80	88	77	85		91.2	95	92	93.2
0.6	Rice straw	0.07	20.7	23	20.3	22.5	0.10	33.5	36	31.9	35	0.15	46	53	45	51.5	0.2	66.3	73.2	63	74.8
	Bagasse pith		23.1	25.8	23.3	25.2		36.6	42	33.8	40		50.3	54.6	52	52.7		74.5	81.0	69.6	77.3

- m = mass of oil, mo = mass of sorbent, A - data for crude oil,

B = data for cotton seed oil., 2 - data for tap water, 3- data for sea water, and I- denotes mass of sorbent/ mass of oil sorbed.