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Crude Oil Sorption from Polluted Waters by Locally Produced Materials

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Abstract

This paper covers the study of using local wood sawdust and polyurethane type polyester which is prepared locally and their capability as a sorbing substance for treating oil pollution of Iraqi waters. The study points directly to the high efficiency of the sorbing substance in treating the oil pollution due to the absence of its hazardous effects on the environment in addition to its economical values. Some of these materials are being extracted from the sorbant and the spilled oil. The paper, also, includes data about the effect of crude oil API gravity and that of temperature on the oil solubility in Iraqi waters plus the loading capacity and the efficiency of the sorbants. The paper stresses on the necessity of treating polluted waters during the early hours of oil leakage or spillage especially where the pollutants are light oils.

إزالة الملوثات النفطية من المياه باستخدام مواد متوفرة محليا"

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الخلاصة

تتضمن الورقة دراسة لاستخدام نشارة الخشب المحلي ورغوة البولي يوريثان نوع بولي استر المحضرة محليا" وقابليتهما كمواد ماصة في معالجة التلوث النفطي في المياه العراقية. تشير الدراسة الى الكفاءة العالية للمواد الماصة في معالجة التلوث النفطي وذلك لانعدام مخاطرها على البيئة إضافة إلـى

اقتصاديتها كون بعضها مسترجعة الاستخلاص لكل من المواد الماصة و النفط المتسرب. تضمنت الورقة بيانات عن تاثير كثافة النفط الخام بمقياس API ودرجة الحرارة على ذوبانية النفط الخام في المياه العراقية وسعة تحميل المواد الماصة وكفاءة استرجاعها. اكدت الورقة على وجوب البدء بمعالجة التلوث خلال الساعات الاولى من عملية التسرب خصوصا" عند التلوث بالنفوط الخفيفة.

Introduction

The problem of water pollution with oil and its products has had an increasing international concern because of the big importance that the watery environment represents to the living species including the human beings. This concern has been concentrated on water pollution due to the increasing progress of oil industries and the increasing numbers of oil refineries and petroleum factories. As a result, oil accidents and spillages lead to hazardous effects and harm to water resources and the worsening of water quality, hence the appearance of unnatural symptoms on the water life (Quiterno & Diaz 1994, UNEP 1993). The accidents occurring to oil tankers or oil well explosions below water surface are considered to be the main causes of oil pollution. But this represents only 10% of the total oily leakage into the international waters, where the operations of oil tankers loading and discharging constitute about 47% (Ali, 1987). The possibility of polluting the Iraqi territorial waters by the oily pollutants can take place indeed, for a number of cases has been recorded and appeared in both river and sea waters (Talal, 1999). The excessive refinery products and greasy rejects into industrial waters from the refining units in addition to the regular cleaning operations of oil tankers and deposits removal, and oil discharge from the oil loading / off loading terminals are considered to be the main sources of polluting Iraqi waters with oil and its products (Bediar & Al-Saad,1992).

The leaked crude oil spreads at a fast rate on the surface of water forming a thin film of about 0.01 inch thickness that covers an area of about 25 square miles within about 8 hours of time (Shell, 1981). Then emulsions form rather quickly after the oil leakage and, in fact, there are two types: i.e. oil in water emulsion where water is the continuous phase and this type breaks up the oily specks and makes them sink below the water surface.

Whereas, the second type is the water in oil emulsion, in which oil is the continuous phase and has a very high consistency and remains afloat on the water surface. This emulsion, usually, stays a few weeks on top of the water surface without disintegrating. It is, here; that the need arises in taking the important decision of removing the possible amount of spilled oil as soon as possible by the use of different means. Such means may include mechanical methods such as floating booms that encircle the oil patches or chemical ways and chemical substances to transform oil into a gel - like matter through the use of dispersants or sorbents. Oily specks are sprayed by materials that have the capability of adsorbing oil and then collected with the adsorbed oil for the purpose of recovering oil and drying the sorbent and render them ready for further use. It was found that some natural materials have the capacity to absorb about ten times its weight of oil (Ali 1987). Such materials include volcanic ash, cellulose wood fibers, and some synthetic polymeric materials like polyurethane foam and urea formaldehyde. In spite of the fact that data indicate the necessity to deal with huge quantities of polluted matter it is, nevertheless, considered one of the best means and less hazardous to the environment. In addition to its economic role where both the sorbents and crude oil can be recovered successfully .The present study is concerned with the use of the locally available wood sawdust and the locally produced polyurethane foam, type polyester, to face the present and future cases of oil pollution and show their feasible application in the Iraqi rivers and estuaries.

Theoretical aspects:

Among the important parameters required for better understanding of the fate of oil in the marine environment is the solubility of oil in water. Hamam et al (1988) confirmed that the dissolution of oil is diffusion controlled. All the correlations available that might be used in estimating diffusion of crude oils in water require parameters which have to be obtained through crude characterization in the laboratory. For the sake of

simplicity the diffusion coefficient, D, is assumed constant since the solution is dilute, hence the differential equation for diffusivities is:

$$dC/dt = D\,(d^2C/dx^2) \quad (1)$$

This can be integrated for large time interval to give:

$$\ln\{1-(C/C_0)\} = \ln 4/\pi + \ln\{\sin(x/2L)\} - (\pi/2L)^2\,Dt \quad (2)$$

An attempt was made to correlate the diffusion coefficient as a function of API, temperature and salinity (Hamam et al 1988). The proposed equation is:

$$D=3.20*10^{-4}\,(API)^{0.67}\,(T)^{1.62}\,e^{1/2} \quad (3)$$

The sorption capacity was often presented in terms of the percent absorption Q of the liquid at time t:

$$Q=(M_t-M_o)/M_o \quad (4)$$

The following relationship has been presented from an analysis of the results of a number of studies on sorption phenomena through the polyurethane foams (Aithal et al 1989):

$$M_t/M_{oo} = kt^n \quad (5)$$

Where k is a constant, which depends on the structural characteristics of the network, and the exponent n depends on the nature of diffusion process.

Experimental work

Crude oil of different API samples were supplied from Nehran Omer laboratories. Polyurethane foams were supplied as cubes with uniform volumes from the national company for plastic industries. An uncovered glass jar of 3-liters capacity and a diameter of 14.8 cm was used. Samples of crude oil of different API ranging from 10 to 30 were studied at temperatures of 20 and 40 C. These ranges would be of an interest to oil pollution problems in Iraqi waters. In each experiment 2 liters of water and 250 ml of an oil sample was placed in the jar; and the jar and its contents

were placed in a thermostatic bath which was controlled at the preset temperature to ± 0.5 C.

In the experiments of oil solubility determination, the test jar was equipped with an electrical stirrer .The stirrer rotation has been chosen so that the interface was generated solely and no oil droplets were dispersed in the oil layer. Water samples of 10 ml each were taken at different time intervals using a hypodermic syringe placed at a fixed distance. The collected samples were analyzed using oil analyzer and pure carbon tetrachloride was used to extract the dissolved portion of the oil. In all measurements, samples were taken and promptly analyzed until a constant concentration value was obtained.

The sorption experiments were performed by submerging polyurethane cubes in the test jar. The dry weights of polyurethane cubes were taken before immersing them into the jar. The samples were periodically removed from the test jar ,the wet surfaces of the cube were dried between filter paper and weighed immediately to the nearest + 0.1 g .The cubes were placed back immediately into the test jar and the experiments were carried out in progress. The experiments were repeated at the same conditions using wood sawdust and the same procedure was followed.

Results and Discussion

For the purpose of obtaining the optimum benefit from the performance of these materials and achieving the most efficient control process, the treatment operation should start as soon as Shatt-el-Arab waters are polluted, see Fig. (1). This is because of the high solubility of crude oil in Shatt-el-Arab waters compared with that in the Arabian Gulf waters. The reason for this is attributed to the existence of marl clays and silts which lead to the formation of soluble petroleum emulsions in these waters. A considerable increase of light oils solubility has been noted especially at the first ten hours of oil spillage as shown in Fig.2. This means, taking the

quality of leaked oil into account and then accelerating the removal process when light oils pollution takes place

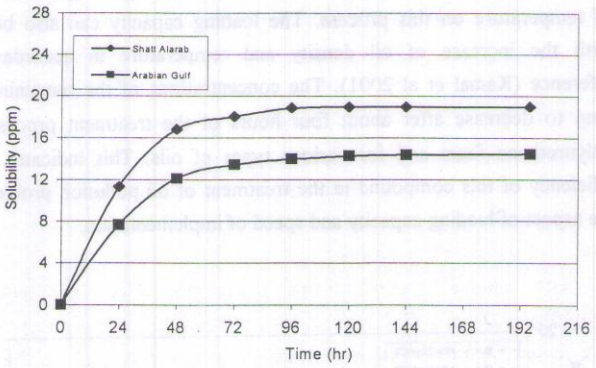

Fig.(1)Crude oil solubility in Iraqi waters

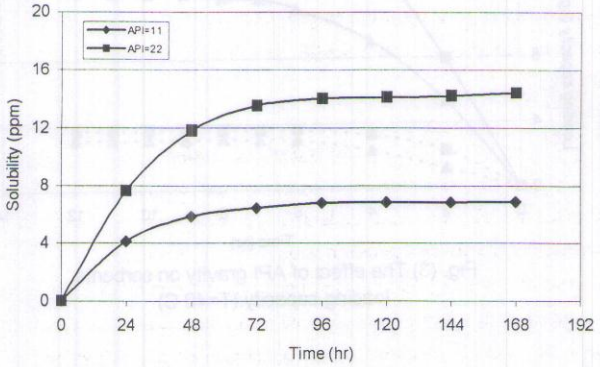

Fig.(2)The effect of API gravity on crude oil solubility.(T=40 C)

Figs. (3) and (4) demonstrate the sorption efficiency of polyurethane foam (PU) and wood sawdust (WD) calculated on the basis of the weight of oil absorbed per kilogram of the sorbent and the effect per degree API and that of temperature on this process. The loading capacity can also be noticed with the increase of oil density and temperature in accordance with reference (Kamal et al 2001). The concentrations of the remaining oil are seen to decrease after about four hours of the treatment process by the polyurethane foam and for various types of oils. This indicates the high efficiency of this compound in the treatment of oil pollution problems from the aspect of loading capacity and speed of implementation.

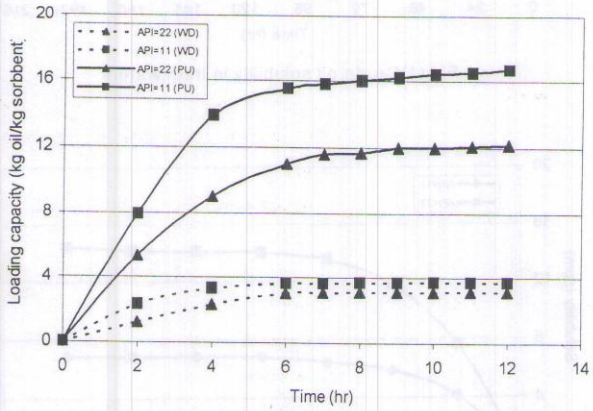

Fig. (3) The effect of API gravity on sorbents loading capacity.(T=40 C)

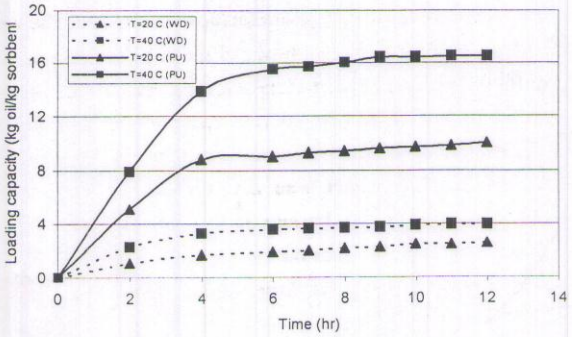

Fig. (4) The effect of temperature on sorbents loading capacity .(API=11)

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