Remediation of Lubricating Oil Waste using Biogenic Silica Granules

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Abstract — Small spills of oils and similar liquid hydrocarbons (such as lubricating oils, fuel oils, cooking oils, and radiator coolants) occur from time to time in workshops, industrial processes, domestic and farming activities. Such spills are sometimes collected using sand, sawdust, 'kitty litter' and similar materials which have limited absorbent capacity, low biodegradability and perform poorly if they become wet, often releasing much of the absorbed pollutants. They also leach downward and contaminate the groundwater if disposed onto soil surface. Recently, specialized biogenic products have been developed which provide a greater absorption and retention capacity than conventional granular materials. These natural based absorbent materials are preferred due to their non-toxicity, excellent biodegradability and non-flammability. Agro-industrial residues are also being used by researchers to produce a new absorbent product which is able to remove toxic elements. The biogenic modified silica produced in aqueous media from rice husk ash has shown excellent sorption. The experimental studies were carried out to study the leaching characteristics at various depths of the soil layers, time intervals and variation in oil- biogenic silica compositions on its sorbent capacity. Also the effect of the oil-laden silica on soil properties was also evaluated. A comparison of these effects with oil-laden sawdust was also carried out.

Keywords: Biogenic silica; Absorption; Waste lubricating oil; Oil-laden silica.

I. Introduction

Often, the oil pollution problems associated with impacts on sea and coastal land environments have been emphasized. This is because marine spillages affect a larger area and they also receive a lot of attention from the public and the media. Very little importance is given to minor spillages of oils and similar liquid hydrocarbons such as lubricating oils, fuel oils, cooking oils, and radiator coolants which occur in workshops, during industrial processes, and domestic and farming activities and which are far more complicated, unpredictable and constitute the vast majority of oil spills in many countries[10]. such spills are mostly collected using sand, sawdust, kitty litter, and similar absorbent materials[7]. however, these materials have limited absorption capacity, high risk of inflammability, low biodegradability and perform poorly if they become wet, often releasing much of the oil and causing it to leach downward and contaminate the groundwater sources once disposed onto soil surface .recently specialised biogenic absorbents have been developed which are biodegradable, non- leaching, non-inflammable and have higher absorption- retention capacity. The MAKSORB™ biogenic silica granules is such a product which is being used in removal of such minor spills. The disposal of the spill collected using such absorbents is another major task. In most cases, since the liquid spilled and absorbed is of small quantity, they are either send for landfilling or are simply thrown onto the land area near to the source of waste generation. This may cause casualties like contamination of surface waters caused by surface runoff during rainy season and deterioration of top soil cover. Hence the development of a feasible, cost-effective, environmentally sound and sustainable method of disposal is essential.

The present paper aims to carry out the initial characterization tests for both the MAKSORB™ biogenic silica granules and the waste lubricating oil as a part of evaluation of environmental friendliness of the MAKSORBTM biogenic silica method for removal of waste oil. The study aims to evaluate the environmental friendliness of the biogenic silica absorption method for removal of used lubricating oil from the environment by evaluating effects of oil-laden silica disposal on the soil surface with respect to the depth of leaching, time, and change in composition. The present work also evaluates the oil sorption capacity of the silica granules and how its efficiency is influenced by oil volume, time, and absorbent weight for used oil clean-up. The study aims to evaluate the effects of the oil absorbent mixture on soil properties and also on the growth properties of the fenugreek plant. Also a comparison of the same with oil sawdust mixture, oil contaminated soil and normal soil was also carried out.

II. Materials and Methods

A. Collection of Materials

The experiment was carried out in the terrace area of the Department of Civil Engineering, Sinhgad College of Engineering , Vadagaon (Bk.), Pune. The soil taken was black cotton soil obtained from a construction site near to the college. The soil was sieved through 4.75mm sieve, was thoroughly mixed and air-dried for a day. Used lubricating oil was obtained from a Two- wheeler repair facility in Ambegaon, Pune. The MAKSORB™ biogenic silica sorbent granules was provided by BIO CARE (INDIA) Pvt. Ltd., Nagpur. The Fenugreek seeds were obtained from a Plant nursery in Nanded City, Pune. The viable seeds were determined using floatation test.

B. Characterization of Oil

Characterization of the oil used for the study is shown in Table 1. The moisture content of the oil was found by the simple oven drying method. Boiling point of the waste engine oil was determined by Thiele's tube method. The viscosity of the waste oil was determined using redwood viscometer apparatus. The carbon, nitrogen, hydrogen content in oil was analyzed using Perkin Elmer 2400 Series II CHN analyzer.

C. Charaterization of Sorbent Material

For characterization studies it was subjected to FESEM JEOL-JSM 7500F to understand the particle size and EDX for elemental analysis of the biogenic silica. The scanning by FTIR Perkin Elmer Spectrum 100 FTIR further reveals the active surface functional groups of the sorbent material. The XRD analysis was done to find the crystalline patterns of the material.

D. Oil Sorption Capacity

For the oil sorption capacity the effect of varying oil volume on the oil sorption capacity was studied by keeping the weight of absorbent constant and the effect of varying weight of the absorbent (biogenic silica granules) on the oil sorption capacity was studied by keeping the oil volume constant and further finding the relationship between time consumed and of each sample, the silica granules were immersed in pure oil and subsequently stirred for 10 minutes. After stirring, the oil-containing sample was placed on top of the SUS wire mesh until no oil droplets were observed to fall for a period of 15 min. The mass of the oil-containing sample was then measured (11).The test was repeated three times in order to obtain the average values. The oil sorption of the sample was evaluated by weighing the samples before and after the absorption.The oil sorption capacity of the sample was calculated using the formula (3):

E. Leaching Characteristics

In the present work the leaching characteristics was monitored at various depths of 6.5 cm, 10 cm, 14 cm, 17 cm and 20.5 cm of the soil layers for time intervals 1st to 4th week. The samples were analysed using FTIR technique for checking oil contamination.

F. Experimental Setup for Determining Effects on Soil Properties

For the experiment, five plastic pots were filled with 1kg soil each. Soil in each pot was mixed with 5% oil laden silica, 5%oil laden sawdust, 5% used oil, 0.5 % used oil and 0% used oil respectively. The pot containing 0% used oil acted as control. Equal number of seeds were sowed in all the pots at the same time. Top soil samples were collected from all the five pots before sowing, at 30^{th} day and 60^{th} day in labelled polythene bags and sealed. The samples were stored in laboratory refrigerator until analyses were made[2]. Survival counts were taken per pot at 60^{th} day and the percentage survival was calculated by the formula:

$$\frac{No:of\ plants\ that\ survived}{No:\ plants\ germinated}\times 100$$

At maturity, other growth parameters were measured including number of leaves, length of leaf and length of stem[1].

III. Result and Discussion

A. Characterization of Sorbent Material

a) The SEM micrograph as shown in Figure 1 reveal that the biogenic silica MAKSORBTM has particle size varying between 1.6 μm to 2.86 μm with a porous structure which is responsible for aiding the sorption of oil sample.

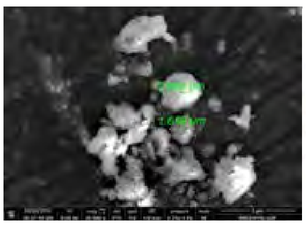

Fig. 1. SEM if biogenic silica

b) EDX studies done on the sample showed 50% of Si, 42% of O with minor amounts of C, Al, Na, Ca. as shown in Figure 2.

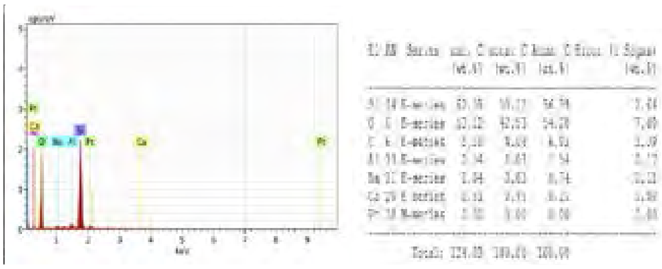

Fig. 2. EDX of biogenic silica MAKSORB™

*c)*Figure 3(a) shows FTIR spectra for biogenic silica and the studies reveal peaks at 1076 cm^{-1}, 460.79 cm^{-1}, 790.08 cm^{-1} indicating presence of □as(Si-O-Si) and □s(Si-O-Si) bonds respectively. Figure 3(b) shows FTIR for used oil. The peaks

obtained at 2920.53 cm-1, 2852.62 cm-1 and 1458.95 cm-1 indicate presence of methylene (C-H), bonds at 1740.74 cm-1

indicate aldehyde and ester groups, while at 1373.41 cm-1 indicate aliphatic nitro groups and at 1223.04 indicate presence of C-C bonds. Figure 3(c) shows FTIR for oil and absorbent.

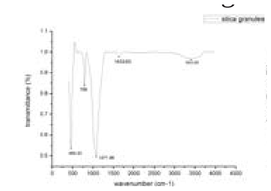

Fig. 3(a). FTIR of biogenic silica

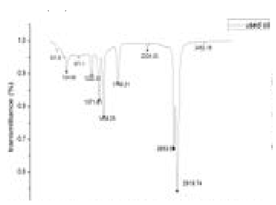

Fig. 3(b). FTIR of used oil

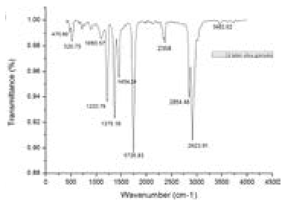

Fig. 3(c). FTIR oil + absorbent

d) XRD pattern of the biogenic silica is shown in Figure 4. The analysis depicts peaks at 2θ values of 20° and 35° respectively in the crystalline pattern characteristic of amorphous SiO2 (12).

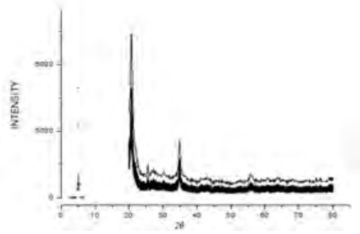

Fig. 4. XRD pattern of biogenic silica

B. Characterization of Lubricating Oil

The CHN analyzer shows that the used oil contains about 85%carbon, 13% hydrogen and only 2% of nitrogen.

Sl. No	Parameters analyzed	Value
1.	Moisture content	2.16%
2.	Specific gravity	0.877
3.	Boiling point	200°C
4.	Kinematic viscosity (31°C)	0.261 stokes
5	Flash point	184°C

The characteristics of the used oil under study are enlisted in Table 1 below:

Table I: Characteristics of used Oil

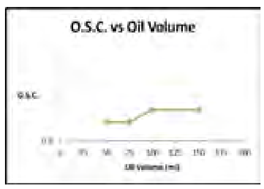

Fig. 9. CHNS Elemental analysis of used oil

C. Oil sorption Capacity

a) The effect of oil volume on the oil sorption capacity was studied by keeping the weight of absorbent constant for varying oil volumes from 50ml to 150ml .From the Figure 5 (a), it is evident that for a constant weight of absorbent, increase in volume of oil does not bring significant deviation in its Oil Sorption Capacity (O.S.C.)

b) The effect of weight of the absorbent on the oil sorption capacity by keeping the oil volume constant for varying absorbent weights from 5g to 50 g. It is observed in Figure 5 (b) that for a constant volume of oil, the O.S.C. is found to be highest for 10 g of absorbent and as the weight increased the O.S.C. was found to decrease. This observation can be correlated to the effect of packing density on oil sorption capacity as reported earlier (13).

c) Relationship between the time consumed and oil sorption capacity as shown in Figure 5 (c) clearly indicates that the oil sorption capacity of the absorbent decreases with passage of time. However beyond one hour, the O.S.C remains constant and no further decrease was observed. The O.S.C. was found be the highest of 0.96 g/g, after 15 min and decreased upto 75 minutes to a value of 0.8 g/g and remained constant after this time.

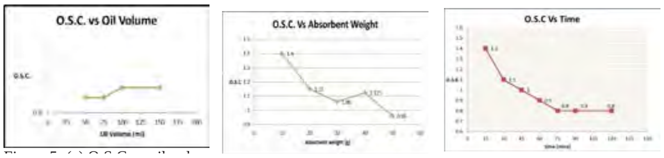

Fig. 5. (a) O.S.C vs oil volume (b) O.S.C vs absorbent weight (c) O.S.C vs time consumed

D) Leaching Characteristic of the Oil Sorbent Mixture

The leaching characteristics was observed at varying depths of 6.5 cm, 10 cm, 14 cm, 17cm and 20.5 cm of the soil layers in the experimental set-up. The samples were withdrawn at time intervals 1st - 4th week to study its sorbent capacity. The results obtained are as shown in Figure 6(a) and 6(b). In the oil sample leaching was observed but not in case of oil biogenic silica mixture.

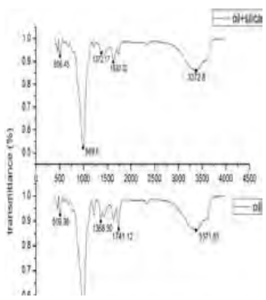

Fig. 6(a). week 1 scenario on both sides

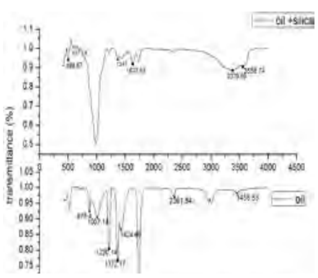

Fig 6. (b). week4 scenario on both sides

Analysing the growth and yield parameters, it can be seen that that plants grown in oil-laden silica and soil mixture survived the extreme summer climate compared to those grown in oil-laden sawdust and soil mixture. It can be also seen that more number of plants survived in silica mixture compare to those grown in control soil as well. This indicates that the absorbent, alongwith holding oil, also forms bonds with water molecules holding it for a longer time, thus resulting in greater yield.It can also be be noticed that there high yield in plants growing in 0.5 % oil contaminated soil. It can also be seen that only 6% of plants grown in oil laden sawdust and soil mixture survived compared to the 82% in oil laden silica and soil mixture. The growth and yield parameters are shown in Table 2.

Table II. Growth and Yield Parameters of Fenugreek After 2 Months of Treatments

Sl No	Type of Mixture	% Survival	Stem length (cm)	Root length (cm)	Number of leaves (for the largest plant survived)
1	5%(oil laden sawdust) +soil	6	2	6.5	1
2	5%(oil laden silica) +soil	82	4.1	12	8
3	5% oil + soil	42	2.2	9.5	3
4	0.5% oil +soil	41	4	10	6
5	0% oil +soil	50	4.3	9.5	11

IV. Conclusions

The present work focuses on the use of biogenic silica granules MAKSORB^{TM} as a potential oil scavenger for cleanup of used lubricating oil. The results show that the oil absorption capacity of the material does not significantly vary with oil volume but decreased with increase in absorbent weight beyond 10g in 100 ml and decreased with time till a saturation level is reached. The leaching characteristics show it to be environmental friendly and economical. The entire life cycle of the biogenic silica needs to be evaluated in due course of time. The study shows that the oil laden silica has higher water retaining capacity which enhance the yield of plant. Studies to evaluate the biological properties of plants grown in oil silica mixture could also be carried out in future

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