PREPARATION OF OLEOPHILIC PERLITE BY POLYMER ENCAPSULATION

by

DURATA BAYRAKTAR

B.S. in Chem., Boğaziçi University, 1982

Submitted to the Institute for Graduate Studies
in Science and Engineering in partial Fulfillment
of the requirements for the degree of
Master of Science
in
Chemistry

Boğaziçi University

1985

PREPARATION OF OLEOPHILIC PERLITE BY

POLYMER ENCAPSULATION

APPROVED BY :

Doç.Dr.Selim KÜSEFOĞLU ______________
(Thesis Supervisor)

Doç.Dr.Haluk ARICAN ______________

Doç.Dr.Salih DİNÇER ______________

Y.Doç.Dr.İbrahim YILMAZ ______________
(Yedek Üye)

Date of Approval : 4.2.1985

ACKNOWLEDGEMENT

This is a welcome opportunity for me to express my sincere gratitude to Doç.Dr.Selim Küsefoğlu for his suggestion of this research problem, his guidance and encouragement throughout this work.

I wish to thank Doç.Dr.Salih Dinçer, Doç.Dr.Haluk Arıcan and Y.Doç. Dr.İbrahim Yılmaz for their advice and criticisms.

I would also like to thank all members of the Chemistry Department who were always helpful and understanding.

Last but not least I want to express my gratitude to my mother without whom this work could have never been completed and to whom I dedicate this work.

ABSTRACT

A new oil adsorbing material was synthezised using expanded perlite. To render perlite oleophilic and hydrophobic it was coated with a suitable hydrocarbon polymer. Perlite was first size classified to assure uniformity and purified from metallic oxide impurities by floatation in ether. After evaporation of adsorbed atmospheric water it was coated using different polymers and different methods. Four substances were chosen for coating: paraffin, polystyrene, high molecular weight polyethylene and low molecular weight polyethylene. These substances were solvent deposited on perlite using appropriate solvents at suitable temperatures and the solvent was subsequently evaporated. Paraffin due to its volatility could be vapor deposited on perlite under vacuum without the use of solvent. Both paraffin and low molecular weight polyethylene were melt deposited on perlite because of their low melting temperatures. Using these techniques samples with various levels of coating of each material were obtained.

These samples were then tested for their oil and water adsorption capability. Further they were compared among themselves with respect to oil adsorption and cost to choose the best adsorbent. A coating method was also chosen to optimize cost and ease of manufacture using the adsorbent with the highest oil adsorption capacity. Reproducility of

the above experiments was tested to calculate accuracy and precision of the work performed.

The best adsorbent was found to be the 48 % low molecular weight polyethylene coated perlite obtained by the melt deposition method. The solid material thus prepared adsorbs 7.4 times its weight in liquid oil, no water, and costs about 108 TL/ Kg. Finally the capacity of the 48 % low molecular weight polyethylene coated perlite for hydrocarbon vapor adsorption was tested by passing n-heptane saturated air through it. The material adsorbed about one to two times its weight in gaseous hydrocarbon.

The results were as expected : coating perlite with hydrocarbon-like polymers considerably decreased its water affinity and increased tremendously its oil adsorption capacity.

This new material can be used as an efficient sorbent for adsorbing oil and other non-polar organic substances from water surfaces and city water, as well as hydrocarbon vapors from flue gases. It can probably be used in any field requiring oil or non-polar substance removal.

ÖZET

Bu çalışmada, genleşmiş perliti uygun hidrokarbon polimerlerle kaplayarak oleofilik ve hidrofobik bir yağ absorblayıcı malzeme sentez edilmiştir. Perlit önce parçacık büyüklüğü uygunluğu sağlamak için elekle klasifiye edilmiş, sonra metal oksitlerden arındırılmak için eterde yüzdürülmüştür ve kurutulmuştur. Daha sonra değişik yöntemler kullanılarak değişik polimerlerle kaplanmıştır. Seçilen kaplama malzemeleri parafin, polistiren, alçak moleküler ağırlıklı polietilen ve yüksek moleküler ağırlıklı polietilendir. Bu maddeler uygun çözücülerle çözülmüş ve perlit parçacıkları üzerine kaplanmış, çözücü daha sonra uçurularak polimer kaplı perlit elde edilmiştir. Parafin uçucu olduğundan çözücü kullanmaksızın buhar halinde vakum altında perlite tatbik edilebilmiştir. Hem parafin, hem alçak moleküler ağırlıklı polietilen erime sıcaklıklarının düşük olması dolayısıyla eriyik halde perlite tatbik edilebilmişlerdir. Bu yöntemlerle değişik miktarlarda polimer kaplanmış perlit örnekleri elde edilmiştir.

Bu örnekler daha sonra su ve yağ absorblama özellikleri açısından incelenmişlerdir. Elde edilen örnekler maliyet fiyatı açısından da en iyi kaplama yüzdesini bulmak üzere testlere tabii tutulmuşlardır. Bulunan en iyi polimer için büyük miktarda üretimde kolaylık ve ucuzluk açısından en iyi kaplama metodu incelenmiştir. Elde edilen sonuçların tekrarlanabilirliğini ve doğruluğunu sağlamak için değişik test

yöntemleri defalarca tekrarlanmıştır.

En iyi absorblayıcı olarak eriyik kaplama yöntemiyle hazırlanmış ; %48 nisbetinde alçak moleküler ağırlıklı polietilen kaplanmış perlit bulunmuştur. Bu yöntemle elde edilen katı madde ağırlığının 7,4 misli sıvı yağ tutmakta, hiç su tutmamakta ve 108 TL/kg bir hammadde fiyatına sahip olmaktadır. Son olarak bu çalışmada % 48 nisbetinde alçak moleküler ağırlıklı polietilen kaplanmış perlitin gaz fazında hidrokarbon absorblaması ölçülmüş ve bu örneğin içinden n-heptan doyurulmuş hava geçirilerek ağırlığının 1,2 misli n-heptan absorbladığı saptanmıştır.

Bütün bu deneylerden beklendiği gibi şu sonuç elde edilmektedir: Perlitin hidrokarbonla kaplanması su absorbsiyonunu azaltmakta, yağ absorbsiyonunu ise çok çok artırmaktadır. Elde edilen bu yeni materyalin yağ ve hidrokarbonlar için çok iyi bir absorban olduğu, deniz ve göl yüzeylerinden, şehir suyundan, baca gazlarından ve su buharından yağ almakta kullanılabileceği meydana çıkmıştır.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

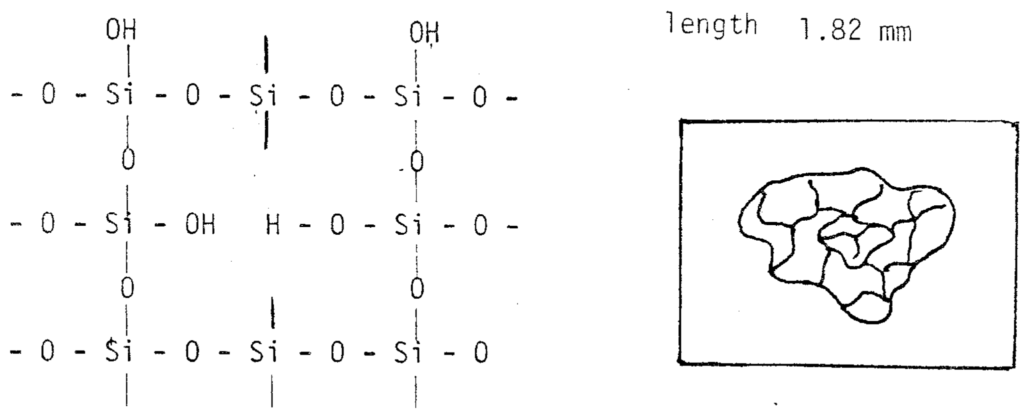
I.1 PERLITE

Perlite is a natural glass of volcanic origin similar to mica and obsidian. It is characterized by its high silica content and is also known as vermiculite (1). The reserves of perlite in Turkey are estimated to reach 8000 million tons (2). It is mainly mined in Cumaovası, İzmir. This mineral is also found in Japan and in a belt ranging from Iceland to Ireland comprising France, Italy and the Aegean Islands. In the United States it is mined in the Western mountains, and the Trans - Carpathian region in the Soviet Union (3). Perlite is mined from open pit, crushed to 1.6 cm and sized. Then it is heated in horizontal or vertical rotary kilns to around 1173 - 1473 ^{o}K, temperature at which perlite expands and forms a frothy mass. The foam obtained is of closed cell structure. The formation of siloxane linkages releases water with enough vapor pressure to expand the molten silica structure to produce a foam, which, upon cooling solidifies to a brittle closed cell foam with exceptionally high specific surface (2). (Fig. I.1.1).

The expansion depends on the composition of the ore : it increases with Al_2O_3 content but decreases with K_2O and SiO_2 content (4).

Perlite is a word used for both the mineral and its expanded form.

To avoid confusion, the word perlite will indicate only expanded perlite throughout this work.



Molecular level Microscopic level

Fig I.1.1. Structure of perlite

I.2 PROPERTIES OF PERLITE

Unexpanded perlite is greyish in colour. It shows concentric shelly structure and has a pearly lustre attributed to reflections from the thin air films formed along the concentric cracks Some of its characteristics are listed below (1):

Specific Gravity	2.2 - 2.4 g/cm^3
Hardness	5.5 - 7.0 on Moh's Scale
Crystalline Substances	3 - 10 %

The chemical composition of the mineral is listed below although it may differ depending on the ore (2).

SiO_2	71 - 75 %
Al_2O_3	12.5 - 18
Na_2O	2.9 - 4
K_2O	4 - 5
CaO	0.5 - 2

Fe_2O_3	0.5 - 1.5
MgO	0.1 - 0.5
Ti_2O	0.03 - 0.2
MnO_2	0.03 - 0.1
SO_3	0 - 0.2
FeO	0 - 0.1
BaO	0 - 0.05
PbO	0 - 0.03
H_2O	2 - 6

The water mentioned in the list is the "free water" loosely bound to the silicate. Expansion is due to "tightly" bound water and expansion ratio depends on its amount (2). Below are listed the temperatures at which different types of water are lost.

Temp °K	Type of water
623-723	Free water
873	Tightly bound water
above 873	Tightly bound water plus CO_2 from decomposition of carbonates.

I.3 USES OF PERLITE

Prior to 1950 perlite was virtually unknown in commerce. It was not until the second - half of this century that it became of widespread use. It is mainly used as agricultural aid, fertilizer extender, filter for drinking and waste waters (5). It is also of expanding use in the building industry; as a fire - resistant insulator (6) or as polymer - perlite composite in lightweight mortars and concrete (2.7) ; low voltage eletro-porcelain raw material (8); and as raw material for the preparation of white pigment (9). Perlite has also been used as petroleum - oil spill remover in different combinations (10).

I.4 PERLITE AS AN OIL SPILL REMOVER

Cleaning up an oil comtaminated area is time consuming, difficult and costly . Many methods have been developed for minimizing contamination of water surfaces. Although there is no completely effective method for dealing with oil spills, the most widely used methods are sorbent surface devices (10), and the physical chemical treatment of oil polluted water (5,11). Sorbent surface devices use a surface to which oil can stick and from which it can be collected afterwards. The Centri - Spray Device, developed by the Centri - Spray Corporation (10) Fig.I.4.1 consists of a belt skimmer driven by a motor. As the belt rotates the oil is scraped off by wipers below the top pulley into a trough where it is screened and dumped into steam heated tanks.

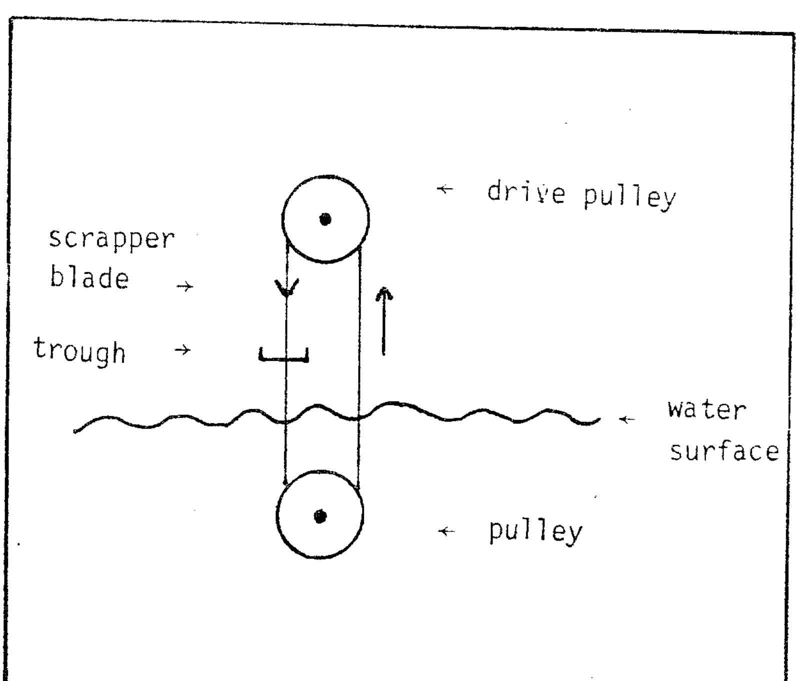


Fig. I.4.1 The Centri - Spray Device

A less sophisticated and ecologically viable alternative consists in the use of solid sorbents. Volcanic pyroclastic rock (slag) has been used (12) as well as aluminosilicates coated liquid glass (13).

Being relatively inexpensive, and non - toxic and having a large specific surface, perlite has been used in the synthesis of sorbing materials. In one research, a blend of 100 parts polyethylene and 50 parts perlite was passed through the conveyer belt of a roll. The sheet thus formed was heated to obtain an oil binding foam (14). No quantitative data is given.

Muntzer succeeded in preparing an oleophilic substance useful for removal of floating oil from water at the five fold of its own weight by mixing perlite, chromic sulfate, water and bitumen. The mix was homogenized, dried and heated with agitation. After use, the activated perlite could be removed from water, burnt and used again as an oil binder (15).

Another sorbent was synthesized by mixing perlite, clay, cellulose and asphalt. It was reported to absorb 7.5 - 12.5 l.petroleum/l (16).

In Funck's work, 66 - 78 % perlite was mixed with 17 - 29 % cellulose fibers and 0.5 - 6 % asphalt. The product could absorb 83 - 95 l.oil / 8.1 Kg. sorbent from a water surface (17).

In another research a mixture was manufactured by blending perlite with paraffin at 200 - 300 C at the ratio 1 to 0.01. It was reported that about 10 Kg of the material could nearly completely remove 5 Kg heavy oil on a 100 m^2 pond (18).

In a different work perlite expanded by heating at 980 C was waterproofed by treatment with aqueous sodium methyl siliconate.

One gram of such perlite could absorb 8 grams petroleum. The rate of absorbtion was markedly faster if applied from below the surface (19).

Perlite could also be rendered oleophilic by treatment with the Methyl silicone Sodium salt. The presence of Aluminium powder greatly increases the efficiency of the reaction of Me silicone with perlite. The adsorbed hydrocarbons may be recovered my mechanical means (20). All of the above mentioned sorbents aim to fulfil the desired characteristics required in an efficent oil adsorbing material.
These characteristics are (10,21):

a) Oleophilicity

b) Hydrophobicity

c) High Adsorbtivity

d) Retention of oil, leakage should be minimum

e) Buoyancy under all conditions

f) Ease of recovery of oil after adsorption

g) Physical form of the adsorbent for ease of storage and transportation

h) Low Cost

Many sorbents however do not have all of these desired characteristics. Some polyurethane foams cannot absorb oil when pre-wetted with water. That is they can be used only under calm weather conditions to remove oil from water surfaces (22). Polyester plastic shavings have a high unit cost, about 100 $ per ton of absorbent. Cheaper sorbents like straw show buoyancy problems, they sink after adsorbing oil if let in contact with water for a long time (10).

Perlite containing sorbents on the other hand not only have all the desired characteristics but are also non-toxic, non-flammable or fire sustaining. Thus, from both academic and economical points of view it would be worthwhile to take advantage of perlite' properties and synthesize new adsorbents by coating perlite with suitable hydrocarbon polymers to render it oleophilic.

II. STATEMENT OF THE RESEARCH PROBLEM

The aim of this work was to synthesize a hydrophobic, oleophilic polymer coated perlite with a potential for oil removal from water surfaces. To accomplish this, perlite was coated with the following substances to render it oil adsorbing:

a) Paraffin

b) Polystyrene

c) High molecular weight polyethylene

d) Low molecular weight polyethylene

Prior to coating the following operations were to be carried on perlite to avoid errors in calculations:

a) Classification of the grain size of perlite

b) Purification

c) Evaporation of external water

The coating methods used were the following:

a) Solvent Deposition

b) Vapor Deposition

c) Melt Deposition

The obtained samples were then investigated for the following properties:

a) Oil adsorption capability

b) Water adsorption capability

c) Hydrocarbon vapor adsorption capability

d) Coating material distribution on the surface of perlite particles

The following points were also investigated:

a) Choosing the best adsorbent with regard to cost and oil adsorption capability.

b) Choosing the best coating method to optimize the cost and synthesis of the best adsorbent.

In summary, this project aims to :

a) Synthesize an efficient oil adsorbent out of perlite

b) Examine the properties of the new material and obtain quantitativ data.

c) Choose the best adsorbent and coating method with regard to efficiency and cost.

III. RESULTS AND DISCUSSION

3.1 PREPARATION OF THE SAMPLES

Coated perlite was prepared by solvent deposition, vapor deposition and melt deposition methods.

3.1.1 SOLVENT DEPOSITION METHOD

Samples were obtained by dipping perlite in solutions of different concentrations of each coating material, namely paraffin, polystyrene, high molecular weight polyethylene and low molecular weight polyethylene, with constant stirring. To avoid inconsistency between percent loading obtained and the amount of coating material used, samples were dried after filtration in the rotary evaporator under vacuum. This insured complete evaporation of the solvent and removed any possible error in material balance. To test oil adsorption capability, perlite samples with wide range of percent coatings were required.

Percent loadings were calculated using the following formula:

Percent loading =

$$\frac{(\text{final weight of coated perlite} - \text{initial weight of perlite}) \times 100}{\text{initial weight of perlite}}$$

The results for each coating material are shown in Figs.3.1.1.1,3.1.1.2, 3.1.1.3,and 3.1.1.4 respectively. In each case 20 ml of the solution was used to coat one gram of perlite.

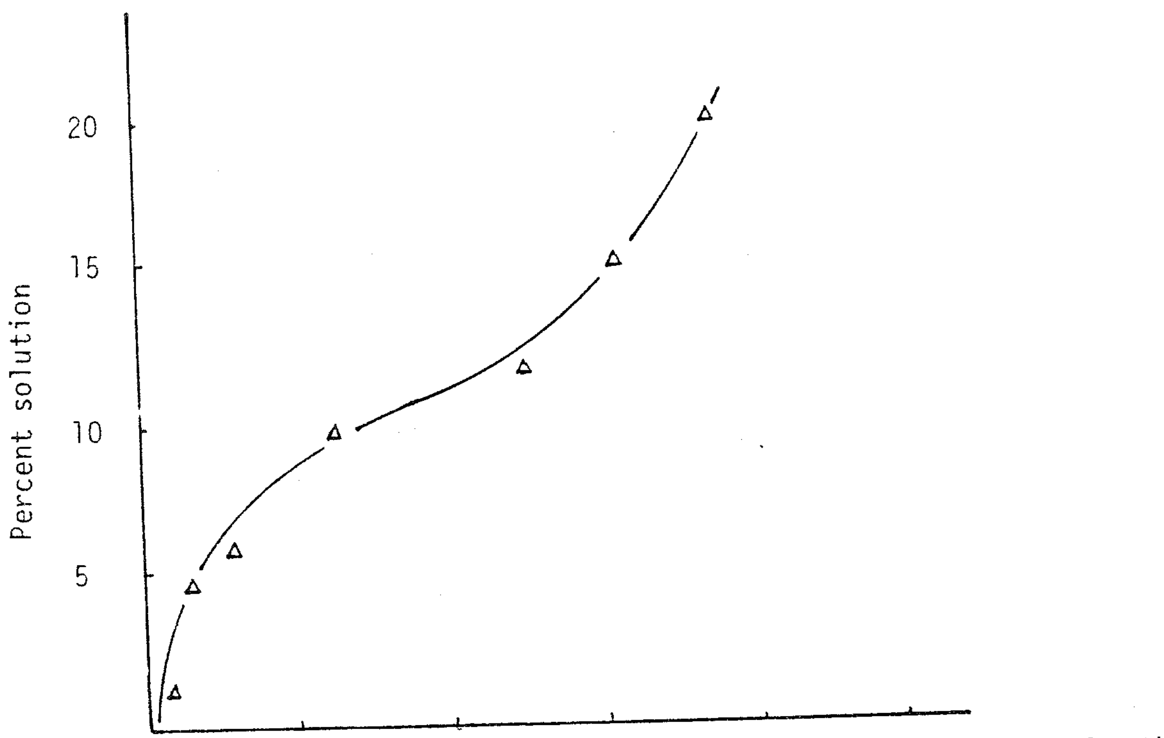


Fig. 3.1.1.1 Loadings of paraffin coated samples

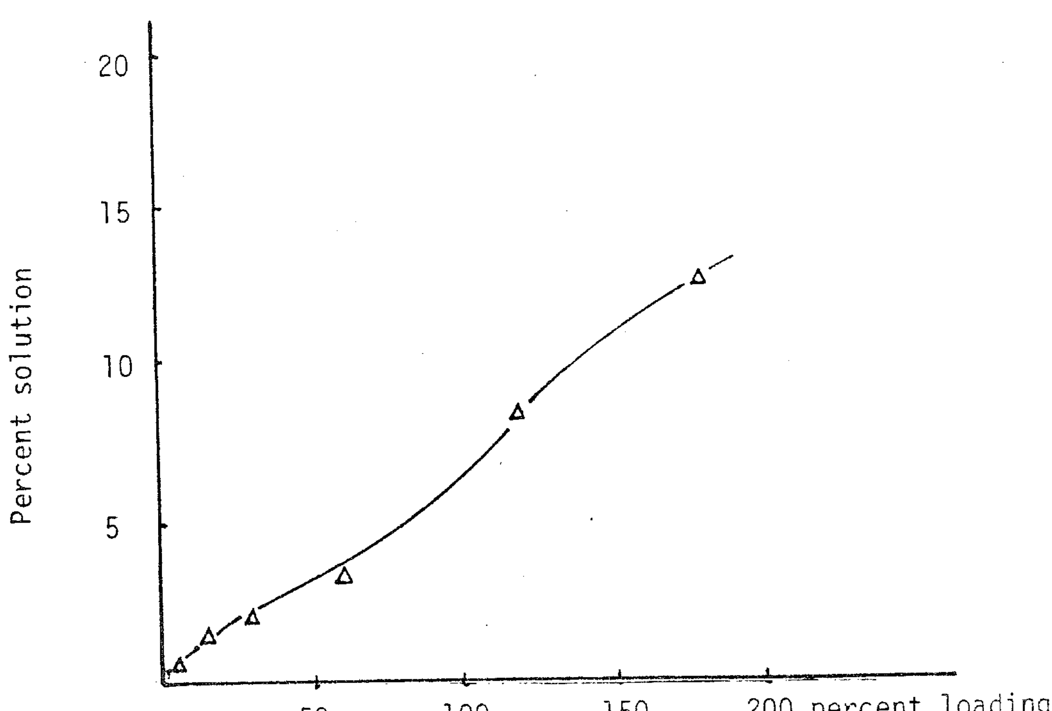


Fig. 3.1.1.2 Loadings of polystyrene coated samples

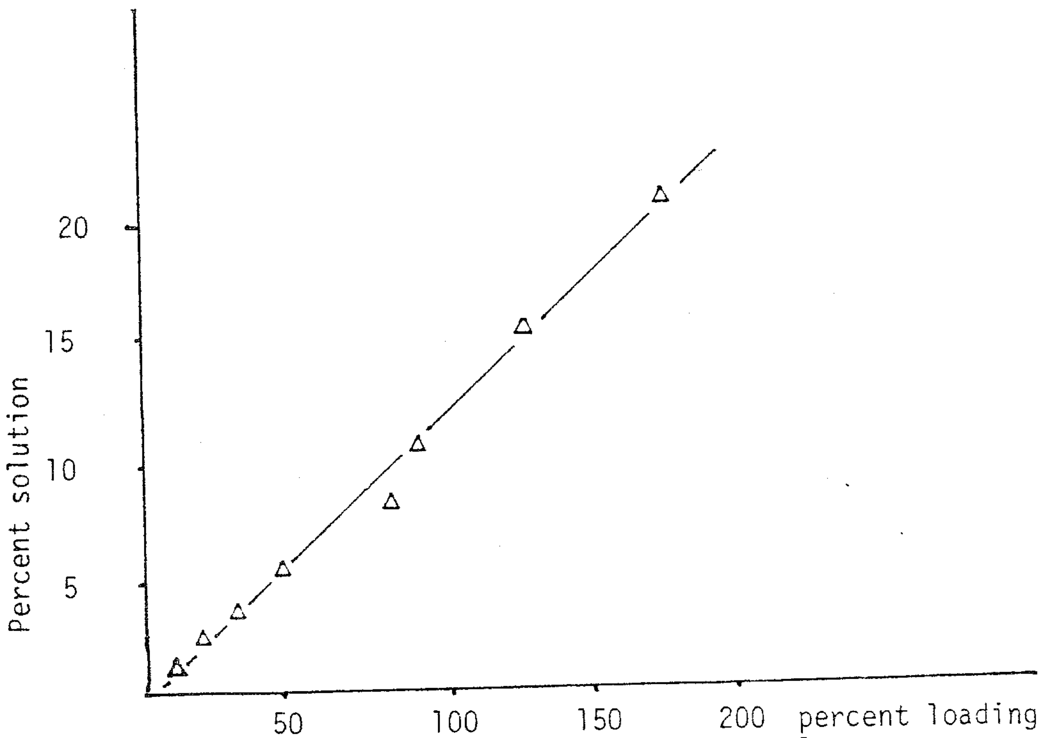


Fig. 3.1.1.3 Loadings of LMPE coated samples

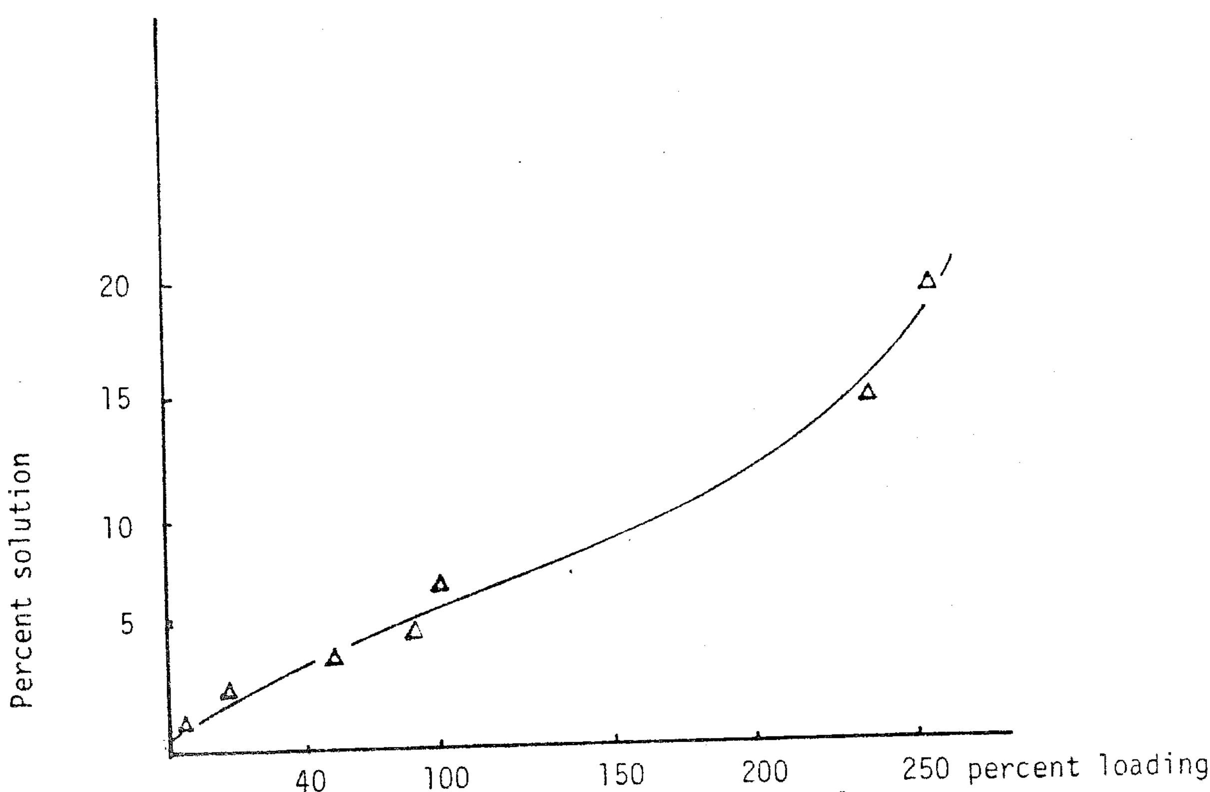


Fig. 3.1.1.4 Loadings of HMPE coated samples

High molecular weight polyethylene and low molecular weight polyethylene will be designated by HMPE and LMPE consecutively throughout the following sections.

All of the paraffin solutions were easily prepared, as paraffin quickly dissolved in chloroform at about 40°C. The first six samples were granular, with particles larger than those of untreated perlite. Granularity decreases with increase in percent loadings, and the last two samples consist of small agglomerations of coated perlite grains as at these high percent loadings, paraffin behaves as a binder for perlite.

Polystyrene in chloroform solutions were difficult to prepare as solubility was low and the polymer tended to precipitate. The 20 percent solution was too viscous to be considered a good impregnation solution. For this reason only seven samples were obtained. Two additional samples were needed, as the samples obtained show a wide percent coating distribution. The physical form of the seven samples was almost similar in nature. Coated grains formed tiny masses which increased in size with the increase in loading.

LMPE which is a sticky gelatinous material dissolves in n-heptane at around 60°C without stirring in a short period of time. The obtained samples were granular in nature and kept this form for all the loadings. The only change was an increase in the grain size with increase in percent loading as expected.

Granular HMPE dissolved with stirring at around 70°C in n-heptane. The first five samples were granular in nature, this characteristics decreases with increase in loading and the last two samples show some mass formation among their grains.

It can be generally seen that as solution concentrations increased percent loadings increased in each case. But, no attempt was made to investigate the correlation between the concentration of the solution used and the loading obtained.

3.1.2 VAPOR DEPOSITION METHOD

Vapor deposition method has the advantage of not using any solvent. It consists of heating the coating material under vacuum and allowing vapors to deposit on continually stirred, cold perlite. After cooling, coated perlite was weighed and percent loading determined.

Polystyrene and HMPE were not used because they have no volatility.LMPE being an impure material in terms of molecular weight distribution evaporated partially. At 40°C and 2 mm Hg pressure one portion evaporated no more evaporation was observed up to 170°C , 2 mm Hg pressure at which time the experiment was stopped. The remaining material, about 80 percent of the original amount, was yellowish and had a penetrating smell. This experiment showed that vapor deposition of LMPE was quite impossible.

Paraffin, on the other hand being a refined sample, boiled at 63°C, at 2 mm Hg pressure. No residueremained in the distilling flask. Along with the perlite, the inside walls of the collecting flask werealso coated. About 21 percent of the paraffin used deposited on perlite, giving a 42 percent loaded sample. The remaining part of paraffin coats the walls of the apparatus, from where it can be removed and used again. Coated perlite obtained by this method was granular.

3.1.3 MELT DEPOSITION METHOD

In this method, the coating material was heated to melt and perlite added to the melt with constant stirring. After cooling, coated perlite was weighed and percent loading determined. This method requires no solvent and no vacuum and promises to be the most economical method of adsorbant deposition.

Polystyrene and HMPE were not used as coating materials because of high melting temperatures required in both cases. Paraffin and LMPE were succesfully used. The results are listed in Table 3.1.3.1

Sample Number	Coating Material g	Perlite g	Percent loading
1	-Paraffin 0.7	1.0	68.99
2	0.7	1.0	69.00
3	-LMPE 0.5	1.0	48.95
4	0.5	1.0	48.90

Table 3.1.3.1 Percent loadings obtained by melt deposition

As can be seen from the table almost all of the coating material deposited on perlite, very little being left on the walls of the container. The reproducility of the results was quite good.

Melted paraffin was less viscous then melted LMPE, but both were quite easy to mix with perlite. The samples obtained were more granular than the samples with the same loading from the solvent deposition method. However, a strong low speed mixer is required as the melts are quite viscous.

3.1.4 COMPARISON BETWEEN THE DEPOSITION TECHNIQUES

Solvent deposition method has the disadvantage of using a solvent that is much more expensive than perlite. The solvent evaporated from the coated perlite can be recovered and reused, but recovery would not be quantitative and some solvent loss is to be expected. Moreover, there is the problem of solvent removal from the coated perlite under vacuum which adds to the cost and the duration of the process. Solvent deposition method, becomes the only workable method, however, when the polymer used has a very high melting point and a low volatility.

Vapor deposition method, on the other hand is easy to perform and needs no solvent. It could only be applied to paraffin though, for reasons mentioned in section (3.1.2) and most of the coating material deposited on the walls of the apparatus.

Melt deposition method has the advantage of not using vacuum or any solvent, and being very simple and straight forward. It only needs stirring with a powerful wall scrapping stirrer, as deposition on the inside walls of the mixer constitutes a very bad heat transfer medium. Almost all of the material deposits on perlite, very little being left on the walls of the container.

It can be deduced that melt deposition method is the most suitable coating technique for preparing oleophilic perlite in large quantities.

3.2 TESTS ON THE SAMPLES

3.2.1 OIL AND WATER ADSORBTION CAPABILITY

The quality of the prepared samples regarding increased oil affinity was tested for each different sample by dipping treated perlite in a mixture of water and oil. The oil used in these experiments is Mobil-therm 705 liquid petroleum oil, chosen to simulate both motor oils and petroleum products from its chemical composition point of view. Its density is 0.92 g /l. The results tabulated below indicate oil and water adsorption as weight percentages, calculated as follows:

$$\text{Percent adsorption} = \frac{\text{weight of oil (or water) adsorbed} \times 100}{\text{weight of sorbent}}$$

Percent loading	Percent oil adsorbed	Percent water adsorbed
1.5	46.8	234.3
8.9	264.4	355.0
13.56	202.3	168.0
34.0	354.3	93.0
65.2	281.3	66.6
66.6	432.8	57.1
141.0	212.0	21.9
186.5	234.3	29.4
217.0	250.6	0.0

Table 3.2.1.1 Oil and water adsorption of paraffin coated perlite

Oil adsorption increases with increased percent loading and reaches a maximum at 66.6 percent loading. This sample adsorbs about 433 percent oil and 57 percent water. Water adsorption however decreases continuously reaching a minimum for the 217 percent loaded sample . The results are illustrated in Fig. 3.2.1.1. It can be deduced that after the 66.6 percent loading, increased paraffin loading does not contribute to increase the oil adsorbing surface anymore.

The results for polystyrene coated samples are shown in table 3.2.1.2

Percent loading	Percent oil adsorbed	Percent water adsorbed
1.4	294.0	600.0
4.9	282.6	396.0
17.0	317.3	442.0
32.0	275.0	245.0
64.0	296.7	241.0
124.0	246.3	48.7
128.0	206.2	52.5

Table 3.2.1.2 Oil and water adsorption of polystyrene coated perlite

Although water adsorption tremendously decreases with increase in loading, oil adsorption does not show a large variation, as seen in Fig.3.2.1.2. The 64 percent and 1.4 percent coated samples adsorb almost the same percentage of oil. It seems that the samples are not uniformely coated, but that polystyrene deposits on regions already coated to produce thick but small coated regions. This may be due to the difficulty in diffusion resulting from the high molecular weight and high entaglement of atactic polystyrene chains (23) . The decrease in water adsorption can be explained by the repulsion between the polar water molecules and non - polar coated regions on the perlite particle which increase in size with increased loading by addition of material on them.

Table 3.2.1.3 gives the results for HMPE coated perlite. Fig 3.2.1.3 shows the oil and water adsorption tendency of HMPE coated perlite. Oil adsorption reaches a maximum at 27 percent loading and then decreases at very high loadings, while water adsorption is almost

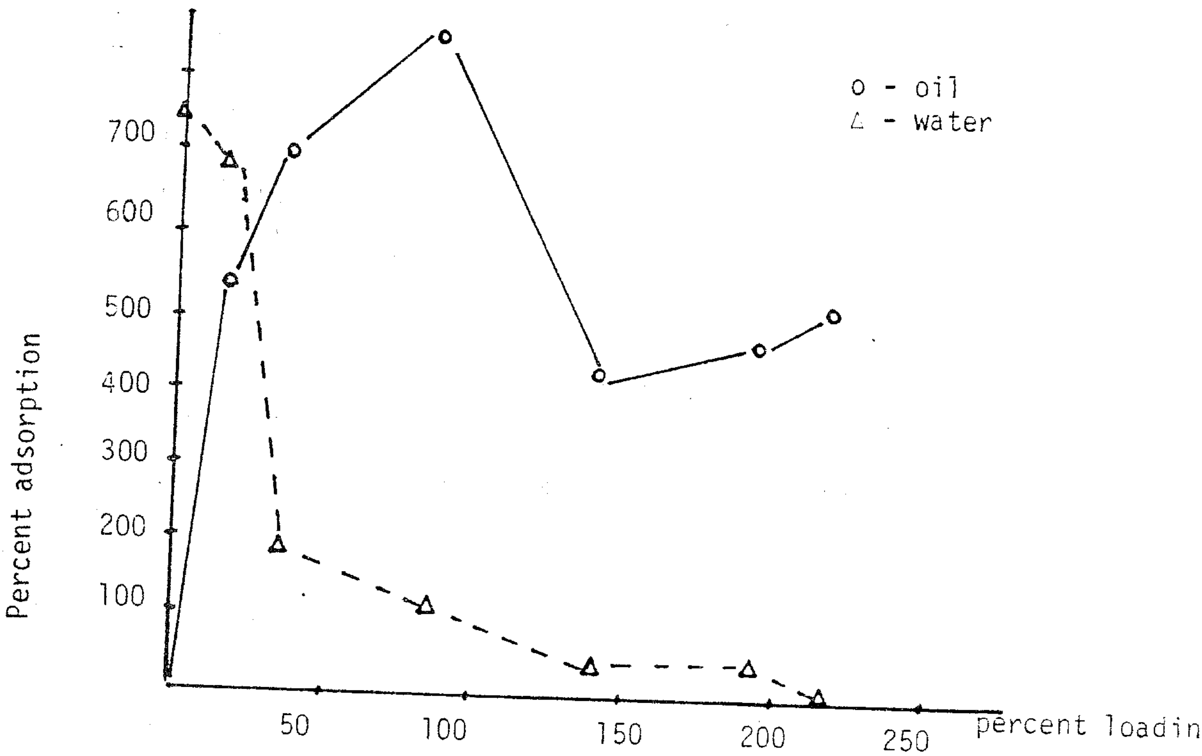


Fig. 3.2.1.1 Oil and water adsorption of paraffin coated perlite

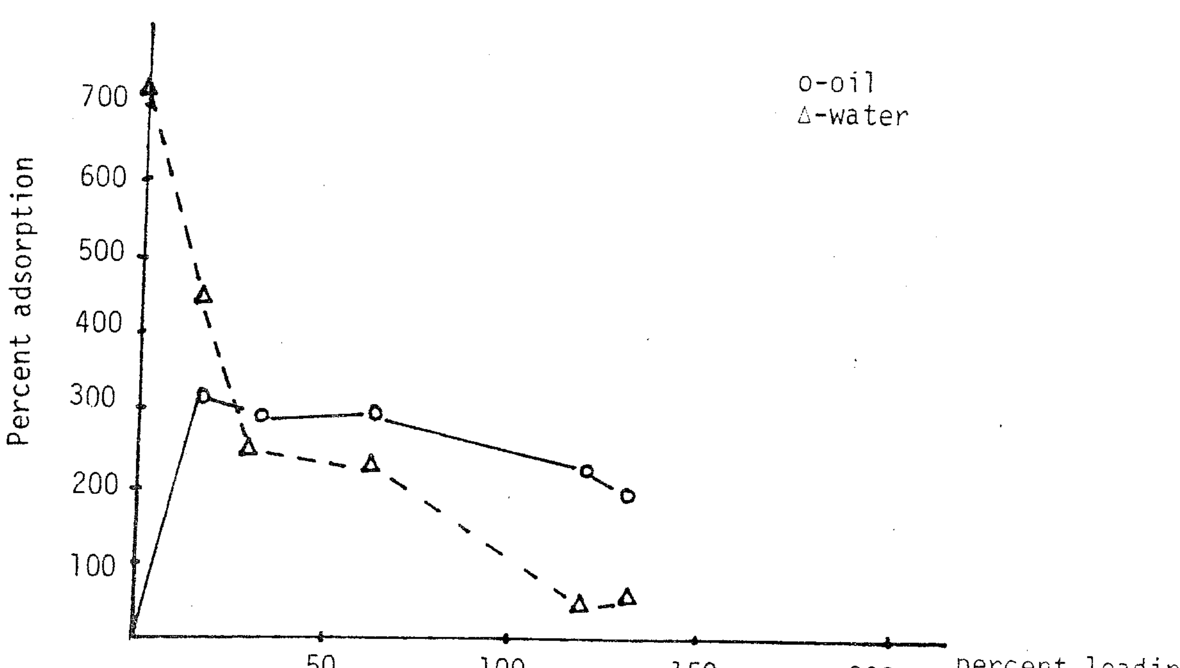


Fig. 3.2.1.2 Oil and water adsorption of polystyrene coated perlite

constant except for the first loading where water adsorption exceeds oil adsorption This means that adding more polyethylene after reaching a 27 percent loading does not improve the oil affinity of the sample.

Percent loading	Percent oil adsorbed	Percent water adsorbed
5.43	103.7	452.8
11.85	489.3	21.2
27.01	591.1	20.0
60.69	448.8	22.2
89.52	492.8	22.0
100.83	514.0	20.0
176.0	302.5	19.6
247.0	169.2	23.8
269.0	109.5	17.5

Table 3.2.1.3 Oil and water adsorption of HMPE coated perlite

It should be noted that at these high loadings, while the amount of oil adsorbed remains the same, the oil adsorption expressed as a percentage shows a decrease because the adsorbent itself gets heavier.

Percent loading	Percent oil adsorbed	Percent water adsorbed
0.52	520.7	116.2
6.39	597.6	113.6
11.5	613.3	18.8
34.0	627.2	10.9
48.0	790.5	0
81.13	333.7	0
93.0	349.3	0
132.0	239.4	0
160.0	223.5	0

Table 3.2.1.4 Oil and water adsorption of LMPE coated perlite

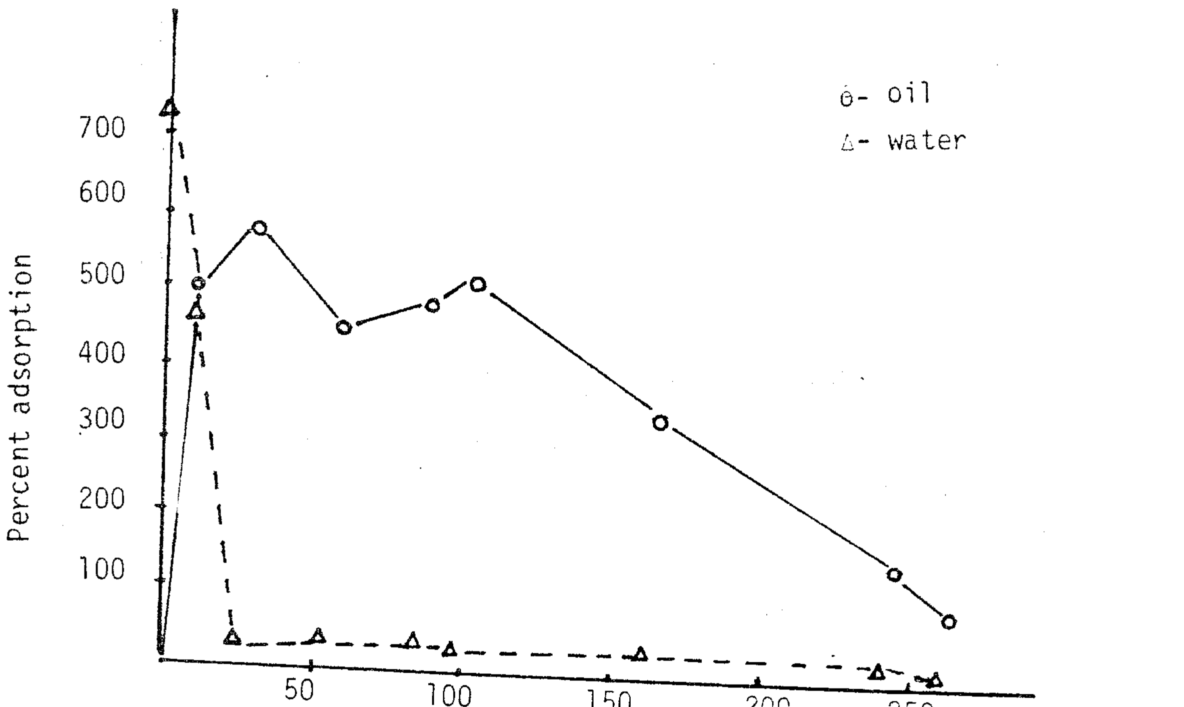


Fig. 3.2.1.3 Oil and water adsorption of HMPE coated perlite

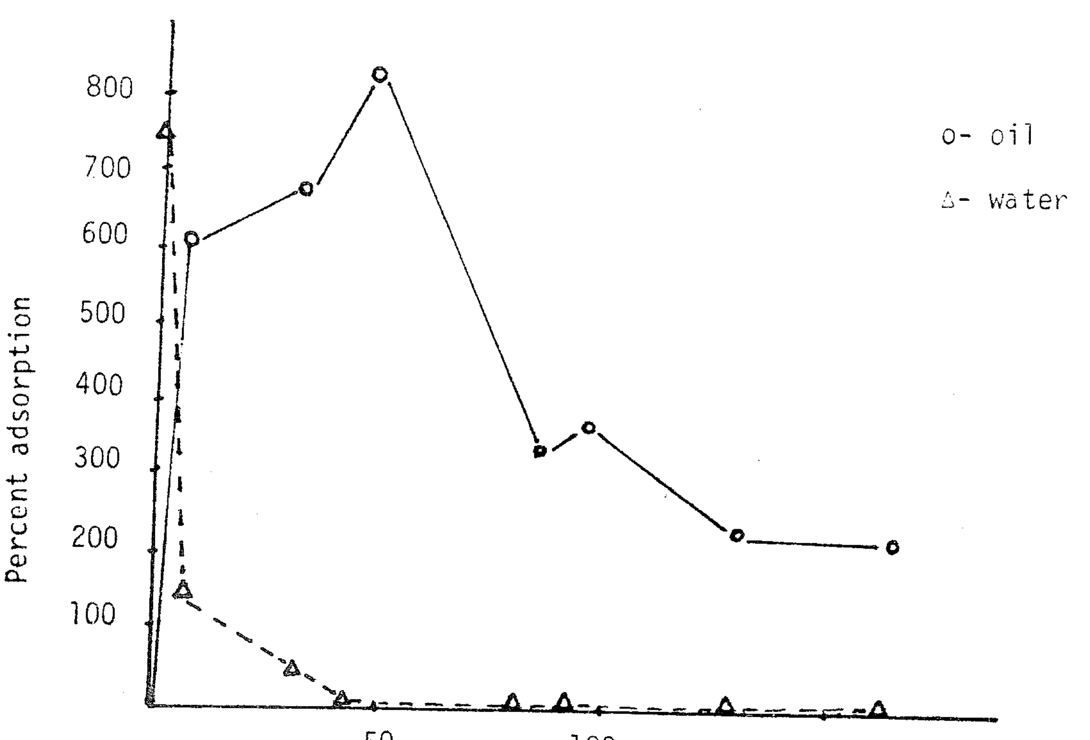


Fig. 3.2.1.4 Oil and water adsorption of LMPE coated perlite

Oil adsorption of the samples is maximum at about 48 percent loading, and water adsorption decreases to zero. This indicates that the coating is uniform, it covers the whole silicate surface, and the material be - comes completely hydrophobic at a 48 percent loading. Any polyethylene added to increase the loading does not affect oil and water adsorption and is wasted. The decrease in oil adsorption percentages at high loadings may again be explained by increase in adsorbant weight. Otherwise, there is no decrease in the actual amount of oil adsorbed.

Compa ring between the four perlite samples coated with different materials, it is noticed that LMPE treated perlite shows the highest percent oil adsorption and lowest percent water adsorption. The efficiency of LMPE coating is probably due to the uniformity of coating resulting from the ease of diffusion of LMPE chains in solution to the perlite surface (24). This increases the "hydrocarbon" specific surface of the sorbent. LMPE is very " hydrocarbon-like" and due to its non-polar nature is most likely to have high Vander Waals forces towards hydrocarbons in oil, making it a very good adsorbant for them. Table 3.2.1.5 gives percent oil adsorption and percent loading of perlite samples coated with about the same percent of each material. To investigate the affinity of the coating material towards oil, the percent oil adsorption was based on coating material weight as follows:

$$\text{Percent oil adsorbed} = \frac{\text{weight of oil adsorbed}}{\text{weight of coating material}} \times 100$$

From the table it can be decuded that LMPE, in addition to its uniform spread on the particles, has also the highest affinity towards oil.

Coating Material	Percent loading of treated perlite	Percent oil adsorbed
Paraffin	34.0	600.0
Polystyrene	32.0	846.1
HMPE	27.0	1925.9
LMPE	34.0	2029.4

Table 3.2.1.5 Percent oil adsorption of the coating materials

3.2.2 REPRODUCIBILITY

To test the reproducibility of oil and water adsorption, the adsorption experiment was repeated for paraffin and LMPE coated samples that show maximum adsorption in each group.

In the LMPE case, four measurements were taken, using two samples prepared by solution deposition and two by melt deposition, of 48 percent loading. Table 3.2.2.1 gives the results.

Sample No:	Weight g	Percent oil adsorbed	Percent water adsorbed
1	0.41	812.4	0
2	0.43	811.6	0
3	0.45	812.0	0
4	0.41	811.0	0

Table 3.2.2.1 Reproducibility of oil and water adsorption of LMPE coated perlite

Water adsorption is zero in the four cases indicating that the uniformity of coating can be obtained by both deposition methods. Average and standart deviation in oil adsorption were calculated using the following formulas : (25)

$$d = \frac{1}{n} \sum_{i=1}^{n} |Xi-\overline{X}|$$

$$s = \left[\frac{1}{n-1} \Sigma (Xi-\overline{X})^2 \right]^{1/2}$$

The results are the following

Average deviation = 0.45 %

Standard deviation = 0.61 %

In the case of paraffin too, samples obtained by different coating methods were used. To check reproducibility samples with 66.6 percent loading were used. Samples one and two were prepared by solution deposition and three and four by melt deposition. Table 3.2.2.2. gives the results.

Sample No:	Weight g	Percent oil adsorbed	Percent water adsorbed
1	0.61	452.4	49.1
2	0.62	451.1	48.3
3	0.59	450.0	50.8
4	0.60	451.3	50.0

Table 3.2.2.2 Reproducibility of oil and water adsorption of paraffin coated perlite.

Average and standard deviation in oil adsorption were found to be:

d = 0.65 %

s = 0.98 %

The results show a good reproducibility in both oil and water adsorption.

3.2.3 ECONOMICS

To choose the best adsorbent among all the samples prepared not only oil adsorption capability but also cost has to be taken into consideration. The major expenditure is due to the coating material used. Perlite costs about 70 TL/Kg. Cost was calculated as follows:

Price / Kg of sorbent =(Percent coating x weight in Kg X Price of coating material / Kg.)+(Percent Perlite x weight in Kg x Price of Perlite/Kg)

Table 3.2.3.1 gives the results of these calculations for paraffin coated perlite. Paraffin price is 200 TL / Kg.

Percent loading	Cost TL / Kg	Percent oil adsorbed
1.5	71.6	46.8
8.9	81.7	264.4
13.5	87.5	202.3
34.0	114.2	354.3
66.6	156.5	432.8
141.0	146.0	212.0
186.5	158.2	234.3
217.0	158.9	250.6

Table 3.2.3.1 Price and oil adsorption of paraffin coated perlite

Figs 3.2.3.1 and 3.2.3.2 show the cost versus percent oil adsorption for paraffin and LMPE coated perlite. From these graphs it can be noticed that the 66.6 percent paraffin coated perlite and 48 percent LMPE coated perlite are the best adsorbents in their groups.

Table 3.2.3.2 lists the results for LMPE coated perlite. LMPE price is 150 TL / Kg.

Percent loading	Cost TL/Kg	Percent oil adsorbed
0.52	70.38	520.7
6.39	74.1	597.6
11.5	79.2	613.3
34.0	97.2	627.2
48.0	108.4	790.5
81.1	134.73	333.7
93.0	144.4	349.3
132.0	116.5	239.4
160.0	119.2	223.5

Table 3.2.3.2 Price and oil adsorption of LMPE coated perlite

Tables 3.2.3.3 and 3.2.3.4 list the results for polystyrene and HMPE coated samples. Polystyrene costs 600 TL / Kg and HMPE 420 TL/Kg. These samples could only be prepared by the solvent deposition method. The price of solvent lost during the operation is not included in the results.

Percent loading	Cost TL/Kg	Percent oil adsorbed
1.4	77.0	294
4.9	95.9	282.6
17.0	160.1	317.3
32.0	287.2	275.0
64.0	409.2	296.7
128.0	367.5	246.3
132.0	371.3	206.2

Table 3.2.3.3 Price and oil adsorption of polystyrene coated perlite

Percent loading	Cost TL / Kg	Percent oil adsorbed
5.4	88.4	103.7
11.8	107.8	489.3
27.0	280.0	591.1
60.6	436.8	448.8
89.5	245.0	492.8
100.8	293.0	514.0
176.0	319.1	302.5
247.0	319.1	169.2
269.0	325.1	109.5

Table 3.2.3.4 Price and oil adsorption of HMPE coated perlite

Prices / Kg are high in both cases compared to paraffin and LMPE coated perlite. Figs.3.2.3.3 and 3.2.3.4 show the cost / Kg versus percent oil adsorption for the two cases. From the graphs it can be deduced that the 17 percent polystyrene coated perlite and 27 percent HMPE coated perlite are the best adsorbents in their respective groups.

The best adsorbants in each group were compared with regard to oil and water adsoption, and to price, Table 3.2.3.5 gives the results.

In this case too price of perlite was also included in the total price of the adsorbent.

It can be decuded from the table that LMPE coated perlite is the best adsorbent. It has the following advantages:

a) High oil adsorption capability, the weight of oil to weight of sorbent ratio is of 7.4 which is satisfactory when compared

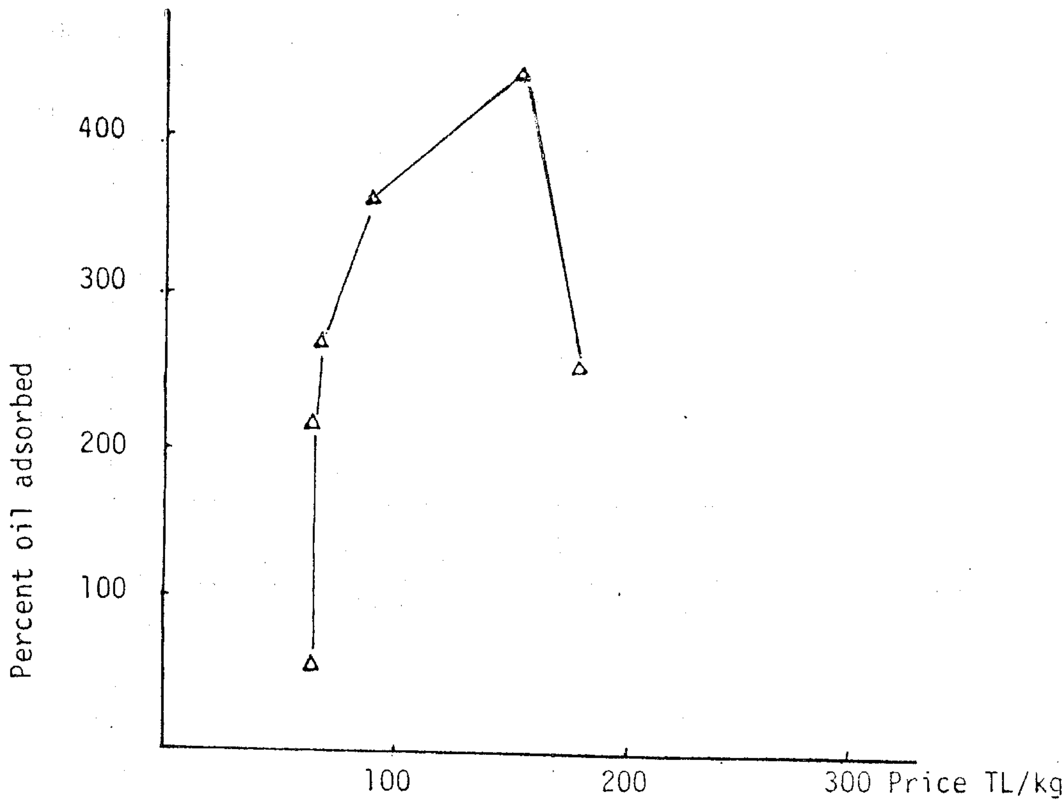


Fig. 3.2.3.1 Price versus oil adsorption of paraffin coated perlite

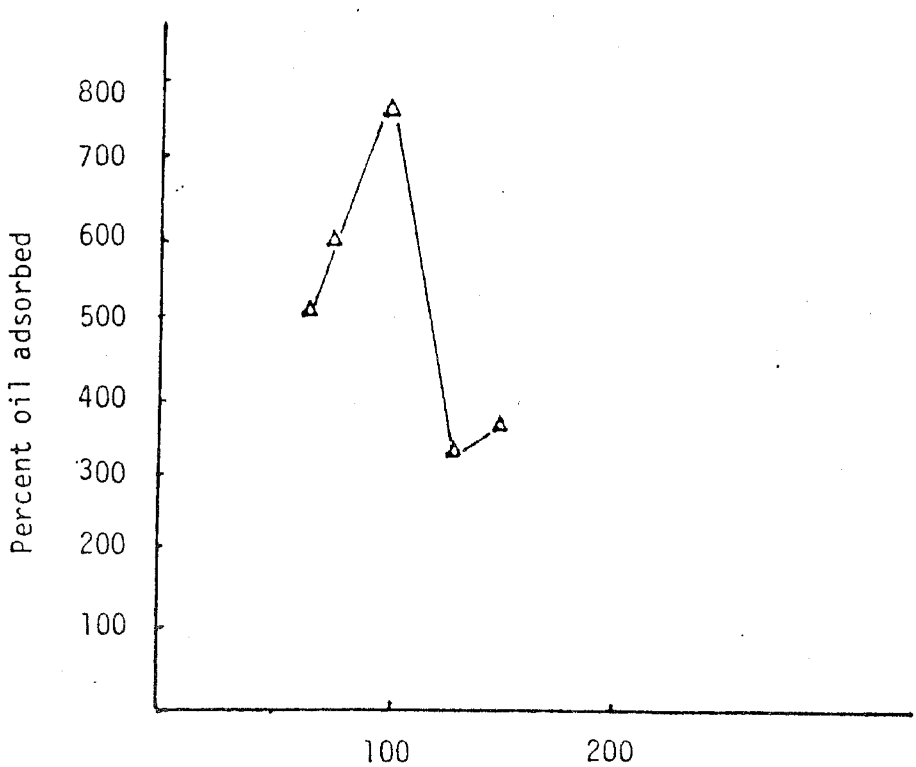


Fig. 3.2.3.2 Price versus oil adsorption of LMPE coated perlite

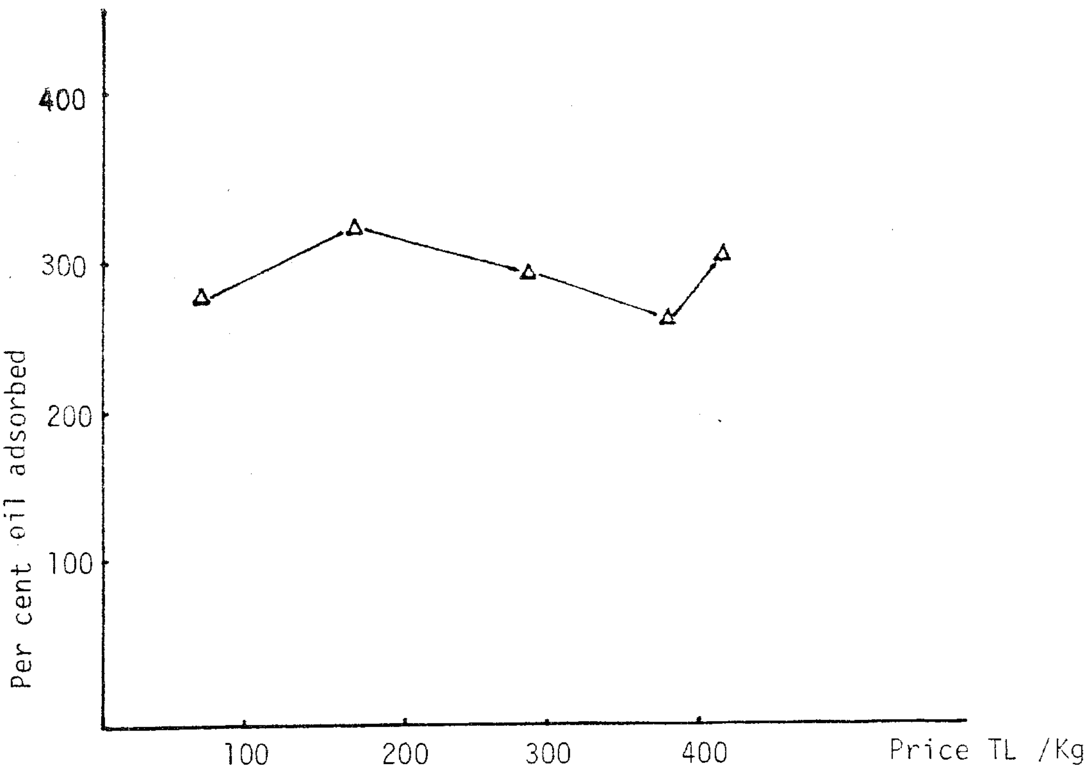


Fig. 3.2.3.3 Price versus oil adsorption of polystyrene coated perlite

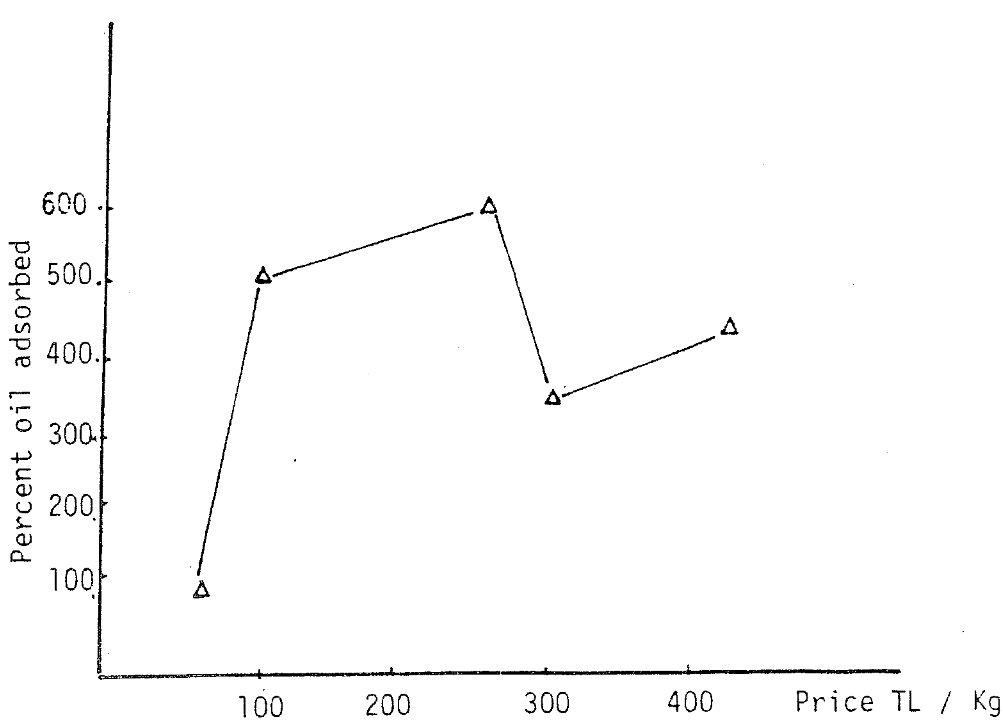


Fig. 3.2.3.4 Price versus oil adsorption of HMPE coated perlite

to other sorbents.

b) Uniformity of coating minimizes water adsorption to zero.

c) The cost / Kg is low : 108 TL / Kg

d) It can be prepared by melt deposition which is a straight-forward and economical method, involving no loss of material no solvent, no vacuum and small amount of energy due to the low melting point of material.

e) The adsorbent is granular: it can be transported on a conveyer-belt, stored either in bulk or bags.

f) It can be easily dispersed on spilled oil, and easily collected. It does not sink after prolonged immersion in water.

Type of sorbent	Percent oil adsorbed	Percent water adsorbed	Price TL/Kg
17 % Polystyrene coated perlite	317.3	442.0	160.1
27 % HMPE coated perlite	591.1	20.0	280.0
66.6 % Paraffin coated perlite	432.8	57.1	156.5
48 % LMPE coated perlite	790.5	0.0	108.4

Table 3.2.3.5 Comparison between differently coated adsorbents.

3.2.4 LARGE SCALE EXPERIMENT USING THE BEST ADSORBENT

In the oil-water adsorption experiments run in the preceeding sections, only small amounts of sorbent, namely one gram or less was used. To check the efficiency and reproducibility of the results, oil and water adsorption capability of the best adsorbent (48 percent LMPE coated perlite) was checked using larger amounts of the substance. Table 3.2.4.1 gives the results.

Sorbent g	Percent oil adsorbed	Percent water adsorbed
6.9	806.0	0
7.0	805.6	0
7.0	808.2	0

Table 3.2.4.1 Oil and water adsorption of the best adsorbent

Average and standard deviations in oil adsorption were calculated to give

d = 1.0 %

s = 1.4 %

The results are reproducible in terms of oil and water adsorption.

3.2.5 HYDROCARBON VAPOR ADSORPTION OF OLEOPHILIC PERLITE

Oleophilic perlite was efficient in adsorbing liquid oil when in direct contact with it. It was interesting to investigate the capacity of treated perlite for hydrocarbon vapor adsorption when hydrocarbon vapor saturated air is passed through it. This property would be useful in utilizing perlite for unwanted hydrocarbon vapor adsorption with subsequent removal of the hydrocarbon from the sorbent by extraction.

This property was investigated using 48 percent LMPE coated perlite and 66.6 percent paraffin coated perlite respectively. The experiment was also run on untreated perlite for comparison. The hydrocarbon used was n - heptane which possessed enough volatility to be swept by air at room temperature. Table 3.2.5.1 gives the results.

Sample	Weight (g)	Time (hrs)	Percent n-heptane adsorbed
. Untreated perlite	2.62	3	0.007
. 48 percent LMPE coated perlite	4.54	2	180.3
. 66.6 percent paraffin coated perlite	6.01	3	119.5

Table 3.2.5.1 N-heptane vapor adsorption of oleophilic perlite

Time indicates the time needed for perlite to reach a constant weight value after vapor charged air is passed through it and the results tabulated are the average values obtained from two experiments on each sample. Figs 3.2.5.1 and 3.2.5.2 show the percent vapor adsorbed with time.

Although adsorption values are good, coated perlite is not retentive of n-heptane. When the used sample is stored at room temperature in open 24 hours after the experiment is stopped, paraffin coated perlite retains 1.37 g of n-heptane and LMPE coated perlite 1.26 g This low retentivity is due to the volatility of n-heptane and if a less volatile hydrocarbon was used higher retentivity would be obtained.

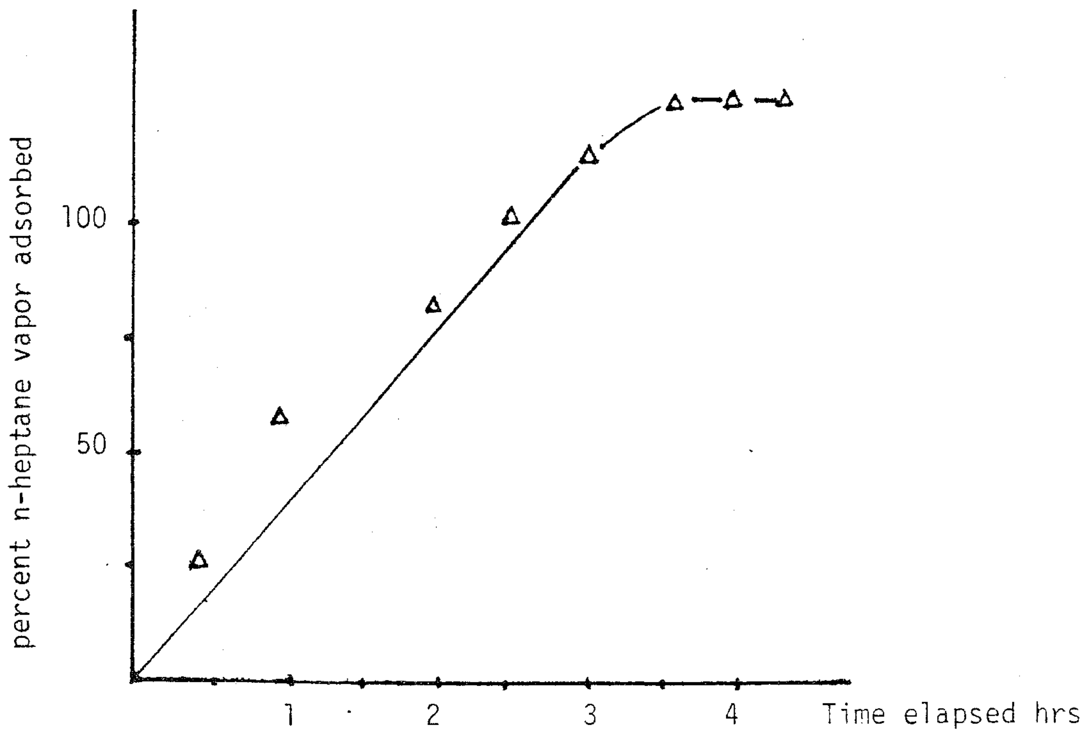


Fig.3.2.5.1 N-heptane vapor adsorbed by paraffin coated perlite

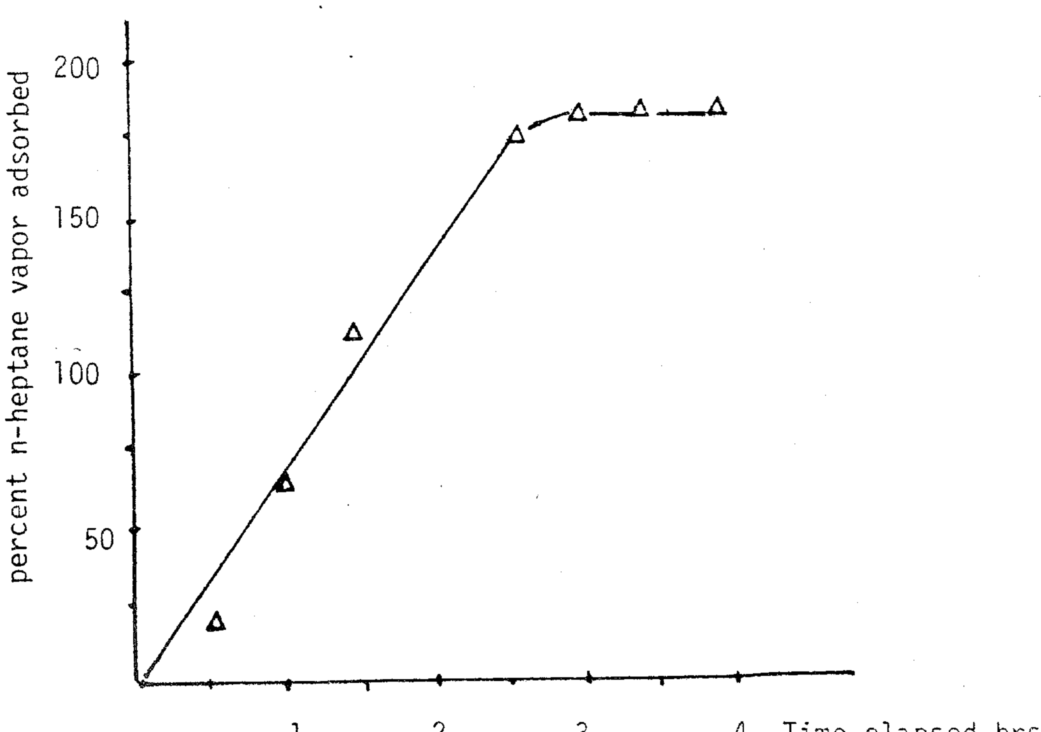


Fig.3.2.5.2 N-Heptane adsorbed by LMPE coated perlite

It is obvious from the results however, that there is a great difference in oleophilicity between treated and untreated perlite.

3.2.6 DISTRIBUTION OF THE COATING MATERIAL ON THE SURFACE OF PERLITE PARTICLES

The uniformity of the coating on perlite particles which is an important factor in determining the amounts of oil and water adsorbed, was investigated by viewing dyed perlite particles of different percent loadings through a bi focal microscope . The dye used was red ink. Being a highly polar pigment, it would produce hydrogen bonds with the -OH groups lying on the surface of the silica structure of untreated perlite (see Fig. 1.1.1). Thus only hydrophilic surfaces could be dyed using red ink. The following diagrams are an attempt to illustrate the coated and uncoated areas on perlite particles. Shaded regions represent dyed (therefore uncoated) portions. Photography would have been more explicit, but lack of equipment made drawing the only resource.

The percent area coated was not possible to calculate, but a general idea may be made from the diagrams. In Fig.3.2.6.1, the whole surface was reddish in colour as expected. Untreated perlite being hydrophilic the dye was hydrogen bonded to all the surface.

Paraffin coated in Fig.3.2.6.2 is not uniformely coated. Small hydrophilic areas are observed.

Fig.3.2.6.3 shows areas of perlite particles with different percent loadings of HMPE. Even in the highest loading HMPE is not uniformely deposited, but hydrophilic areas are present.

In polystyrene Fig. 3.2.6.4 the coating is regional and thick, hydrophilic areas being more numerous than in the other cases. This agrees with the high percent water adsorption of polystyrene coated perlite.

Fig 3.2.6.5, illustrates LMPE coated perlite. No colouration was observed. The coating was thin and uniform. The absence of uncoated areas agrees with the fact that 48 percent LMPE coated perlite adsorbs no water. Furthermore, it is a proof of the uniformity of the coating in the case of LMPE which is a most important factor for the success of this material as an oil adsorbent.

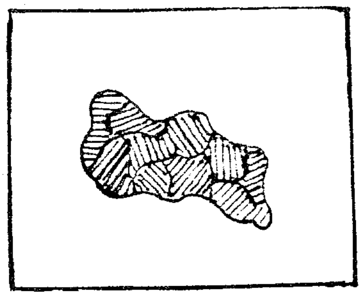
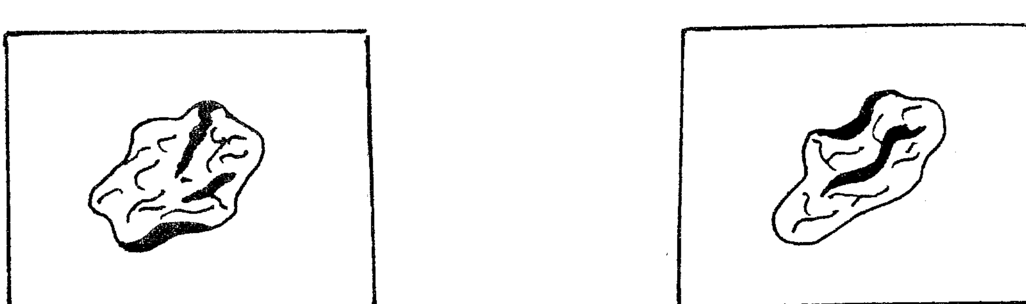


Fig. 3.2.6.1 Untreated Perlite

Solvent deposition

Melt deposition

Fig.3.2.6.2 66.6 Percent Paraffin Coated Perlite



89 percent loading

269 percent loading

Fig.3.2.6.3 HMPE Coated Perlite

64 percent loading 128 percent loading

Fig.3.2.6.4 Polystyrene Coated Perlite

Melt deposition Solvent deposition

Fig.3.2.6.5 48 Percent LMPE Coated Perlite

IV. EXPERIMENTAL

4.1 INTRODUCTION

The experiments done in this work consisted of three main parts:

a) Experiments run on perlite

b) Preparation of the samples

c) Tests carried on the prepared samples

The Apparatus and the techniques used are described in the following sections.

4.2 EXPERIMENTS RUN ON PERLITE

Perlite used was obtained in its expanded form from PABALCK company under the trade name "Perlisol 08"

4.2.1 SIZE CLASSIFICATION

Perlite was reported to be 0-2 mm in size.To obtain a uniform sample with a uniform size distribution, perlite was sieved through US Standard sieves with square orifices according to ASTM standards. The samples were classified as follows.

Grain Size	Orifice Opening mm	Taylor Mesh No:
1	0.840	20
2	0.590	30
3	0.297	50
4	0.149	100

Grain size No:2 having a diameter between 0.595 and 0.840 mm were retained for use The average length of the particles was obtained by taking measurements on 15 particles through a monofocal microscope, and was found to be 1.82 mm.

4.2.2 SEPARATION OF IMPURITIES BY FLOATATION

The sieved sample was mixed with ether thoroughly and let stand The floating portion fas separated for use. The material that sank was discarded; it consisted of metallic oxide impurities and heavy unexpanded particles which are unfit for the subsequent steps and could cause errors in weighing and calculations.

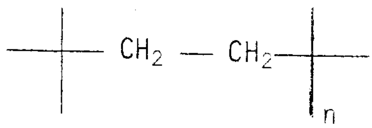
4.2.3 EVAPORATION OF EXTERNAL WATER

Untreated expanded perlite is a very hydrophilic substance. To remove any water that may have been adsorbed from the atmosphere, the sample was heated in the oven at 90-100°C to constant weight and kept in dessicators till use.

4.3 PREPARATION OF THE SAMPLES

All of the chemicals used in this work except LMPE and Mobiltherm 705 liquid petroleum oil, were pure grade chemicals. The coating materials used were the following:

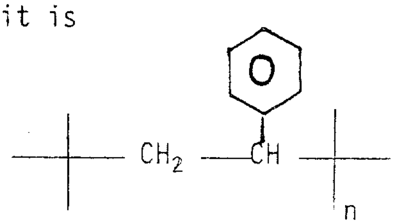
a) HMPE: Commercial high density polyethylene manufactured by Petkim A.Ş. , Kocaeli. It has a number average molecular weight of 300.000 . The repetating unit is the following:



b) LMPE: By-product of polyethylene manufacture at Petkim A.Ş., obtained as the toluene soluble fraction during manufacture. Its molecular weight is about 1200.

c) Paraffin: A refined de-oiled embedding paraffin of about 23 to 30 carbon atoms per molecule, its molecular weight is about 420 units and contains less branching then LMPE.

d) Polystyrene: Commercial granular atactic polystyrene manufactured by Petkim A.Ş. , Kocaeli. Its molecular weight is about 100.000 units and the repeating unit is



4.3.1 SAMPLE PREPARATION BY SOLVENT DEPOSITION METHOD

Solutions were prepared by dissolving the coating materials in the appropriate solvent at the appropriate temperature as listed below:

Temp°C	Solvent	Coating Material
40-45	Chloroform	Paraffin
50-55	Chloroform	Polystyrene
70-75	N-heptane	HMPE
60-65	N-heptane	LMPE

Weighed perlite was then added with constant mixing and kept in the solution at the indicated temperature for 30 min. The solutions were then filtered and perlite dried in the oven to constant weight at the boiling temperatures of each solvent: 98.8°C for n-heptane and 61°C for chloroform. The percent loading was determined by weighing. When coating material was recovered from the remaining solution by the evaporation of solvent it was found that material balance was not met. The amount of coating material remaining in solution after filtration, and the amount supposed to be on perlite, added upto an amount greater than the initial weight of coating material used. This was especially striking in the case of low and high molecular weight polyethylenes. But there were discrepancies in weight in some paraffin and polystyrene coated samples too. To account for these errors the purity of the solvents used was checked ; no impurities were found. It was assumed then that the problem arose from incomplete evaporation of the solvents from the coated perlite, especially n-heptane. Being a hydrocarbon it was adsorbed by the oleophilic perlite. To remove excess solvent coated perlite was dried after filtration in a Buchi rotary evaporator under 2 mm Hg. pressure at room temperature in the case of chloroform, and about 40-45°C for n-heptane. The final weight of perlite was determined and the results were acceptable in terms of material balance. These operations were repeated for 1, 2, 3, 5, 10, 15, 20 percent solutions of each coating material, in order to obtain a wide distribution of percent loadings. Additional samples were obtained in the same way.

4.3.2 SAMPLE PREPARATION BY VAPOR DEPOSITION METHOD

This method was used to prepare paraffin coated perlite. The apparatus used is shown in Fig.4.3.2.1.

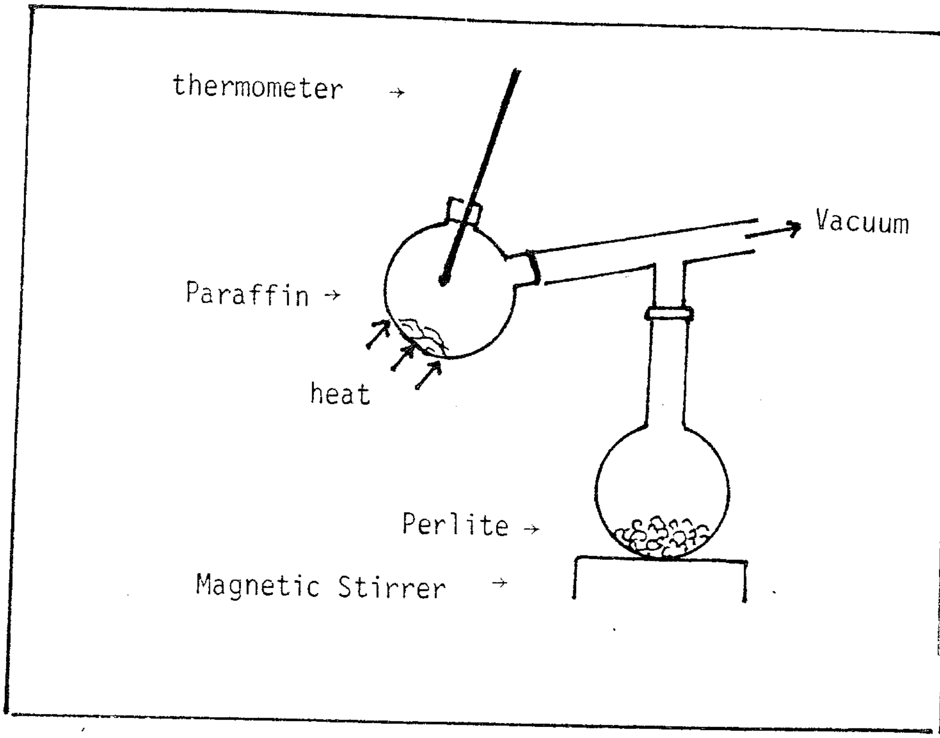


Fig. 4.3.2.1 Apparatus for Vapor Deposition of Paraffin on Perlite

Under 2 mm Hg pressure paraffin boiled at 63°C and vapors deposited on perlite. Perlite, which was kept at a colder temperature than paraffin was continually stirred by a magnetic stirrer to assure deposition on all particles. After all paraffin has evaporated, the perlite was let to cool and loading determined by weighing.

4.3.3 SAMPLE PREPARATION BY MELT DEPOSITION METHOD

Paraffin and low molecular weight polyethylene were deposited on perlite using this method. The procedure consisted of heating the coating material till it melts and adding a weighed amount of perlite with continous and through mixing for five min at the melting temperature. The mixture was cooled and loading determined by weighing. Paraffin melted at 55°C and low molecular weight polyethylene at 52°C. Minute amounts of coating material remained on the walls of the flask while most of it deposited on perlite.

4.4 TESTS RUN ON THE SAMPLES

The experiments described in this section aim to measure the oil and water adsorbtion capability of the prepared samples and the differences in oleophilicity between them.

4.4.1. UNSUCCESSFUL TRIALS

Experiment 1 : A 5 ml graduated burette (Fig 4.4.1.1) was filled with a known volume of n-octane. A thin walled test tube of 4 cm length, 1 cm diameter filled with perlite was fitted under the tip of the burette.

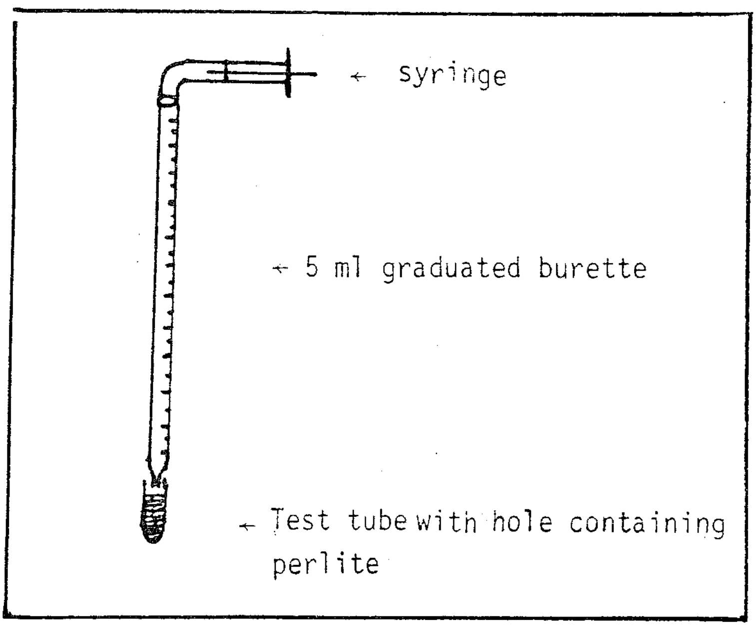


Fig. 4.4.1.1 Apparatus used in experiment one

By using the syringe n-octane was dropped into the tube till the first drop comes out of the hole in the bottom of the test tube. Air was blown through the tube to take out excess oil. The volume of adsorbed octane could be measured taking readings from the burette and adding the excess drops. The experiment was repeated using untreated perlite and 70 % paraffin coated perlite. Then n-octane was replaced by mineral oil. No difference could be measured to indicate a change in oleophilicity between treated and untreated perlite. The difficulty in this case probably arose from the fact that oil physically trapped between particles exceeded oil adsorbed by the coated perlite.

Experiment 2 : The glass stopper of the apparatus (Fig. 4.4.1.2) was filled with 40% high molecular weight polyethylene coated perlite and closed at the open end with some thin wire gauze from car gasoline filters. The narrow end of the tube was closed with a rubber cork. The tube was filled with water partially and topped up with oil enough to fill the neck of the bottle.

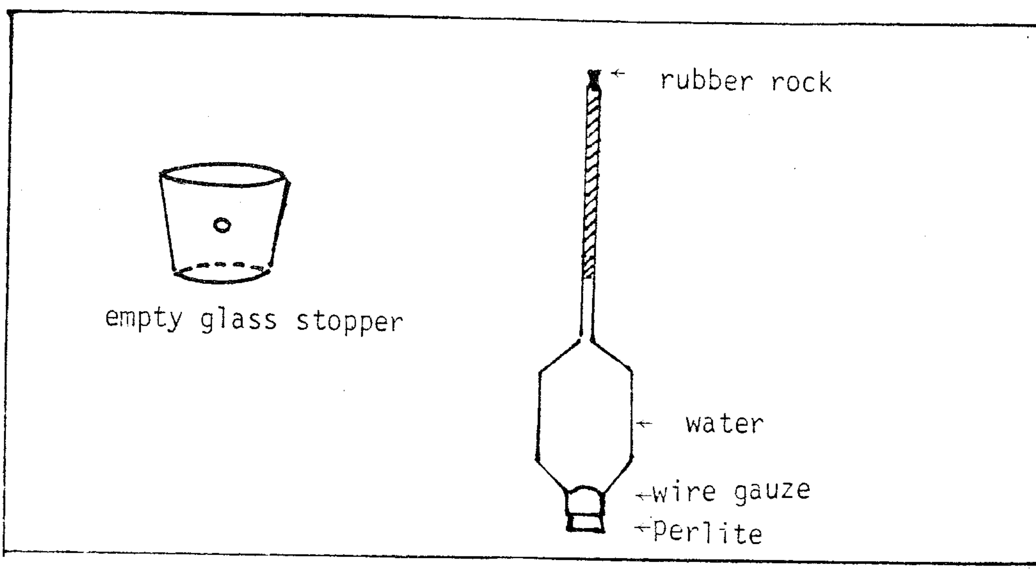


Fig. 4.4.1.2 Apparatus used in experiment two

Perlite was first in contact with water. By inverting the tube it came into contact with oil. Then the tube was inverted again to make oil return to its original position. The difference between the initial and final oil column heights should have given the amounts of oil adsorbed. This was not possible however as most of the oil adhered to the walls of the tube after coming into contact with perlite and didnot turn back to its original position.

4.4.2 SUCCESSFUL EXPERIMENTS

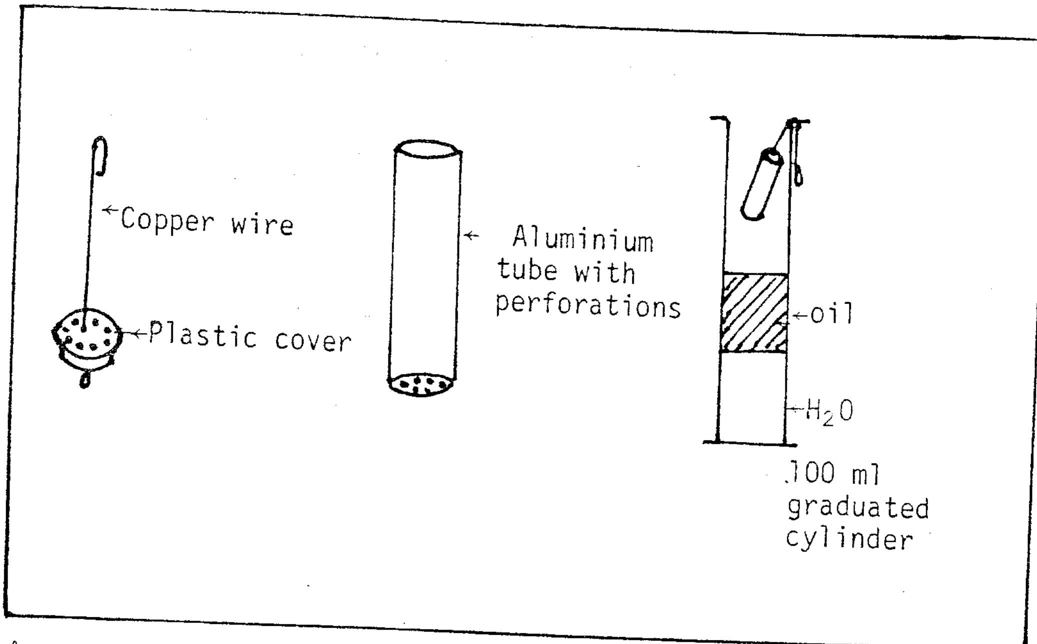


Fig.4 .4.2.1 Apparatus used in graduated cylinder experiment

The perlite container consisted of an aluminium medicine tube. It was first cleaned with chloroform then its bottom was perforated as shown in (Fig. 4.4.2.1). The original plastic cover of the tube was used as a cover for this container after making holes in it with a hot wire and passing a thin wire through it for hanging.

A 100 ml graduated cylinder was filled with a known volume of water and a known volume of oil. The perlite container was dipped into the water layer and shaken in it for some time., then in the oil layer in the same way. The container was then hanged on the side of the cylinder and let drip for a night. The difference between the initial and final volumes of the oil and water layers gave the amounts adsorbed.

The experiment was repeated for each sample and the reproducibility of the results was tested.

4.4.3 LARGE SCALE EXPERIMENT

The graduated cylinder experiment was repeated using larger amounts of substances. 48 percent low molecular weight polyethylene coated perlite was the sorbent used.

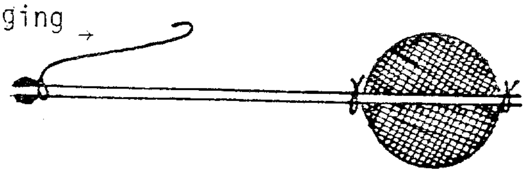


Fig.4 .4.3.1 Apparatus used in the large scale experiment

The container in this case was made by filling two tea sieves with perlite and closing both ends with thin copper wire(Fig.4 .4.3.1). A one liter graduated flask was filled with known volumes of oil and water. The container was dipped in the 2 layers consecutively and shaken in them. It was then let to drip for a night. The adsorbed oil and water were determined from the differences in volumes.

4 .4.4 HYDROCARBON VAPOR ADSORBTION OF OLEOPHILIC PERLITE

This experiment aimed to measure the capability of coated perlite to adsorb hydrocarbon vapor when a hydrocarbon vapor saturated air flow is passed through it. The apparatus used is shown in (Fig 4.4.4.1)

The ends of the tube containing perlite were closed with glass wool and stoppers. The valve was necessary for adjusting the air flow through perlite.

A measured volume of n-heptane was heated to 20-30 °C by adjusting the air flow using the trap, n-heptane vapor charged air was led through perlite.

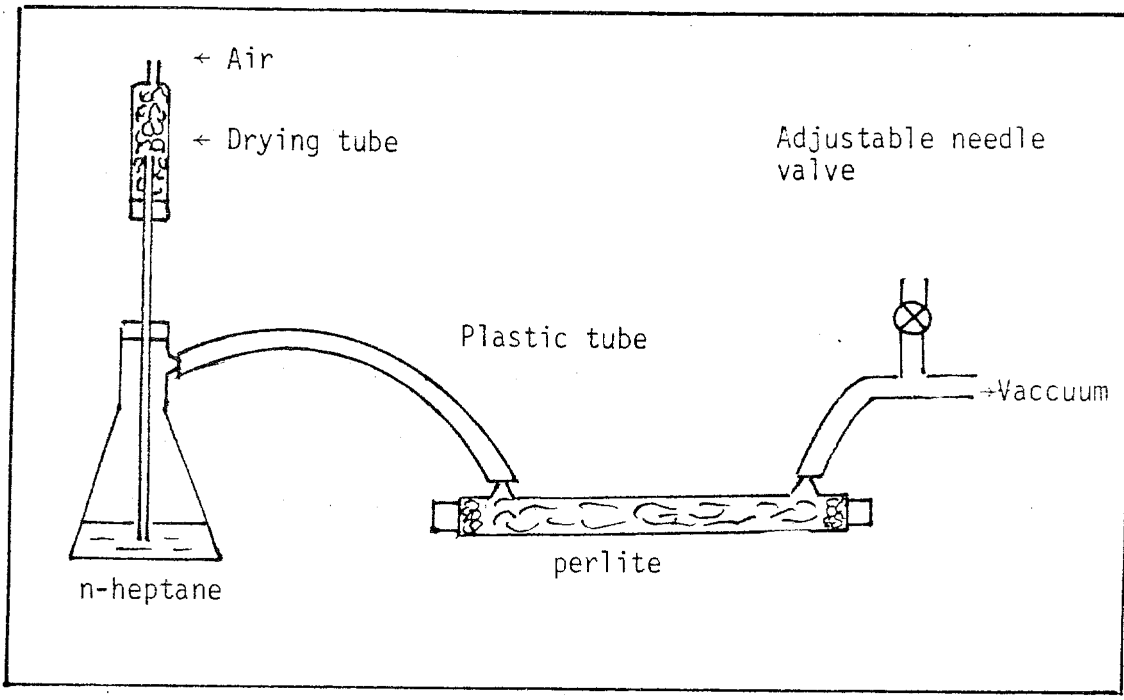


Fig. 4.4.4.1 Apparatus used to measure hydrocarbon vapor adsorption of coated perlite.

The sorbent and the adsorbtion tube was weighed every 30 min till a constant weight was reached. The sorbent container was disconnected from the apparatus and its ends opened. Sorbent was then weighed every 10 min, to check the retention capability of perlite for n-heptane vapor it had adsorbed. The experiment was run on untreated perlite, 48 % low molecular weight polyethylene coated perlite and 66.6% paraffin coated perlite.

4.4.5 DISTRIBUTION OF COATING MATERIAL ON PERLITE PARTICLES

In order to determine the distribution of the coating materials on perlite particles, different samples including untreated perlite were dipped in a red ink solution, dried on a filter paper, and observed through a monofocal microscope. Ink used being water based only hydrophilic surfaces could adsorb it and appear pink. The shades of pink observed on perlite particles were drawn in an attempt to show the percent of the surface coated by the different coating materials and rendered oleophilic. The microscope used was a Euromex EB type bifocal microscope.

V. CONCLUSION

The results obtained show that the aims of this work were reached. A new oil adsorbing material was synthesized from perlite by encapsulation with hydrocarbon like polymers.

The best adsorbent obtained (48 percent LMPE treated perlite) has the advantages of low cost and high oil adsorption. It costs 108 TL /Kg and has an oil adsorption to weight of sorbent ratio of 7.4. Melt deposition technique allows preparation of large quantities of the sorbent in an economical and straight forward way. In addition to that, the sorbent is non-toxic and easily handled. The high oil affinity of 48 percent LMPE coated perlite results from the following factors:

a) Perlite itself has a very high specific surface (surface area/weight)

b) All of this surface can be utilized for oil adsorption, because of the uniformity of coating in the case of LMPE treatment

c) LMPE is a good oil adsorbing material due to its hydrocarbon structure.

Other points in the advantage of the new sorbent are the utilization of perlite which is a natural resource of Turkey, and the use of LMPE , a cheap and otherwise useless by-product as a coating material.

In addition to its utilization in oil and organic substance removal from water surfaces and city waters, oleophilic perlite can also be used in removal of oil from tank bottoms and from floors in factories and car service stations, preventing thus any fire hazards. Flue gases released to the atmosphere by factories could be purified from hydrocarbon vapors by the use of the new sorbent.

Although re- extractability of the oil adsorbed was not investigated, the sorbent plus oil adsorbed could be burnt as a fuel and the perlite could be reused.

To verify the results of oil adsorbtion experiments, large scale experiments on actual sea and lake surfaces need to be carried out.

BIBLIOGRAPHY

1. Benton, W. ed.,"Pitchstone " ,Encyclopedia Britannica, Vol. 17, p.117, 1971

2. Yüksel, K.Ümit, " Perlite PMMA Composites" , M.S. Thesis, Boğaziçi University, 1979

3. Buzhevich, G.A., etal., "Basic Properties of Expanded Perlite Sands.", Legk. Silikat Betony, Vol 6, 181, 1969

4. Barrer, R.M., Zeolites and Clay Minerals as Sorbent and Molecular Sieves, pp 425-426,New York: Academic Press, 1978

5. Ciaccio, L. ed, Water and Water Pollution Handbook, pp. 129-130, New York: Marcel Dekker. Inc., 1972

6. Dorn, Karlheinz, "Fire Resistant Insulators from Perlite Sands", Ger.offen. Vol, 3, 142, 1983

7. Gülerman, H., "An nvestigation of Perlite as Structural Lightweight Concrete", M.S. Thesis, Robert College, 1965

8. Gorbunova, K.N., et.al, "Low Voltage Electroporcelains", Steklo Keram. Vol. 6, 20-1, 1983

9. Maslennikov I.A., "White Pigment Preparation from Perlite ", Izobret. Prom . Obraztsy,14, 102, 1983

10. Sitting, M., Oil Spill Prevention and Removal Handbook, pp 290, London, Noyes Building, 1974

11. Wolfe, A.Douglas, Fate and Effects of Petroleum Hydrocarbons in Marine Organis ms and Ecosystems. No: 8-10

New York: Pergamon Press Inc., 1977

12. Emelina, Z.G., "Volcanic Pyroclastic Rock as a Sorbent", Vodosnabzh Sanit. Tekh., Vol 6 , 202, 1983

13. Rutkonsky, M., "Granulated Porous Sorbents From Aluminosilicates", Politechnika Wrodanska, 116, 1982

14. Yamano, Y., etal., "Polyethylene Foams containing Perlite as Sorbents." Japan, Kokai , 464, 1976

15. Muntzer, E., Muntzer, P., " Disperse Solids for Oil Removal from Water", Ger. Offer., Vol 2, 149, 1971.

16. Preus, Paul, " Separation of Hydrocarbons from water", Ger. offen., P 2459378.0, Dec. 1974

17. Funk, Richard S., "Hydrophobic Absorbents for Petroleum", Ger offen., Vol 2, 205, 1972

18. Manago, T. etal, "Water Repellent from Rock and Volcanic Ash", Japan, Kokai,Vol 9, 790, 1973

19. Bezorud ' ko, O.V. etal, "Use of Waterproofed Perlite for the Removal of Petroleum from the Surface of Waters", Ukr. Khim. Zh.,Vol 1, 46, 1980.

20. Le Dorze, Daniel , "Adsorbents for Controlling Oil Pollution on Large Expanses of Water", Fr.Appl., 7100, 435, 08,1971

21. Rodier, Jean, Analysis of Water, pp 839, 870, New York: Wiley and Sons Inc., 1975

22. Orhan, metin, " A Study of Penetration of Oil into Sorbents", M.S. Thesis, Boğaziçi University, 1982

23. Segal, Charles L., ed., High Temperature Polymers, pp 45-46, New York: Marcel Dekker Inc., 1967

24. Boening, Herman V., Polyolefins: Structure and Properties, pp. 160-161, New York: Elseiver Publishing Company, 1966

25. Fritz, James S, Schenk, George H., Quantitative Analytisal Chemistry, pp. 30-33 London: Allyn and Bacon Inc., 1977