

REMOVAL OF OIL SPILLS FROM SALT WATER BY MAGNESIUM, CALCIUM CARBONATES AND OXIDES

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ABSTRACT: Magnesium, calcium carbonates and oxides which are widely used in cement industries were employed in studying sorption of petroleum oil spills from salt water at different condition parameters such as temperature, loading weight, degree of salinity. Treatment of magnesium, calcium carbonates and oxides by dedecylbenzene sulphonic acid alcohol was studied to enhance the sorption efficiency. Results obtained showed that treated $MgCO_3$, $CaCO_3$, MgO and CaO with dodecyl benzenesulphonate can sorb oil by 0.95, 1.25, 78, 0.56 times its weight respectively; untreated materials can sorb oil by 0.49, 0.76, 0.44, 0.32 its weight. Characteristics of crude oil and the used materials were investigated by FTIR, X – Ray Fluorescence, Inductive Coupled Plasma, Pour Point and Thermostatic Water Bath instruments. Determination of the amount of crude oil in water was done by extraction the crude oil in trichlorotrifluoroethane and measuring absorbance by FTIR spectrometer.

1. INTRODUCTION

Many researches had been forwarded towards organic sorbents for removing oil spills from the surface of salt water such as, de-oiled petroleum asphalt bottoms (Ralph S. Wilcox, 1979), turkey's feathers, pre-cooked puffed cereals (Emile Arseneault and Hervey Tremblay, 1990), paraffin wax (John Bartha and Gyorgy Cscapo, 1992), ground corn-cobs (Adria Brown; and West Bloomfield, 1992), synthetic polymer (Glenn R. Rink, et al., 1999), peat-moss (Annapolis Valley Peat Moss Co. Ltd., 2001), recycled wool – based non woven material (Maja et al., 2003) and other carbon products. Organic sorbents are loose particles and are difficult to collect after they have spread on water. Getting rid of those materials are a real problems for all whom concern to the environment.

So, many other researches had been concentrated their efforts to use inorganic sorbents. Clays are the most popular materials which are used as sorbents for oil spills. Clays such as kaolinite (Tarrasevich, 1986, Sayed et al., 2002), bentonite (Laura Kajita, 1997), smectite (Steven Kemnetz and Charles A. Cody, 1998) have been used. Inorganic sorbents have an advantage over organic sorbents in that they can be re-sued again in many industries (EPA, 1999).

A little work had been done to use metal carbonates and oxides to sorb oil spills from the surface of salt water (Sayed and Zayed, 2002; Sayed et al., 2003).

2. EXPERIMENTS

As the Crude oil is a very complex mixture of many different chemicals, consequently the effects of an oil spill on the marine environment is dependent on the exact nature and quantity of the oil spilled, as well as such other factors as the prevailing weather conditions and the ecological characteristics of the affected region (Doerffer, 1992; Roy, 1996). According to the complex nature of oils, they do not behave as the same in the environment. Some constituents are noted for they tendency to vaporize while others clearly prefer to bind to solids; some oil hydrocarbons extremely unreactive while other interacts with light, so they have different toxicological effects on the aquatic life and hence on human being (Rene, 1993).

Gulf of Suez mixture crude oil is used for the purpose of our study since it represents about 60% of the mass production of Egyptian crude oil, which, is transferred directly to oil refining companies or for exportation along Suez Canal. It is a mixture of crude oils produced from nearly 33 fields located at the Red Sea area. Analyses figures for the tested crude oil according to the institute of petroleum (IP) test methods are listed in Table (1) (IP, 2001).

Table 1. Physical properties of Gulf Suez mixture crude oil

Test	Test Method	Results
Density at 15°C kg /L	IP 160	0.8544
Sediment % mass	IP 53	NIL
Water %Volume	IP 74	0.35
Salt % mass	IP 77	0.004
Sulphur % mass	IP 336	1.42
Pour point °C	IP 15	-3
Viscosity Redweed at 37.8°C Sec.	IP 212	31
Iron µg/ml	Inductive Coupled Plasma	130
Vanadium µg/ml		70
Chromium µg/ml		30

I.R spectra (FT/IR-410 Spectrometer, Jasco) of the tested petroleum crude oil was demonstrated in Table (2). Inspection of these spectra reveals the presence of the following two peaks at wave no. 2923 cm^{-1} and 2853 cm^{-1} represent $-\text{CH}_3$ and $-\text{CH}_2-$ stretching frequencies; two peaks at wave no 1462 cm^{-1} and 1377 cm^{-1} represent $-\text{CH}_3$ and $-\text{CH}_2-$ bending frequencies and peak at 722 cm^{-1} for aliphatic hydrocarbons of chains containing carbon atoms equal or greater than seven . These data indicate that the crude oil has a paraffinic nature (Wauquier, 1995; Silverstein, 1991).

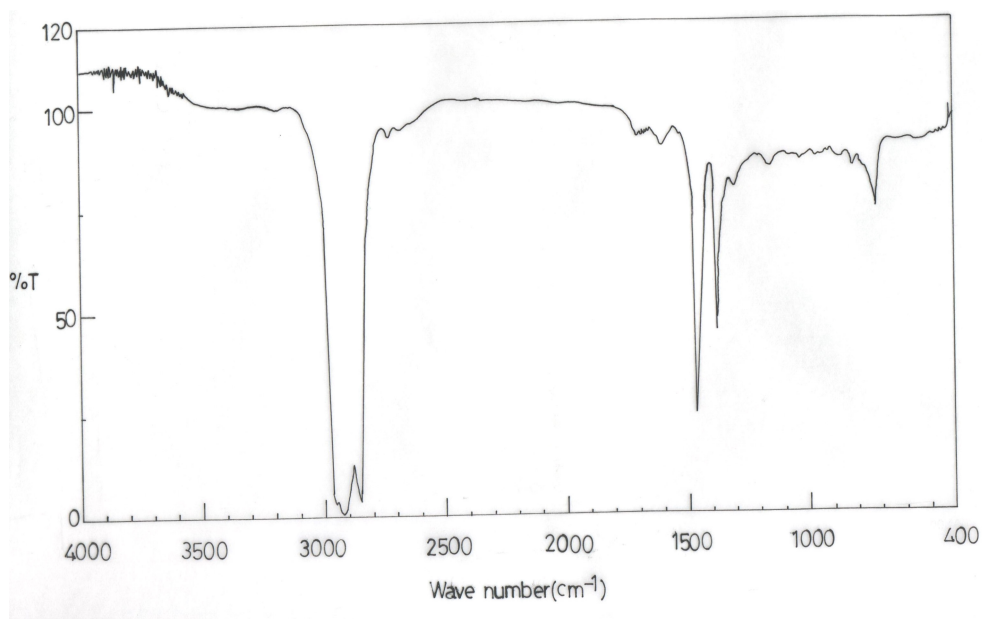


Fig. 1. Infra Red spectra (FT/IR-410 Spectrometer, Jasco) of the tested crude oil

Table 2. I.R signals and assignments of the used materials

Wave number (cm ⁻¹)	Assignment of chemical groups
3600 – 3700	Bounded Water
3400	Free Water
1000 – 1100	Ionic Phosphates
900	Ionic Carbonates
800 – 850	Silicon Carbide
700	Si or P or S
550	Conjugated Nitrite
550	Ionic Nitrite

Determination of petroleum hydrocarbons in water was done by using the American society for testing and materials ASTM D-3921, 2002.

A calibration curve for determining the amount of oil on the surface of saline water was constructing by following these steps. Prepare a stock solution of crude oil by rapidly transferring 1 ml of the crude oil to a tared 100 mL volumetric flask. Stopper flask and weigh to nearest milligram. Add trichlorotrifluoroethane solvent to dissolve and dilute to mark. Using volumetric techniques, prepare a series of standards. Select a pair of matched near-infrared silica cells. A 1-cm-path-length cell is appropriate. Scan standards and samples from 3200 cm⁻¹ to 2700 cm⁻¹ with solvent in reference beam and record results on absorbance paper. Measure absorbances of samples and standards by constructing a straight base line over the scan range and measuring absorbance of the maximum peak at 2930 cm⁻¹ and subtracting base line absorbance at that point. Use scans of standards to prepare a calibration curve as in Figure (2).

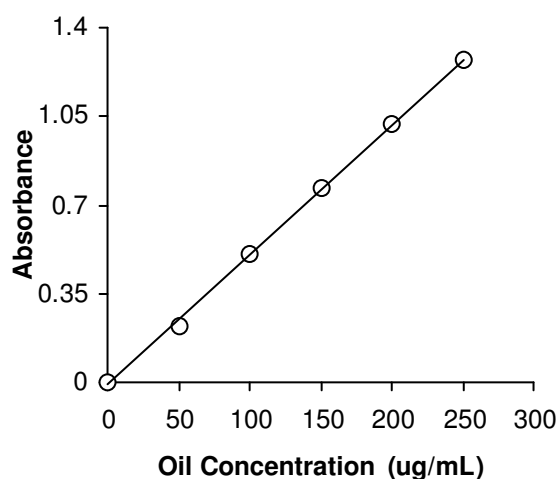


Fig. 2. Calibration curve of the tested crude oil

Procedure of determination was done by transferring the water sample to a separatory funnel coated with silicone oil, and extracting the petroleum crude oil by shaking the water sample with 30 mL trichlorotrifluoroethane solvent. Drain the solvent from bottom. Shake the water sample with another 30 mL of the solvent. Repeat with a final 30 mL of the solvent. Transfer extracts to 100 ml volumetric flask and dilute to the mark. Measure the absorbance. Measure the volume of extracted water. Calculate the concentration of the crude oil in water according to the following equation:

$$C = (R \times D) / V$$

where,

C ; Concentration of crude oil, mg/L.

R; Amount of crude oil in 100 mL of untreated extract, mg.

D; Dilution factor;

$$D = (\text{Volume of diluted extract}) / (\text{Volume of undiluted extract}).$$

V; Volume of extracted water.

The uptake efficiency of the petroleum crude oil on *Cynanchum acutum* L. plant was calculated according to the equation:

$$\text{Uptake efficiency \%} = ((C_o - C_w)/C_o) \times 100$$

where,

W_o is the initial concentration and W_w is the final concentration.

The adsorption isotherm in dilute solution is formulated by Freundlich (Kin H. Tan, 1998) as:

$$C_s = K C_w^n$$

where

C_s is the amount of oil retained by unit mass of sorbent

C_w ; the amount of oil in water

K, n ; constants

Another version of Freundlich is

$$K_d = C_s / C_w$$

Where the distribution ratio (K_d) describes the portioning of the oil between adsorbent and liquid phases. Strongly adsorbed oil exhibits high K_d values. The K_d is also affected by temperature, degree of salinity, material weight, and concentration of some cations and anions that is commonly present in water.

3. PROCEDURE OF TREATMENT

A sample of 0.6 g of crude oil was added to a 1 L-Beaker containing 750 mL saline water at. The Beaker walls were coated formally, with silicone oil to prevent crude oil from sticking to the walls. The Beaker content were shaken using a thermostatic water bath at different condition parameters of degree of salinity, temperature, sorbing time and sorbent weight to simulate sea waves. A weighed sample of the used materials was spread over the surface of water to sorb crude oil from the surface, where substantial amounts of crude were seen to sink. A fixed volume of trichlorotrifluoroethane was carefully added to the surface of water to extract the remaining crude, if present. Trichlorotrifluoroethane layer was subsequently siphoned off the water surface and subjected to quantitative analysis.

4. RESULTS AND DISCUSSION

The uptake efficiency percent of magnesium, calcium carbonates and oxides to remove oil spills from the surface of saline water was studied at various condition parameters of degree of salinity, expressed as sodium chloride concentration, contacting time, permanent hardness, expressed as calcium and magnesium chloride and temporary hardness expressed as sodium bicarbonate and carbonate. Also, the used materials were studied after soaking in dodecylsulphonic acid.

The effect of the contacting time, expressed in minutes, on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with 2 g of 63 µm particle size of the used materials for different contacting times. Fig. 8.; shows that uptake efficiency percent of the used materials increases as contacting time increases till it reaches a maximum value 79, 92, 89,71% for $MgCO_3$, $CaCO_3$, MgO , CaO respectively at 5 minutes.

The effect of loading weight, expressed in grams, on sorption of oil spill from the surface of saline water was studied by contacting a saline water of 5 M sodium chloride of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with different weights of MgCO₃, CaCO₃, MgO, CaO for 7 minutes. Fig. 4 shows that as the loading weight increases, the uptake efficient percent increases till it reaches maximum value of 79, 92, 89, 71% for MgCO₃, CaCO₃, MgO, CaO at 1.6, 1.2, 2, 2.4 g, respectively. This due to the surface area increase as the weight increases.

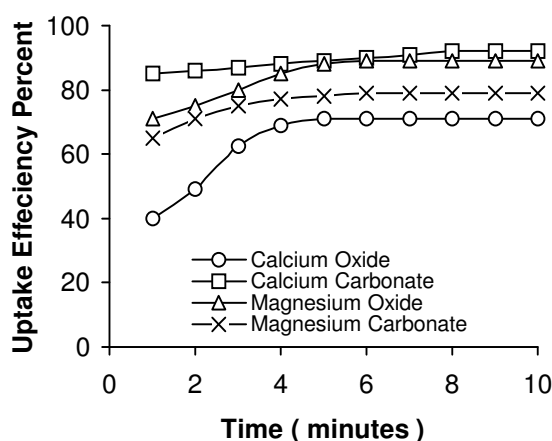


Fig. 3. Effect of contacting time on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 5 M NaCl, 30°C, 0.6 g crude oil and sorbent weight 1.6, 1.2, 2, 2.4 g of 63 μ m particle size for each respectively

The effect of the degree of salinity, expressed in sodium chloride concentration units, on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of different concentrations of sodium chloride, expressed in molarity of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with 1.6, 1.2, 2, 2.4 g of MgCO₃, CaCO₃, MgO, CaO for 7 minute. Fig. 7 shows that as the concentration of sodium chloride increases, the uptake efficiency percent of the used materials increases till it reaches a value of 79, 92, 89, 71% for MgCO₃, CaCO₃, MgO, CaO respectively at which, the maximum concentration is 5 M. This is due to the increase of the sedimentation rate of the used materials towards the bottom of water, which decreases contacting with the oil spill (ASTM D-4920, 2002).

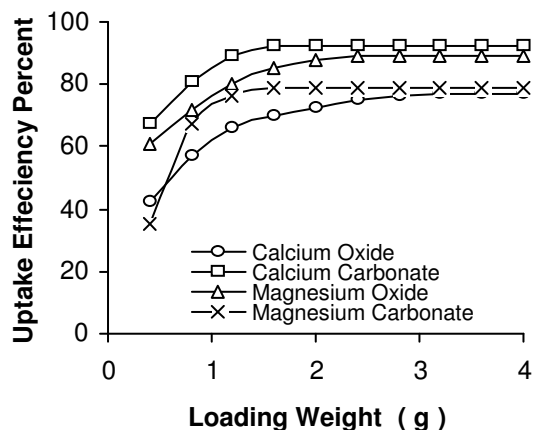


Fig. 4. Effect of loading weight on the uptake percent of magnesium, calcium oxides and carbonates sorbents at 5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and 63 μm particle size

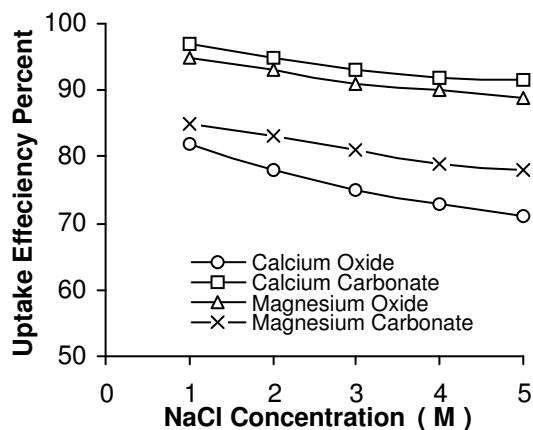


Fig. 5. Effect of NaCl concentration on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 30°C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of 63 μm particle size for each respectively

The effect of the temperature, expressed in degree C, on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of volume 750 mL that contains 0.6 g crude oil on its surface with 1.6, 1.2, 2, 2.4 g of MgCO_3 , CaCO_3 , MgO , CaO for 7 minute at different temperatures. Fig. 9 shows that the optimum temperature range of the used materials to sorb oil spills is 20 - 40°C indicating that the sorption process is an adsorption process and depends on the temperature.

The effect of particle size, expressed in μm , on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of volume 750 mL that contains 0.6 g crude oil on its surface with 1.6, 1.2, 2, 2.4 g of MgCO_3 , CaCO_3 , MgO , CaO for 7 minute at 30°C. Fig. 9.; shows that as the particle size increases the uptake efficiency percent of the used materials decreases till it reaches a value of 79, 92, 89, 71% for MgCO_3 , CaCO_3 , MgO , CaO respectively. This behavior was attributed to the increase of sedimentation rate with the increase in particle size.

The effect of permanent hardening calcium and magnesium cations, expressed as calcium and magnesium chloride and temporary hardening bicarbonate and carbonate anions, expressed as sodium bicarbonate and carbonate on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with 1.6, 1.2, 2, 2.4 g of MgCO_3 , CaCO_3 , MgO , CaO for 7 minutes. Figures (8-11) show that as the concentration of MgCl_2 , CaCl_2 increases the uptake efficiency percent decreases slightly to the slightly solubilization of the used materials and as NaHCO_3 and Na_2CO_3 increases, the uptake efficiency percent increases slightly. This

due to as the concentrations of these materials increase, the oil spill tends to be more viscous and not spread over a large area that enhance the contact between the oil spill and the used materials (Singh and Pandey, 1991; EPA, 1999).

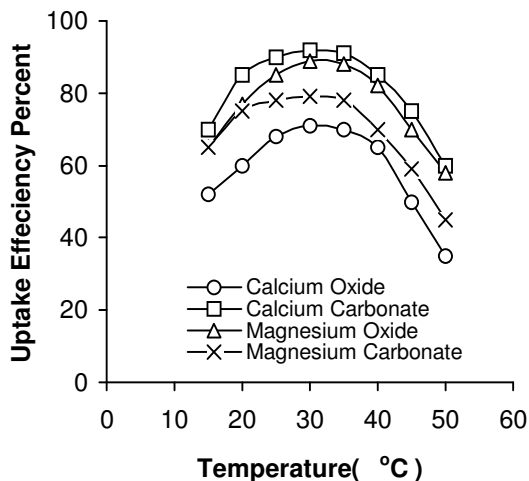


Fig. 6. Effect of temperature on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 5 M NaCl, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of 63 μm particle size for each respectively

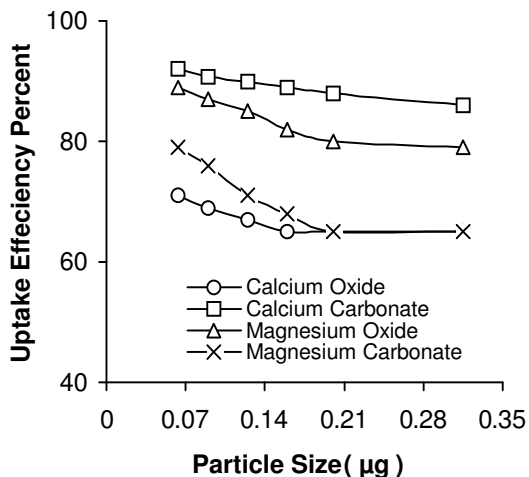


Fig. 7. Effect of particle size on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of different particle size for each respectively

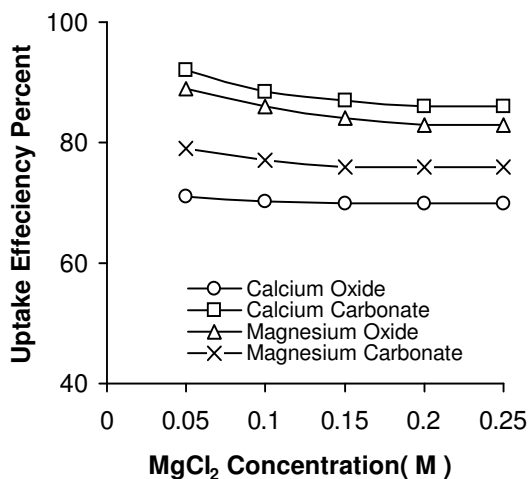


Fig. 8. Effect of magnesium chloride concentration on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of 63 μm particle size for each respectively

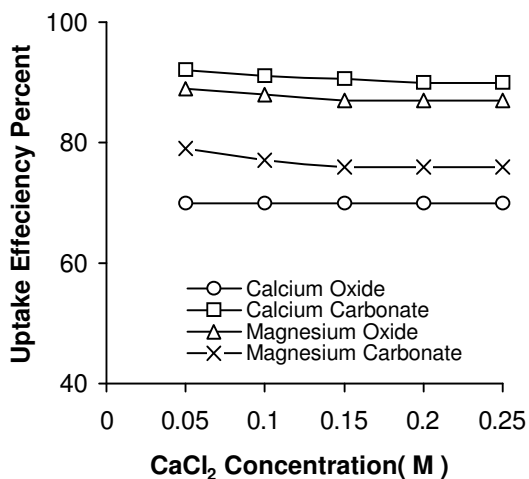


Fig. 9. Effect of calcium chloride concentration on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of 63 μm particle size for each respectively

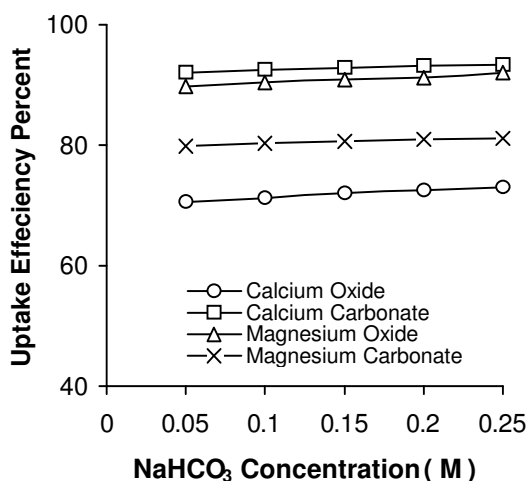


Fig. 10. Effect of sodium bicarbonate concentration on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of 63 μm particle size for each respectively

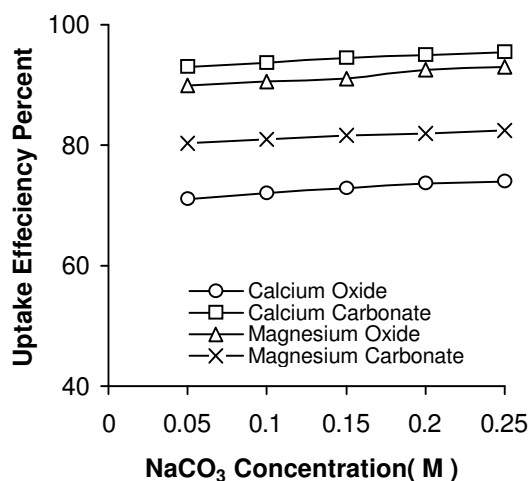
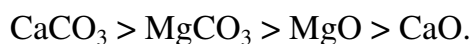


Fig. 11. Effect of sodium carbonate concentration on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of 63 μm particle size for each respectively

Distribution ratio (K_d) of the amount of oil retained by unit mass of the used materials to the amount of oil in water was studied by plotting C_s versus C_w at optimum conditions of contacting time 7 minutes, temperature 30°C, sodium chloride concentration 5 M and 1.6, 1.2, 2, 2.4 g of MgCO_3 , CaCO_3 , MgO , CaO respectively, as in Fig. 12, where the slope of the resulting straight line is K_d . It is clear from Fig. 12 that K_d is 0.49, 0.76, 0.44, 0.32 for MgCO_3 , CaCO_3 , MgO , CaO respectively. Since strongly adsorbed oil exhibits K_d values. Sorbed phases according to values obtained can be arranged in the following order:



The effect of treating of the used materials with different concentrations of dodecyl benzenesulphonic acid (where the used materials was soaked in different concentrations of dodecyl benzenesulphonic acid for 24 hours and dried with a dry stream of air), on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with the treated materials with dodecyl benzenesulphonic acid for 7 minutes. Fig. 13 shows that uptake efficiency percent increases as concentration of dodecyl benzenesulphonic acid increases till it reaches maximum value of about 95, 100, 95, 80 % for MgCO_3 , CaCO_3 , MgO , CaO at dodecyl benzenesulphonic acid concentrations 60, 30, 50, 40 $\mu\text{g/mL}$ respectively.

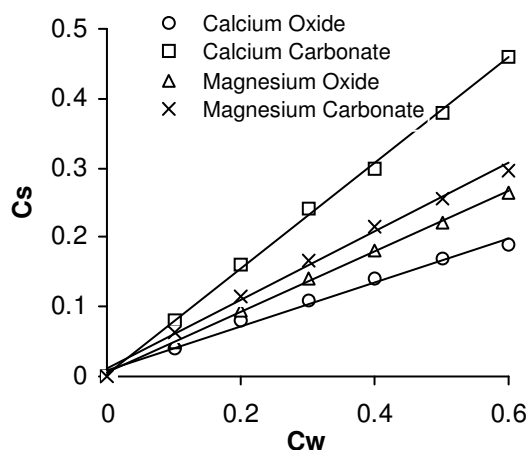


Fig. 12. Distribution ratio (K_d) between magnesium, calcium carbonates and oxides sorbed phases and the saline water at 5 M NaCl, 30°C, 0.6 g crude oil and 7 minutes and sorbent weight 1.6, 1.2, 2, 2.4 g for each respectively of 63 μm particle size

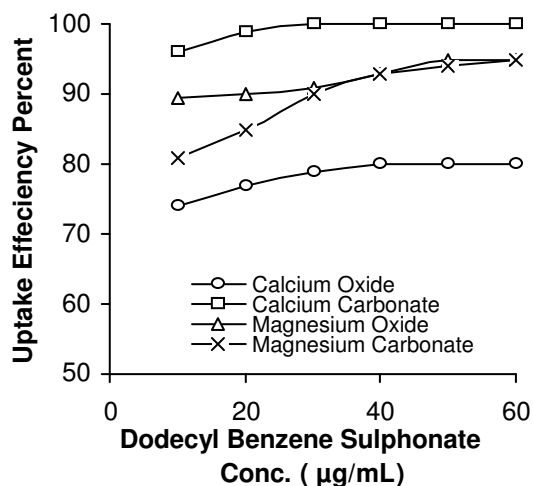


Fig. 13. Effect of treating of magnesium, calcium carbonates and oxides sorbents with dodecyl benzenesulphonic acid at 5 M NaCl, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of 63 μm particle size for each respectively on the uptake percent

The effect of the loading weight of those treated materials at the previous conditions is illustrated as in Fig.14. It is clearly seen that as the loading weight increases, the uptake efficient percent increases till it reaches maximum value of 79, 92, 89, 71% for the treated MgCO_3 , CaCO_3 , MgO , CaO at 1, 0.8, 1.2, 1.4 g respectively. Distribution ratio (K_d) of the amount of oil retained by unit mass of the used materials to the amount of oil in water was studied by plotting C_s versus C_w at optimum conditions of contacting time 7 minutes, temperature 30°C, sodium chloride concentration 5 M and 1, 0.8, 1.2, 1.4 g of the treated MgCO_3 , CaCO_3 , MgO , CaO respectively, as in Fig. 15, where, the slope of the resulting straight line is K_d . It is clear from Fig. 15 that K_d is 0.95, 1.25, 0.78, 0.56 for MgCO_3 , CaCO_3 , MgO , CaO respectively. Comparing those values of the K_d with that of the untreated forms, one can predict that the treating process rises the uptake efficiency twice more.

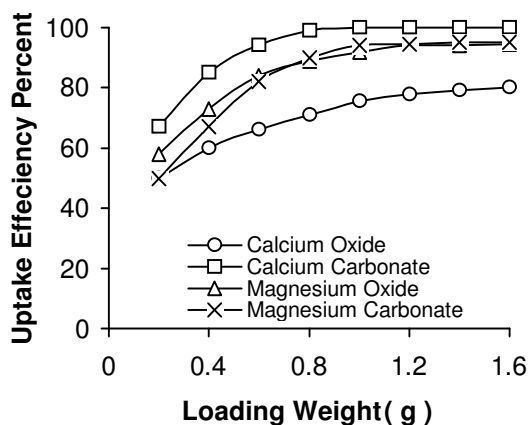


Fig. 14. Effect of loading weight on the uptake percent of magnesium, calcium carbonates and oxides sorbents at 5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and 63 μ m particle size

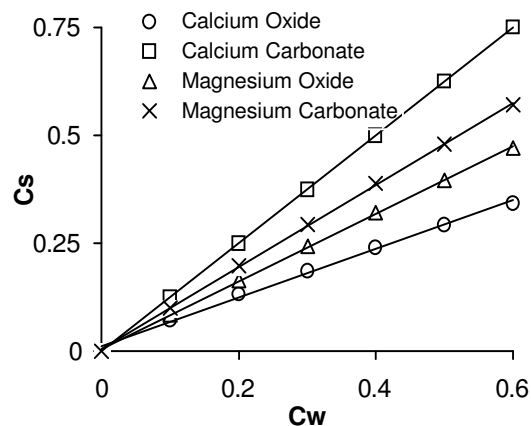


Fig. 15. Distribution ratio (K_d) between treated magnesium, calcium oxides and carbonates with dodecyl benzenesulphonate sorbed phases and the saline water at 5 M NaCl, 30°C, 0.6 g crude oil and 7 minutes and sorbent weight 1.4, 0.8, 1.2, 1 g of 63 μ m particle size for each respectively

Sorbed crude oil can be stripped from the used materials by naphtha (a petroleum product of boiling range 30-165°C) or kerosene (a petroleum product of boiling range 150-220°C). Kerosene is much cheaper than naphtha. The stripped materials are charged to reuse again. Contaminated naphtha or kerosene is distilled and is returned for further reuse. The residue is pumped to crude oil as a feed for refineries. Figures (16, 17) show that two minutes is sufficient to strip about 87, 55, 80, 60 % from $MgCO_3$, $CaCO_3$, MgO , CaO respectively, in case of using naphtha as a stripper and 9 minutes is sufficient to strip about 48.5, 47, 50, 46.5 % from $MgCO_3$, $CaCO_3$, MgO , CaO respectively, in case of using kerosene as a stripper. Figures (18, 19) show that 25 mL is sufficient to strip about 94, 90, 92, 94 % from $MgCO_3$, $CaCO_3$, MgO , CaO respectively, in case of using naphtha as a stripper and 15 mL is sufficient to strip about 61, 57, 63, 59 % from $MgCO_3$, $CaCO_3$, MgO , CaO respectively, in case of using kerosene as a stripper. So, using naphtha as a stripper is much more efficient than kerosene.

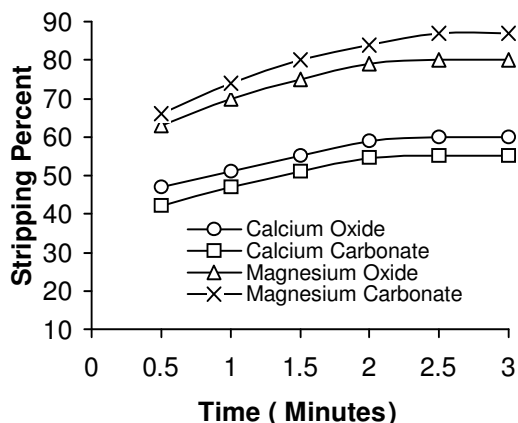


Fig. 16. Stripping time of petroleum crude oil from 1.6, 1.2, 2, 2.4 g of magnesium, calcium carbonates and oxides by 5 mL naphtha respectively

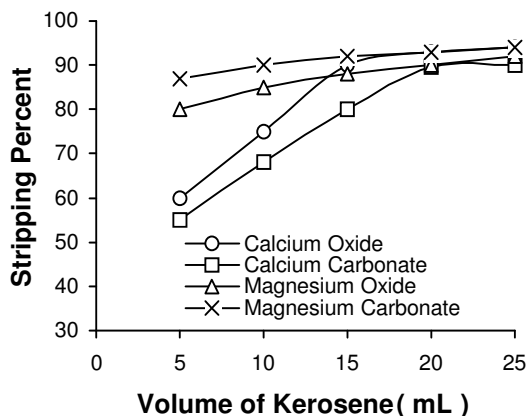


Fig. 17. Stripping volume of petroleum crude oil from 1.6, 1.2, 2, 2.4 g of magnesium, calcium carbonates and oxides by naphtha respectively at 2 minutes stripping time

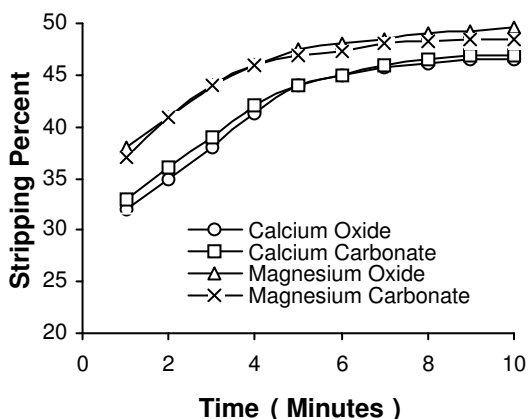


Fig. 18. Stripping time of petroleum crude oil from 1.6, 1.2, 2, 2.4 g of magnesium, calcium carbonates and oxides by 5 mL kerosene respectively

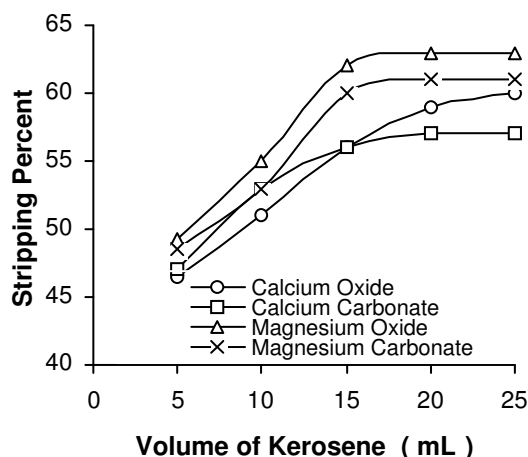


Fig. 19. Stripping volume of petroleum crude oil from 1.6, 1.2, 2, 2.4 g of magnesium, calcium carbonates and oxides by kerosene respectively at 9 minutes

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