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Removal of Oil Spills from Salt Water by Magnesium, Calcium Carbonates and Oxides

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ABSTRACT: Magnesium, calcium carbonates and oxides that 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 dodecyl benzene sulphonic acid alcohol was studied to enhance the sorption efficiency. Results obtained showed that treated $MgCO_3$, $CaCO_3$, MgO and CaO with dodecyl benzene sulphonic 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 extracting the crude oil in tricholorotrifluoroethane and measuring absorbance by FTIR spectrometer. @*JASEM*

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). 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). Therefore the aim of this research work is to examine the effectiveness of $MgCO_3$, $CaCO_3$, MgO and CaO to cleanup oil spills.

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EXPERIMENTAL

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
Sulfur % 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 were demonstrated in Table (2) and were shown in our earlier publication as Fig 1 (Sayed *et al* 2003) and is not shown here for brevity. Inspection of these spectra reveals the presence of the following two peaks at wave no. 2923 cm^{-1} and 2853 cm^{-1} represent $–CH_3$ and $–CH_2–$ stretching frequencies; two peaks at wave no 1462cm^{-1} and 1377cm^{-1} represent –CH3 and $–CH_2–$ bending frequencies and peak at 722cm^{-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 (Silverstein, et al., 1991.; Wauquier, 1995).

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

Table 2. Infra Red signals and assignments of the crude oil.

Wave number (cm^{-1})	Assignment of chemical groups
2923	$–CH_3$ stretching
2853	$–CH_2–$ stretching
1462	$–CH_3$ bending
1377	$–CH_2–$ bending
722	Aliphatic hydrocarbons of chains containing carbon atoms ≥ 7

Determination of petroleum hydrocarbons in water was done 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 1,1,2 tricholoro-1,2,2 trifluoroethane 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-lenghth 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).

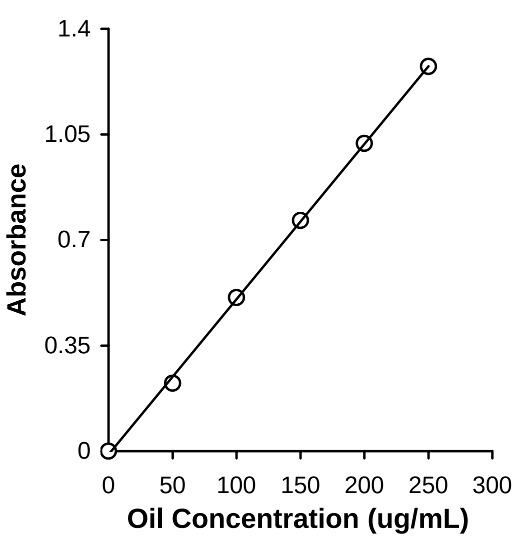


Fig. 2. Calibration curve of the tested crude oil.

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 1,1,2 tricholoro-1,2,2 trifluoroethane 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:

$$C = \frac{RxD}{V}$$

Where,

C = Concentration of crude oil, mg/L.

R = Amount of crude oil in 100 ml of untreated extract, mg.

V = Volume of extracted water.

D = Dilution factor;

$$D = \frac{V_d}{V_a}$$

V_d = Volume of diluted extracted water; V_a = Volume of undiluted extracted water.

The uptake efficiency of the petroleum crude oil on $MgCO_3$, $CaCO_3$, MgO and CaO was calculated according to the equation:

$$\text{Uptake efficiency \%} = \frac{C_o - C_w}{C_w} x100$$

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:

$$C_s = KC_w^n$$

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

$$K_d = \frac{C_s}{C_w}$$

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 are commonly present in water.

PROCEDURE OF TREATMENT

A sample of 0.6 g of crude oil was added to a 1 L-Beaker containing 750mL saline water at. The Beaker walls were coated formally, with silicone oil to prevent crude oil from sticking to the walls. The Beaker content was 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 1,1,2 tricholoro-1,2,2 trifluoroethane was carefully added to the surface of water to extract the remaining crude, if present. The solvent 1,1,2 tricholoro-1,2,2 trifluoroethane layer was subsequently siphoned off the water surface and subjected to quantitative analysis.

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 contacting time, loading weight, degree of salinity, temperature, temporary and permanent hardness. Also, the used materials were studied after soaking in dodecyl benzene sulphonic acid. The effect of the contacting time on sorption of oil spill was studied by contacting 0.6 g crude oil on a saline solution; 750 ml of 0.5 M NaCl at 30°C with 2 g of $MgCO_3$ or $CaCO_3$ or MgO or CaO of particle size less than 63 µm for different contacting times. Fig.3 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 and CaO respectively at 7 minutes. The effect of loading weight on sorption of oil spill was studied by contacting 0.6 g crude oil on a saline solution; 750 ml of 0.5 M NaCl at 30°C with different weights of $MgCO_3$, $CaCO_3$, MgO and CaO of particle size less than 63 µm 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 $MgCO_3$, $CaCO_3$, MgO and CaO at 1.6, 1.2, 2, 2.4 g of each respectively. This due to the surface area increase as the weight increases.

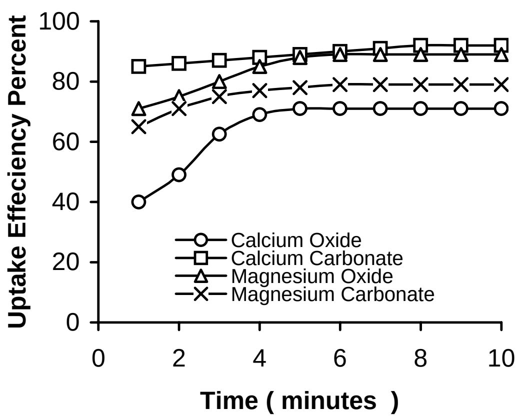


Fig.3. Effect of contacting time on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 0.5 M NaCl, 30°C, 0.6 g crude oil and 1.6, 1.2, 2, 2.4 g of particle size less than 63 µm for each respectively.

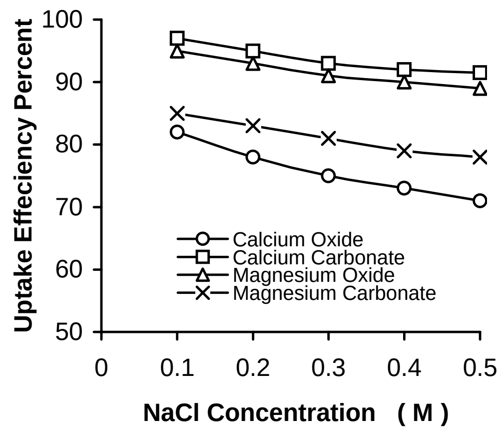


Fig.4. Effect of loading weight on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 0.5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and particle size less than 63 µm.

The effect of the degree of salinity on sorption of oil spill was studied by contacting 0.6 g crude oil on a saline solution; 750 ml of different concentrations of NaCl at 30^{o}C with 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO of particle size less than 63 µm for 7 minutes. Fig.5 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 the adsorbents; $MgCO_3$, $CaCO_3$, MgO and CaO respectively at which, the maximum concentration is 0.5 M, where water is considered to be saline if it at least contains 0.5 M NaCl. This is attributed to the increase of increase the sedimentation rate of $MgCO_3$, $CaCO_3$, MgO and CaO towards the bottom of water which decreases contacting with the oil spill (Foss and Nilsen, 1996; ASTM D-4920, 2002).

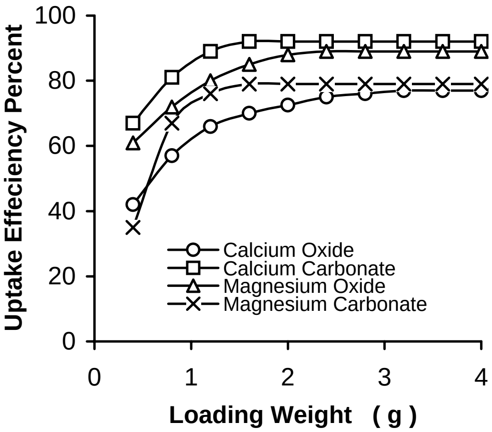


Fig.5. Effect of NaCl concentration on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 30^{o}C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of particle size less than 63 µm for each respectively.

The effect of the temperature sorption of oil spill was studied by contacting 0.6 g crude oil on a saline solution; 750 ml of 0.5 M NaCl with 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO of particle size less than 63 µm for 7 minutes at different temperatures. Fig.6 shows that the optimum temperature range of the used materials to adsorb oil spills is 20 - 40^{o}C indicating that the sorption process is an adsorption process and depends on the temperature. The effect of particle size on sorption of oil spill was studied by contacting 0.6 g crude oil on a saline solution; 750 ml of 0.5 M NaCl with 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO of particle size less than 63 µm for 7 minutes at 30^{o}C. Fig.7 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 and CaO respectively. This behavior was attributed to the increase of sedimentation rate with the increase in particle size. The effect of temporary hardness; bicarbonate and carbonate anions expressed as sodium bicarbonate and carbonate and permanent hardness; calcium and magnesium cations, expressed as calcium and magnesium chloride on sorption of oil spill was studied by contacting 0.6 g crude oil on a saline water; 750 ml of 0.5 M NaCl that contains different concentrations of sodium bicarbonate and carbonate, calcium and magnesium chloride at 30^{o}C with 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO of particle size less than 63 µm for 7 minutes. Figs. (8-11) show that as the concentration of $MgCl_2$, $CaCl_2$ increases the uptake efficiency percent decreases slightly due to the exchange of calcium and magnesium ions with the $MgCO_3$, $CaCO_3$, MgO and CaO which hinders the adsorption of crude oil molecules and as $NaHCO_3$ and Na_2CO_3 increases, the uptake efficiency percent increases slightly. This due to as the concentrations of $NaHCO_3$ and Na_2CO_3 increase, the oil spill tends to not spread over a large area that enhance the contact between the oil spill and $MgCO_3$, $CaCO_3$, MgO and CaO (Singh and Pandey, 1991; EPA, 1999). Distribution ratio (K_d) of the amount of oil retained by unit mass of $MgCO_3$, $CaCO_3$, MgO and CaO to the amount of oil in water was studied by plotting Cs versus Cw at optimum conditions of contacting time 7 minute, temperature 30^{o}C, 0.5 M NaCl and 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO of particle size less than 63 µm respectively, as in Fig. 12, where, the slope of the resulting straight line is distribution ratio K_d . It is clear from the Fig.12. that K_d is 0.49, 0.76, 0.44, 0.32 for the adsorbents $MgCO_3$, $CaCO_3$, MgO and CaO respectively. Since strongly adsorbed oil exhibits K_d values. Sorbed phases according to values obtained can be arranged in the following order:

CaCO3 > MgCO3 > MgO > CaO. The effect of treating $MgCO_3$, $CaCO_3$, MgO and CaO with different concentrations of dodecyl benzene sulphonic acid (where the used materials was soaked in different concentrations of dodecyl benzene sulphonic acid for 24 hours and dried with a dry stream of air), on sorption of oil was studied by contacting 0.6 g crude oil on a saline solution; 750 ml of 0.5 NaCl at 30^{o}C with 1.6, 1.2, 2 and 2.4 g of the treated $MgCO_3$, $CaCO_3$, MgO and CaO with dodecyl benzene sulphonic acid for 7 minutes. Fig.13 shows that uptake efficiency percent increases as concentration of dodecyl benzene sulphonic acid increases till it reaches maximum value of about 95, 100, 95, 80 % for $MgCO_3$, $CaCO_3$, MgO, CaO at dodecyl benzene sulphonic acid concentrations 60, 30, 50, 40 µg/ml respectively. 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 treated $MgCO_3$, $CaCO_3$, MgO and CaO with dodecyl benzene sulphonic acid to the amount of oil in water was studied by plotting Cs versus Cw at optimum conditions of contacting time 7 minute, temperature 30^{o}C, sodium chloride concentration 0.5 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 the Fig.15. that K_d is 0.95, 1.25, 0.78, 0.56 for $MgCO_3$, $CaCO_3$, MgO and CaO respectively. Comparing those values of the K_d with that of the untreated forms, one can predict that the treating process raises the uptake efficiency twice more. Adsorbed crude oil can be stripped from the used materials by naphtha (a petroleum product of boiling range 30-165^{o}C) or kerosene (a petroleum product of boiling range 150-220^{o}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. Figs.(16,17); show that two minutes is sufficient to strip about 87, 55, 80, 60 % from $MgCO_3$, $CaCO_3$, MgO and 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 and CaO respectively, in case of using kerosene as a stripper. Figs.(18,19); show that 25 mL is sufficient to strip about 94, 90, 92, 94 % from $MgCO_3$, $CaCO_3$, MgO and 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 and CaO respectively, in case of using kerosene as a stripper. So, using naphtha as a stripper is much more efficient than kerosene. Also, $MgCO_3$, $CaCO_3$, MgO and CaO can be reused again to adsorb further crude oil or can be charged to the cement factories to be reused in the manufacture of cement.

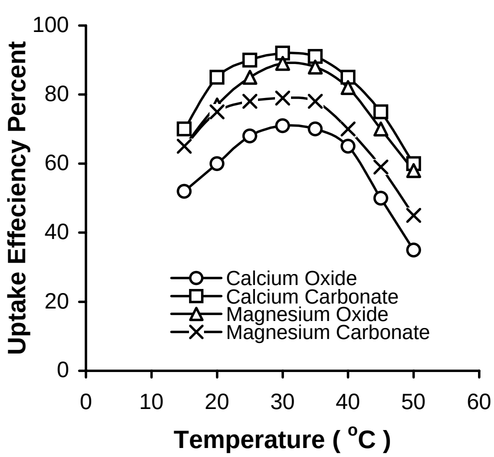
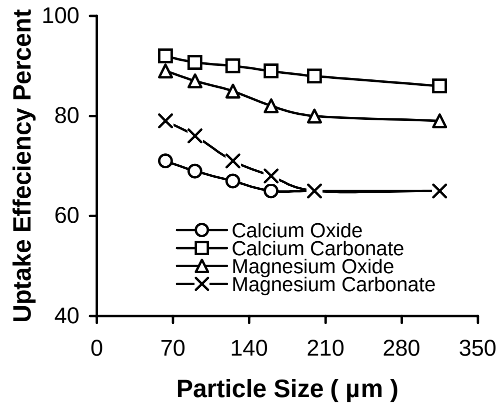


Fig.6. Effect of temperature on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 0.5 M NaCl, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of particle size less than 63 µm for each respectively.



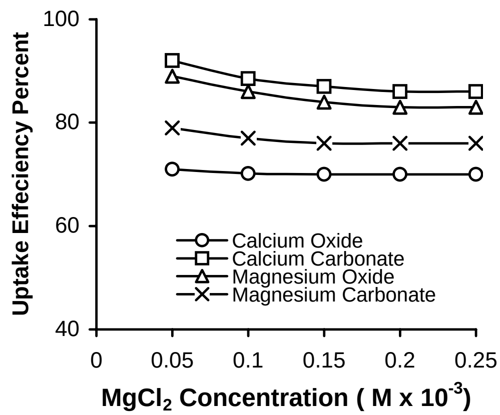


Fig.7. Effect of particle size on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 0.5 M NaCl, 30^{o}C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of different particle size for each respectively

Fig.8. Effect of magnesium chloride concentration on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 0.5 M NaCl, 30^{o}C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of particle size less than 63 µm for each respectively.

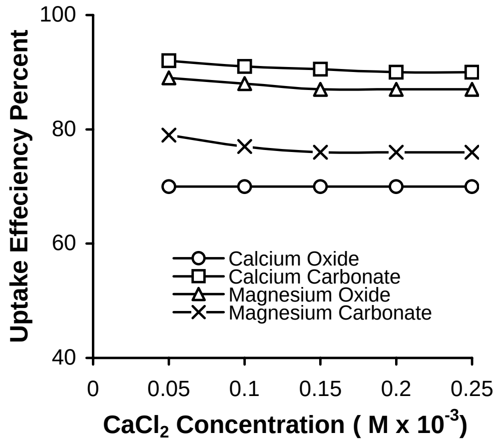


Fig.9. Effect of calcium chloride concentration on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 0.5 M NaCl, 30^{o}C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of particle size less than 63 µm for each respectively.

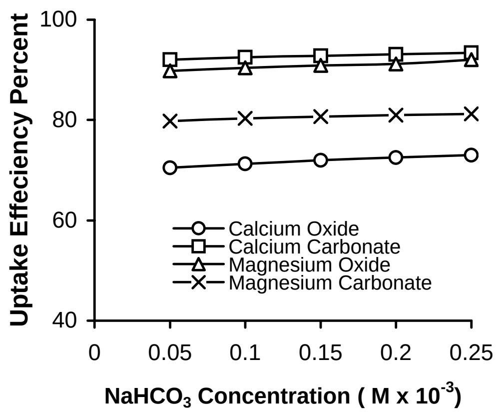


Fig.10. Effect of sodium bicarbonate concentration on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 0.5 M NaCl, 30^{o}C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of particle size less than 63 µm for each respectively.

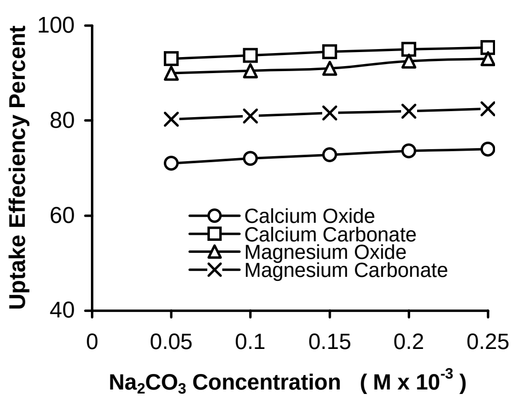


Fig.11. Effect of sodium carbonate concentration on the uptake efficiency percent of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents at 0.5 M NaCl, 30^{o}C, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of 63 µm particle size for each respectively.

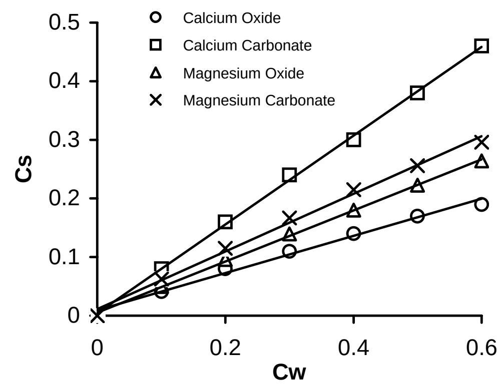


Fig.12. Distribution ratio (Kd) between $MgCO_3$, $CaCO_3$, MgO and CaO adsorbed phases and the saline water at 0.5 M NaCl, 30^{o}C, 0.6 g crude oil and 7 minutes and 1.6, 1.2, 2, 2.4 g of particle size less than 63 µm for each respectively.

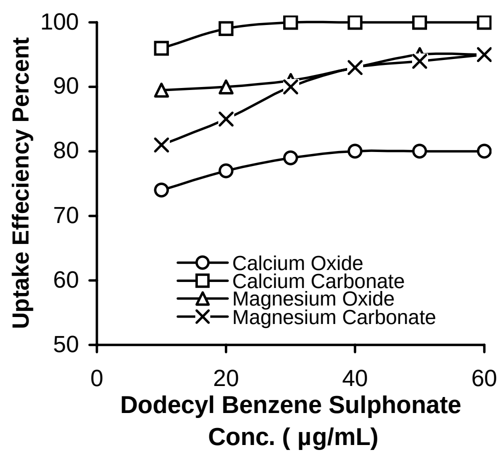


Fig.13. Effect of treating of $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents with dodecyl benzene sulphonic acid on the uptake efficiency percent at 0.5 M NaCl, 0.6 g crude oil, 7 minutes and 1.6, 1.2, 2, 2.4 g of particle size less than 63 µm for each respectively.

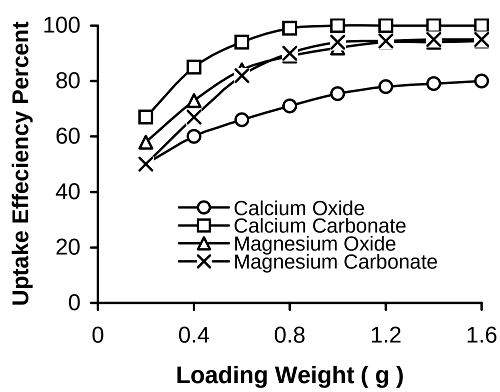


Fig.14. Effect of loading weight on the uptake efficiency percent of the treated $MgCO_3$, $CaCO_3$, MgO and CaO adsorbents with dodecyl benzene sulphonic acid adsorbents

at 0.5 M NaCl, 30°C, 0.6 g crude oil, 7 minutes and particle size less than 63 µm.

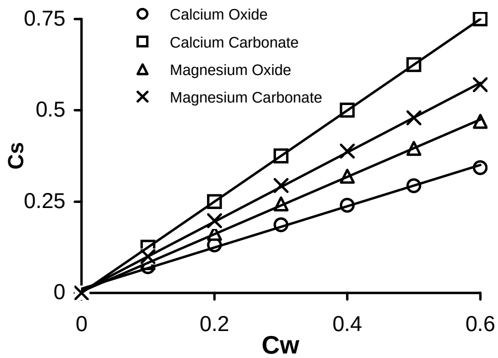


Fig.15. Distribution ratio (Kd) between treated $MgCO_3$, $CaCO_3$, MgO and CaO with dodecyl benzene sulphonic acid adsorbed phases and the saline water at 0.5 M NaCl, 30°C, 0.6 g crude oil and 7 minutes and 1.4, 0.8, 1.2, 1 g of particle size less than 63 µm for each respectively.

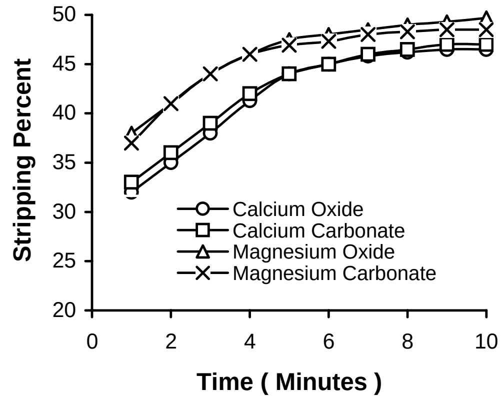


Fig.18. Stripping time of petroleum crude oil from 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO by 5 mL kerosene respectively.

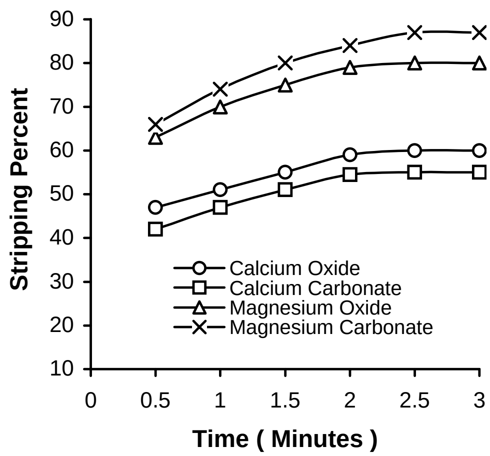


Fig.16. Stripping time of petroleum crude oil from 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO by 5 mL naphtha respectively.

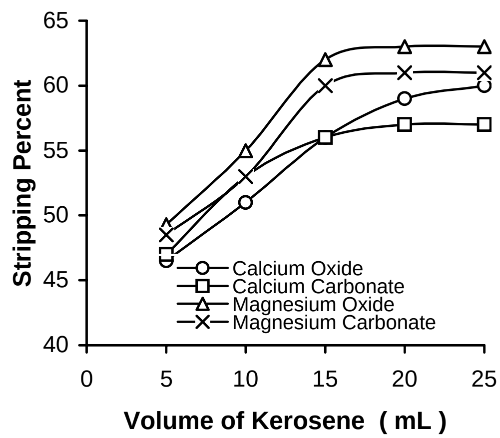


Fig.19. Stripping of petroleum crude oil from 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO by kerosene respectively at 9 minutes.

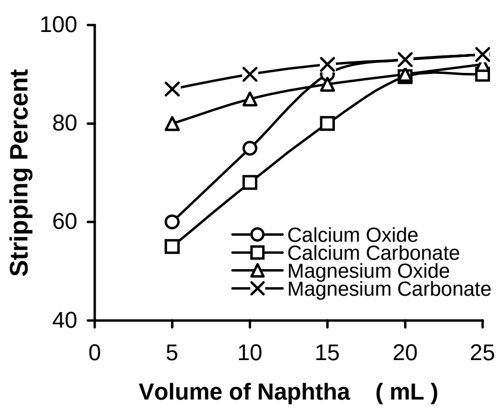


Fig.17. Stripping of petroleum crude oil from 1.6, 1.2, 2, 2.4 g of $MgCO_3$, $CaCO_3$, MgO and CaO by kerosene respectively at 9 minutes.

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