



Treatment of Liquid Oil Spill by Untreated and Treated Aswanly Clay from Egypt

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ABSTRACT: The aim of this work is to use cheap, available and recyclable sorbents for oil spill clean - up. α -SiO₂-Quartz, Na₂Si₂O₅(OH)₄, CaCO₃, MgCO₃, BaCO₃, CaO, MgO, and Fe₂O₃ are used individually or mixed with Aswanly clay to identify the sorption activity of these materials and to show the effect of incorporation of these materials into the Aswanly clay. Results were 63, 75, 100, 93, 95,75, 92, 100, 80, 98, 90, 71, 90 and 97% on using 1.0 g α -SiO₂-Quartz, 0.9 g Na₂Si₂O₅(OH)₄, 0.07 g CaCO₃, 0.05 g MgCO₃, 0.08 g BaCO₃, 0.05g CaO, 0.1 g MgO, and 0.08 g Fe₂O₃, 0.1 g clay mixture of 50% CaCO₃, 0.1 g clay mixture of 10% MgCO₃, 0.1 g clay mixture of 50% BaCO₃, 0.1 g clay mixture of 50% CaO, 0.1 g clay mixture of 10% MgO, and 0.1 g clay mixture of 50% Fe₂O₃ respectively, to remove 14.07 mg crude oil, below which mechanical means for removing crude oil from oil contaminated water becomes less more effective, from oil contaminated water of volume 25 ml from oil contaminated water at pH 6 and temperature 30°C. All of these materials were treated by naphtha, a petroleum product of boiling range 30°C - 165°C, to remove sorbed crude oil from its surface for further reuse and contaminated naphtha are processed to be distilled for reuse. Characteristics of crude oil and Aswanly clay were investigated by FTIR, X - Ray Fluorescence, X - Ray Diffraction, pour point and centrifuge instruments. Determination of amount of crude oil in water was done by extraction the crude oil with 10 ml n-hexane and measuring absorbance by UV - VIS. 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 (Berridge, 1968; Piwoni and Banerjee, 19899 and William and Morse, 1979). According to the complex nature of oils, they do not behave as the same in the environment. Some constituents are noted for their tendency to vaporize while others clearly prefer to bind to solids; some oil hydrocarbons are extremely unreactive while other interacts with light,

so they have different toxicological effects on the aquatic life and hence on human being (Bo, 1987; Ralph, 1955; Rene, 1983).

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

Parameters	Test method	Results	
Density at 15°C	kg /l.	IP 160	0.8544
Sediment	% mass	IP 53	NIL
Water	% Vol.	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		130
Vanadium	µg/ml	Inductive Coupled Plasma	70
Chromium	µg/ml		30

Figure 1 shows the I.R spectra (FT/IR-410 Spectrometer, Jasco) of the tested petroleum crude oil. Inspection of these spectra reveals the presence

of the following two peaks at wave no. 2923 cm⁻¹ and 2853 cm⁻¹ represent -CH₃ and -CH₂- stretching frequencies; two peaks at wave no 1462cm⁻¹ and

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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 of the following physical properties (Wauquier *et al.*, 1995).

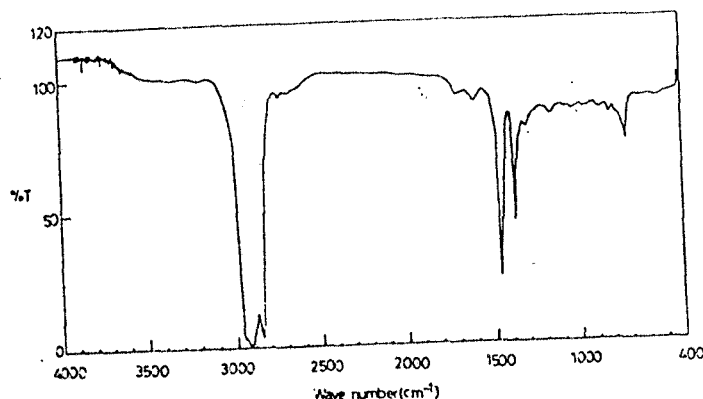


Fig.1. I.R spectra (FT/IR-410 Spectrometer, Jasco) of the tested petroleum crude oil

Bryk and Yakovenco, (1987), showed that treating water with oil spills necessitated the use of an oleophilic adsorbent, which must have magnetic properties to permit ready collection. Fuel oil and clay with a high content of iron oxides underwent thermal oxidation destruction to produce a uniform, black, powdery, porous hydrophobic product whose capacity for petroleum adsorption is 3.5 – 4 g/g. The iron oxides were reduced to ferromagnetic forms, and the magnetic susceptibility of the thermally treated composition reached a maximum after 90 minutes of treatment at 360°C. Complete restoration of the magnetic and sorption properties of the adsorbent is achievable at 350°C for 2 hours.

James and Shan, 1996 removed spilled oil from shorelines or from the surface of a body of water by adding to the surface a mixture of fine hydrophilic mineral solids dispersed in an aqueous liquid that interacts with the oil to form buoyant mineral fines-oil floccules. These floccules reduce the tendency of the oil to adhere to solid surfaces or to recombine, thus facilitating dispersion and removal of the oil.

A chemical composition and method for treating oil-contaminated wastewater and more particularly, waste water in the form of oily emulsions that may also contain dissolved metal ions, and/or metal solids, to sorb (adsorb and/or absorb) the contaminants between and within platelets of sodium bentonite clay particles, and calcium bentonite clay particles, and the contaminants are encapsulated or trapped in a mixture of calcium bentonite platelets and sodium bentonite platelets that are flocculated by a flocculent, such as cationic polymer, so that leaching of contaminants into the wastewater, or subsequently

into a liquid portion of a landfill is unexpectedly reduced (Laura 1997).

Among many different clays spread all over our country, Egypt (Abou El Naga *et al.*, 1998), Aswanly clay (which is mechanically grounded to 160-micron mesh size) is selected for the purpose of treatment of oil spills and industrial wastewater, because of its wide use in the ceramic industry. X-ray fluorescence analysis (Sequential XRF, Applied Research Laboratories, ARL 9400) by fusing the Aswanly clay with potassium tetra-borate as diluent is given in details in Table 2; in order to identify other impurities present within the clay structure, which may affect the uptake of oils.

X-Ray diffraction (Phillips X - Ray diffraction, PW 1010) with scanning limited from $2\theta = 6$ to $2\theta = 62$ on the copper target with nickel filter of the untreated clay is presented in Table 2. It is obvious that the main components are α - SiO_2 -Quartz, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, FeO , γ - Fe_2SiO_4 , $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$ and Fe_2O_3 which are designated by capital letters A, B, C, D, E, F respectively Nelson-Smith, 1973 and Wauquier, 1995). The observable signals of the infrared spectra of the applied material - untreated clay is given in Table 3.

Aswanly clay was used formerly to sorb crude oil from oil-contaminated water in a previous work Sayed and Abu Bakr, 2002. Uptake efficiency percent were 65% on using 0.1 g untreated Aswanly clay, 89% on using thermally treated Aswanly clay at 1200°C and 90% on using chemically treated Aswanly clay with hot concentrated phosphoric acid.

Table 2. X-ray fluorescence analyses of the Aswanly clay

Oxide	Mass %	Element	Mass %	Oxide	Mass %	Element	Mass %
SiO ₂	58.5	Si	27.35	HfO ₂	0.0773	Hf	0.0656
Al ₂ O ₃	27.58	Al	14.6	MnO	0.0690	Mn	0.0534
Fe ₂ O ₃	7.76	Fe	5.43	V ₂ O ₅	0.0347	V	0.0194
TiO ₂	1.75	Ti	1.05	ZrO ₂	0.0322	Zr	0.0238
K ₂ O	1.03	K	0.859	S	0.0297	S	0.0297
CaO	0.916	Ca	0.655	Cr ₂ O ₃	0.0247	Cr	0.0185
Na ₂ O	0.867	Na	0.643	SrO	0.0199	Sr	0.0168
MgO	0.745	Mg	0.449	Nb ₂ O ₅	0.0077	Nb	0.0054
ZnO	0.312	Zn	0.251	CuO	0.0042	Cu	0.0034
Cl	0.125	Cl	0.125	Ga ₂ O ₃	0.0028	Ga	0.0021
P	0.0952	P	0.0952				

Table 3. 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

EXPERIMENTAL

Ultra violet spectra of tested crude oil (Sayed and Abu Bakr, 2000) (Double beam UV-Spectrophotometer, Shimadzu 160A) in 10 ml n-hexane; at various concentrations, varied from 50 µg/ml to 1200 µg/ml. The mean peak occurs at wavelength range 285nm - 300nm.

A calibration curve of the tested crude oil in the Ultra violet range (Badr, *et al.*, 1988) in 10 ml n-hexane; at various concentrations, varied from 50 µg/ml to 1200 µg/ml; by measuring absorbance values using n-hexane as reference solution which obeys Beer's law up to 600 µg/ml. Above 600 µg/ml there is a negative deviation due to the impurities incorporated within the tested crude oil and chemicals and reagents were of a guaranteed grade used without further purification.

Then varied weights of the tested materials were contacted with aqueous solutions (25 ml) of different concentrations and constituents for different times and temperatures in a Macarity tubes and shackled in a thermostatic water bath shaker. The phases were separated by centrifugation and then the oil was extracted in n-hexane and then determined by measuring the absorbance value.

The uptake efficiency of the petroleum crude oil on the different used materials was calculated according to the equation:

$$\text{Uptake efficiency \%} = \left(\frac{W_o - W_w}{W_o} \right) \times 100$$

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

The adsorption isotherm in dilute solution was formulated by Freundlich (Kin 1998; Rene *et al.*, 1993) as:

$$C_s = K C_w^n$$

Where C_s is the amount of oil retained by unit mass of adsorbent C_w is the oil concentration and K, n are 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 pH, temperature, loading weight, and concentration of some cations and anions that are commonly present in water.

RESULTS AND DISCUSSION

The different parameters such as pH, temperature, loading weight, concentration of some cations and anions that are commonly present in water and affect the employed materials sorption activity were studied.

α-SiO₂ quartz and sodium silicate: α -SiO₂ quartz and sodium silicate form the greatest clay composition percent as shown from X.R.D and X.R.F analyses of the Aswanly clay, so that, the effect of pH and loading weight on sorption of oil on their surfaces were studied (Sayed and Abu Bakr, 2002).

Effect of pH: sorption process was studied by using an aqueous solution (25ml) covering all the pH range, containing 14.07 mg oil, 0.1 g loading weight, at 15min shaking time and at 30°C. The relation between the uptake efficiency percent and solution

pH is given in Fig. 2. It is clear that α -SiO₂ quartz and sodium silicate recorded high uptake efficiency percent at pH ≤ 3 , where the surface is positively charged and at pH ≥ 5 α -SiO₂ quartz shows slight gradual increase in the uptake efficiency percent increase due to the formation of colloidal silica and formation of silicate (Duncan, 1992) as the pH

increases till it reaches a maximum value at pH 11 and then decreases slightly as they are settled down and also the same behavior is observed for sodium silicate which settles down over pH 7, while at pH range from 3 to 5 a lower uptake is observed because the sodium silicate surface is going to be neutrally charged (Ralph 1955).

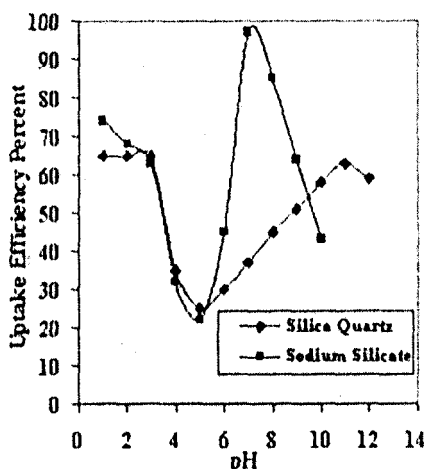


Fig. 2. Effect of pH on the uptake efficiency percent of oil-contaminated water on α -SiO₂ Quartz and Sodium silicate

Effect of loading weight: The loading weight effect on sorption of oil contaminated water on the α -SiO₂ quartz and sodium silicate are studied by using an aqueous solution (25 ml) of pH 6, containing 14.07 mg oil, loading weight range (0.1 g -1.5 g), 15 min shaking time at 30°C. The effect of loading weight on the uptake efficiency percent of α -SiO₂ quartz and sodium silicate to the oil is given in Fig. 3, which shows an increase of the uptake efficiency percent with increasing loading weight till it approaches a constant value at 1.1 g and 0.9 g for α -SiO₂ quartz and sodium silicate respectively. This is due to the increase of the adsorbing surface.

Incorporation of Ca, Mg and Ba carbonates: Ca, Mg and Ba carbonates are also incorporated within the clay. Sample solution (25 ml), which contaminated with 17.04 mg petroleum oil, shaken for 15 min shaking time and temperature (30°C) are maintained as for the untreated Aswanly clay. While pH and loading weight effects are studied separately so, it is found previously (Ralph 1955) that it is the main determining factors affecting the uptake efficiency percent of the petroleum oil.

Effect of pH: The pH effect on sorption of oil contaminated water on the Ca, Mg and Ba carbonates is studied using an aqueous solution (25ml) of pH range from 4 to 14 to minimize

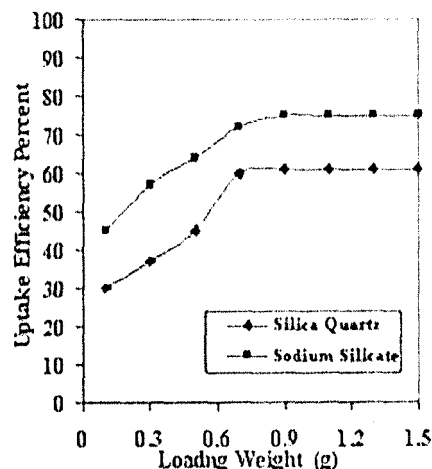


Fig. 3. Effect of loading weight on the uptake efficiency percent of oil contaminated water on α -SiO₂ Quartz and sodium silicate

carbonate solubility, that contains 14.07 mg oil, 0.1 g loading weight, 15 min shaking time at 30°C. The relation between the uptake efficiency percent and solution pH was given in Fig. 4. At pH range from 4 to 8 the uptake efficiency percent increases by increasing pH value where at pH range from 8-10.5 the uptake efficiency percent decreases by increasing pH. The uptake efficiency percent increases in the first region due to sorption on solid CaCO₃ and decrease in the second region is due to solid CaCO₃-solid and Ca(OH)₂ equilibrium (Vernon and David 1980) while, in the third region the gradual increase is due to Ca(OH)₂ formed precipitate which, has a great surface to occlude the oil.

Effect of loading weight: The loading weight effect on sorption of oil contaminated water on the Ca, Mg and Ba carbonates was studied using an aqueous solution (25 ml) of pH 6, containing 14.07 mg oil, loading weight range (0.01-0.13 g), 15 min shaking time, at 30°C. The effect of loading weight on the uptake efficiency percent of the Ca, Mg and Ba carbonates to the oil is given in Fig. 5; The highest values of uptake efficiency percents are 95, 100 and 95% at loading weight greater than 0.04, 0.05 and 0.08 g of MgCO₃, CaCO₃, BaCO₃, respectively, i.e., as the weight of solid carbonates increases the uptake efficiency percent increases till it reaches a constant value because of the increase of surface area.

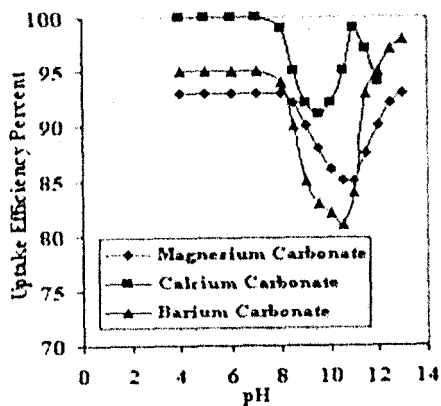


Fig. 4. Effect of pH on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium and Barium Carbonates.

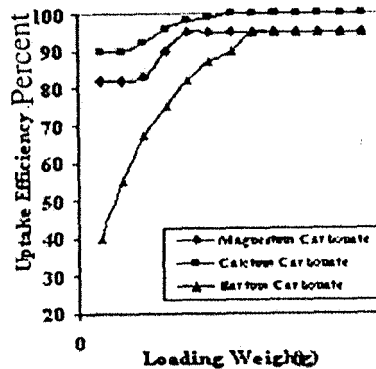


Fig. 5. Effect of loading weight on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium and Barium Carbonates.

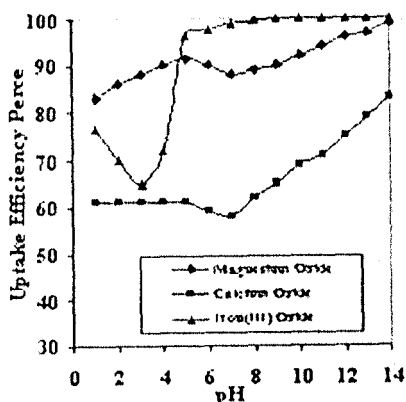


Fig. 6. Effect of pH on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium and Iron (III) Oxides.

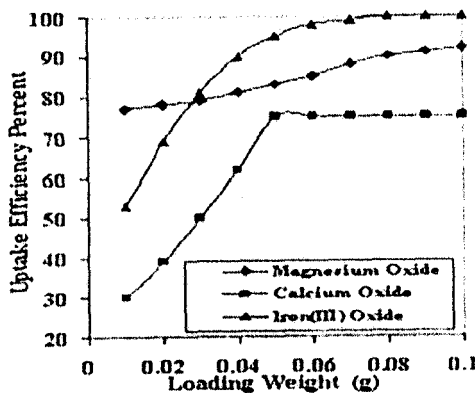


Fig. 7. Effect of loading weight on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium and Barium Oxides.

Ca, Mg and Fe(III) oxides: Ca, Mg and Fe(III) oxides are also incorporated in clay composition as shown from X.R.F analyses. The best conditions of sample volume (25 ml), which is contaminated with 17.04 mg petroleum oil, 15 min shaking time and temperature (30°C) are maintained as for the untreated clay. While pH and loading weight effects are studied separately because.

Effect of pH: The pH effect on sorption of oil contaminated water on the Ca, Mg and Fe(III) oxides

was studied using an aqueous solution (25 ml) of pH range from 1 to 14, contains 14.07 mg oil, 0.1 g loading weight, 15 min shaking time, at 30°C. As shown in Fig. 6; in case of Ca and Mg oxides, a little increase is observed with pH increase because of the gradual formation of Ca and Mg hydroxides. While in case of Fe(III) oxide at pH lower than 5, a decrease in the uptake efficiency percent is recorded with Fe(III) oxide dissolution and at pH which is greater than 5 the uptake efficiency percent increased due to the colloidal iron hydroxide formation (Duncan, 1992).

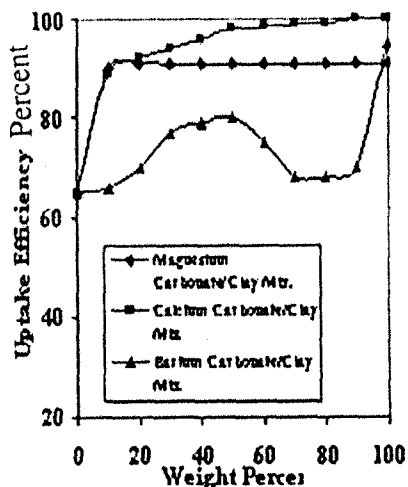


Fig. 8. Effect of weight percent on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium and Barium Carbonates.

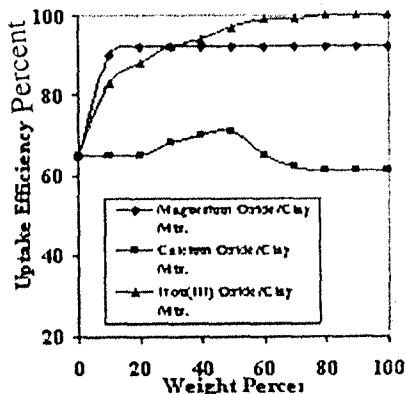


Fig. 9. Effect of weight percent on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium and Iron (III) Oxides.

Effect of loading weight: The loading weight effect on sorption of oil contaminated water on the Ca, Mg and Fe(III) oxides is studied using an aqueous solution (25ml) of pH 6, contains 14.07 mg oil, loading weight ranges from 0.01 to 0.1g, 15 min shaking time, at 30°C. The effect of loading weight on the uptake efficiency percent of the Ca, Mg and

Fe(III) oxides to the oil was given in Fig. 7; the highest values of uptake efficiency percent 95, 100 and 95% are at loading weight greater than 0.04, 0.05 and 0.08 g for MgO, CaO and Fe₂O₃, respectively, i.e., as the weight of solid oxides increases the uptake efficiency percent increases till it reaches a constant value because of the increase of surface area.

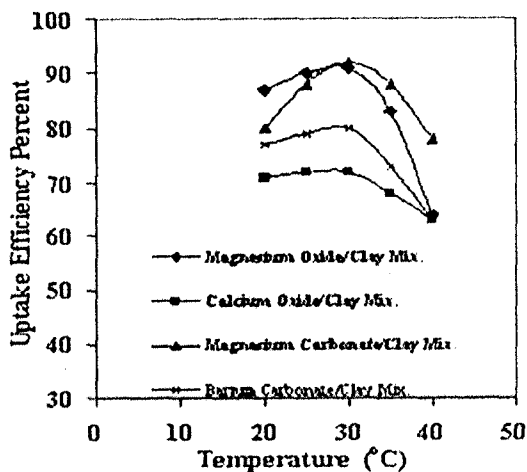


Fig. 10. Effect of Temperature on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium Oxides and Magnesium, Barium Carbonates/Clay mixtures

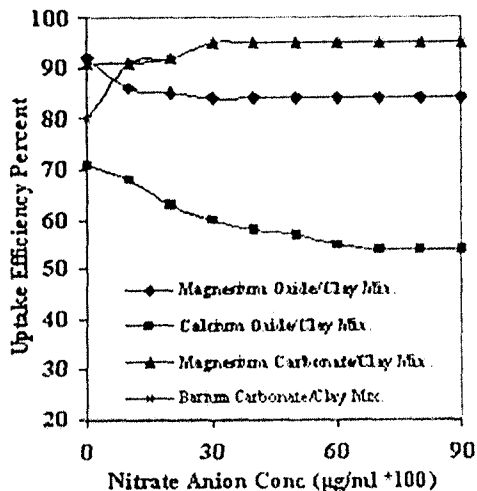


Fig. 11. Effect of Nitrate anion concentration on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium Oxides and Magnesium, Barium Carbonates/Clay mixtures.

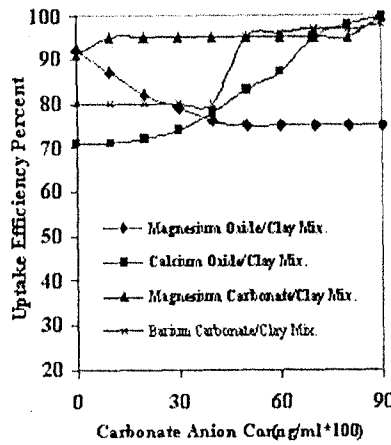


Fig. 12. Effect of Carbonate anion concentration on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium Oxides and Magnesium, Barium Carbonates/Clay mixtures.

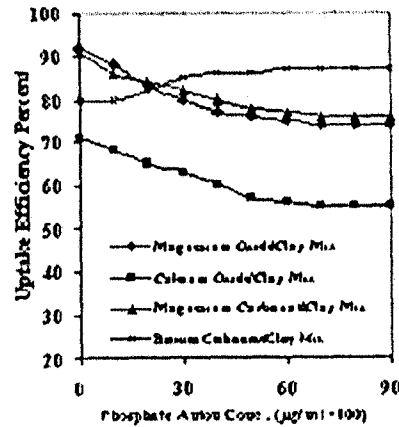


Fig. 13. Effect of Phosphate anion concentration on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium Oxides and Magnesium, Barium Carbonates/Clay mixtures.

Uptake efficiency percent of metal carbonates or oxide/clay solid sorbents mixtures: An attempt to improve sorption process of petroleum oil on the untreated clay, some metal carbonates and oxides which show excellent uptake efficiency percent, as studied before, are added to the untreated clay to reduce the quantity of metal carbonates and oxides, hence costs and keeps using of untreated clay which shows good adsorption properties to heavy metals. The sorption effect of petroleum oil on solid CaCO_3 , MgCO_3 , BaCO_3 , MgO , CaO , Fe_2O_3 /Clay mixtures are studied by using a different continuous variation of solid metal oxide or carbonate / clay mixture

percents where the total weights was 0.1g. The study is conducted using an aqueous solution (25ml) of pH 6, contains 14.07mg oil, 0.1g loading weight, 15min shaking time, at 30°C. The relation between uptake efficiency percent and metal oxide or carbonate weight percent [(weigh of oxide or carbonate /0.1) x*100] were shown in Figures 8 - 93. As shown in these figures, 10, 50, 40, 10, 40, 50 weight percents of MgCO_3 , CaCO_3 , BaCO_3 , MgO , CaO , Fe_2O_3 respectively are preferable to raise uptake efficiency percent of the untreated clay from 65% to 91, 98, 79, 92, 71 and 97%.

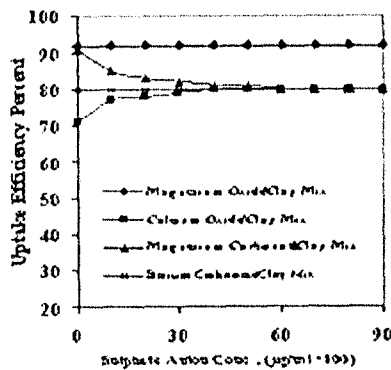


Fig. 14. Effect of Sulphate anion concentration on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium Oxides and Magnesium, Barium Carbonates/Clay mixtures.

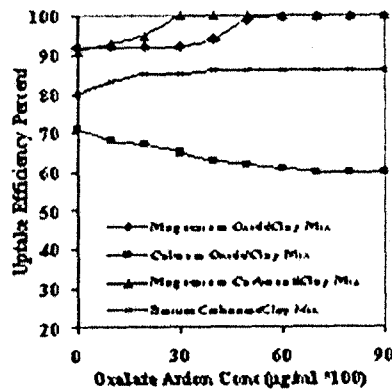


Fig. 15. Effect of Oxalate anion concentration on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium Oxides and Magnesium, Barium Carbonates/Clay mixtures.

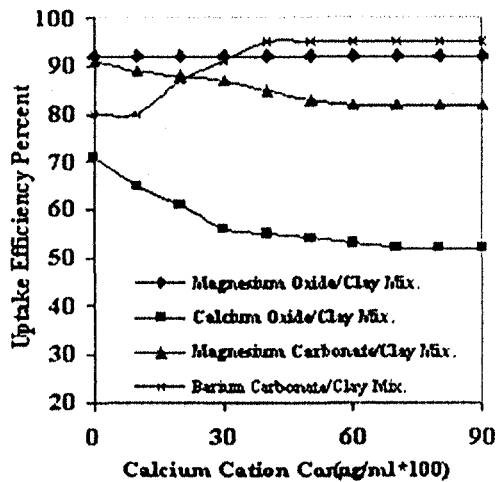


Fig. 16. Effect of Calcium cation concentration on the uptake efficiency percent of oil contaminated water on Magnesium, Calcium Oxides and Magnesium, Barium Carbonates/Clay mixtures.

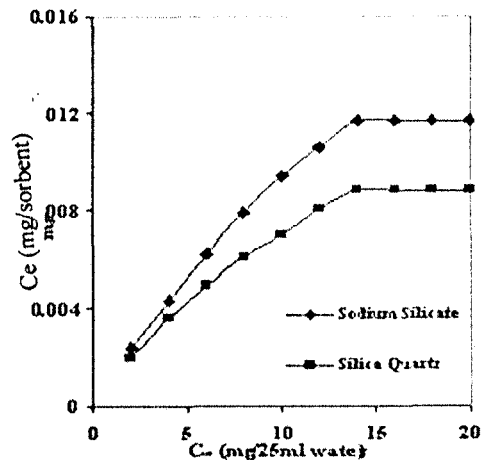


Fig. 17. Distribution ratio (K_d) between α -SiO₂, Quartz and Sodium silicate sorbed phases and the aqueous phase.

Some factors affecting the oil sorption process on some selected solid mixtures: Some factors affecting the oil sorption process on some selected solid mixtures MgCO₃, BaCO₃, MgO and CaO/Clay mixtures are studied at the best conditions of the untreated clay using aqueous solution (25ml) of pH 6, contains 14.07 mg oil, 0.1 g loading weight, 15 min shaking time, at different anion and calcium cation concentrations.

Effect of temperature on some selected adsorbing mixtures: The temperature effect on sorption of oil contaminated water on the MgCO₃, BaCO₃, MgO and CaO/Clay mixtures are studied using an aqueous solution (25 ml) of pH 6, contains 14.07 mg oil, 0.1 g loading weight, 15 min shaking time, temperature range from 20°C to 40°C and at optimum conditions of 10, 50, 10 and 50% weight percents for MgCO₃, BaCO₃, MgO and CaO/Clay mixtures. The effect of temperature on the uptake efficiency percent of the MgCO₃, BaCO₃, MgO and CaO/Clay mixtures to the oil was given in Fig. 10; as the temperature increases the uptake efficiency percent increases till it reaches maximum at 30±3°C and after that decreases i.e., the sorption process is an endothermic process, while with temperature increase higher than 30°C the adsorbed oil tends to be less viscous and steadily leaves the solid sorbent/clay mixtures surface.

Effect of some anions on some selected adsorbing mixtures: The effect of some anions (nitrate, dihydrogenphosphate, bicarbonate, sulphate and oxalate) concentration on sorption of oil contaminated water on MgCO₃, BaCO₃, MgO and

CaO/Clay mixtures are studied using an aqueous solution (25 ml) of pH 6, contains 14.07 mg oil, 0.1 g loading weight, 15min at 30°C and at optimum conditions of 10, 50, 10 and 50% weight percents for MgCO₃, BaCO₃, MgO and CaO/Clay mixtures, respectively. The relation between selected anion concentration and uptake efficiency percent was given in Figures 11 -15. This may be attributed to the adsorption surface interaction between the clay and the solid added with a great influence of the anion free energies on the crystal structures of both the clay and the added solid. As shown in Figures, as the concentration of nitrate anions increases the uptake efficiency percent increases slightly in case of MgCO₃ and BaCO₃/Clay mixtures till it reaches a constant value and decreases slightly till it reaches a constant value in case of MgO and CaO/Clay mixtures. As the concentration of carbonate anions increases the uptake efficiency percent increases in case of MgCO₃, CaO and BaCO₃/Clay mixtures till it reaches a constant value and decreases till it reaches a constant value in case of MgO/Clay mixture. As the concentration of phosphate anions increases the uptake efficiency percent increases in case of BaCO₃/Clay mixture till it reaches a constant value and decreases till it reaches a constant value in case of MgCO₃, CaO and MgO/Clay mixtures. With sulphate ions concentration the increase of the uptake efficiency percent of petroleum oil on MgO and BaCO₃/Clay mixtures has not any effect where the uptake efficiency percent of petroleum oil on MgCO₃/Clay mixture increases and decreases in case of CaO/Clay mixture.

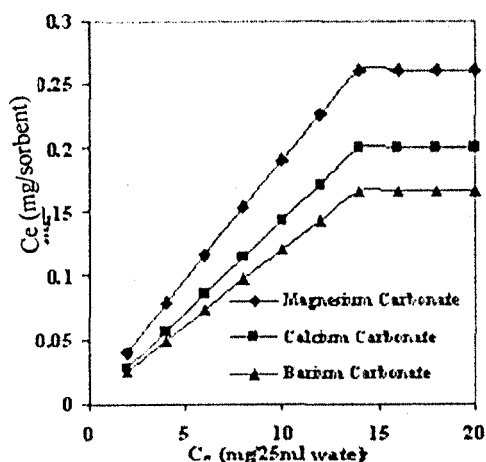


Fig. 18. Distribution ratio (K_d) between Calcium, Magnesium and Barium Carbonates sorbed phases and the aqueous phase.

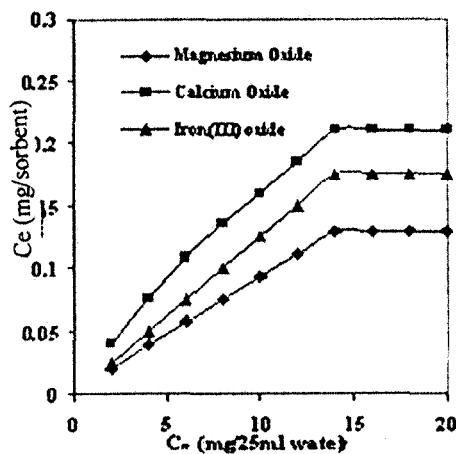


Fig. 19. Distribution ratio (K_d) between Calcium, Magnesium and Iron (III) Oxides sorbed phases and the aqueous phase.

Effect of calcium (II) ion concentration on some selected adsorbing mixtures: The effect of calcium (II) ion concentration on sorption of oil contaminated water on the $MgCO_3$, $BaCO_3$, MgO and $CaO/Clay$ mixtures were studied using an aqueous solution (25 ml) of pH 6, contains 14.07 mg oil, 0.1 g loading weight, 15min shaking time, at $30^\circ C$ and at optimum conditions of 10, 50, 10 and 50% weight percents for $MgCO_3$, $BaCO_3$, MgO and $CaO/Clay$ mixtures. The relation between calcium ion concentration and uptake efficiency percent was given in Fig. 16; which may be attributed to the surface interaction between the clay and the solid added with a great influence of the anions free energies on the crystal structures of both clay and solid. As shown in Fig 16, as the concentration of calcium ion concentration increases the uptake efficiency percent increases slightly in

case $BaCO_3/Clay$ mixture till it reaches a constant value and decreases till it reaches a constant value in case of $MgCO_3$ and $CaO/Clay$ mixtures and has not any effect in case of $MgO/Clay$ mixture. Finally, distribution ratio (K_d) was calculated at optimum condition of pH 6, temperature $30^\circ C$, and loading weights 0.1 g for 1.0 g α - SiO_2 -Quartz, 0.9 g $Na_2Si_2O_5(OH)_4$, 0.07 g $CaCO_3$, 0.05 g $MgCO_3$, 0.08 g $BaCO_3$, 0.05g CaO , 0.1 g MgO , and 0.08 g Fe_2O_3 , 0.1 g clay mixture of 50% $CaCO_3$, 0.1 g clay mixture of 10% $MgCO_3$, 0.1 g clay mixture of 50% $BaCO_3$, 0.1 g clay mixture of 50% CaO , 0.1 g clay mixture of 10% MgO , and 0.1 g clay mixture of 50% Fe_2O_3 . Distribution ratio (K_d) was calculated by plotting C_s versus C_w as shown in Figures 17 – 21, where, the slope of the resulting straight line is K_d . Values were calculated and presented in Table 4

Table 4: Distribution ratios (K_d) between sorbed phases and aqueous phase

Material	K_d	Material	K_d
SiO_2	0.0006	Fe_2O_3	0.0125
$Na_2Si_2O_5(OH)_4$	0.0008	$MgCO_3/Clay$ Mixture	0.0088
$MgCO_3$	0.0184	$CaCO_3/Clay$ Mixture	0.0098
$CaCO_3$	0.0143	$BaCO_3/Clay$ Mixture	0.0125
$BaCO_3$	0.0117	MgO Clay Mixture	0.0089
MgO	0.0090	$CaO/Clay$ Mixture	0.0089
CaO	0.0139	$Fe_2O_3/Clay$ Mixture	0.0097

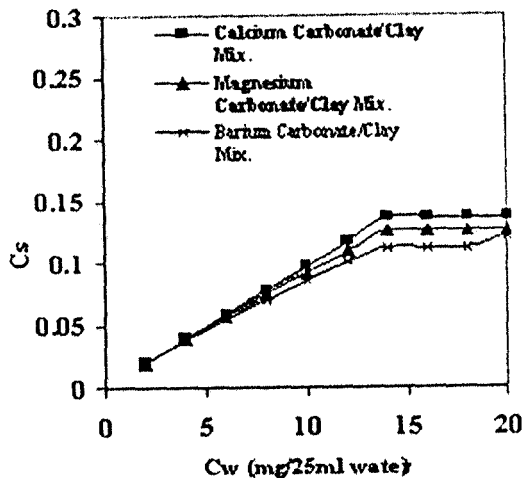


Fig. 20. Distribution ratio (K_d) between Calcium, Magnesium and Barium Carbonates/Clay mixtures of 50% Calcium Carbonate, 10% Magnesium Carbonate and 50% Barium Carbonate sorbed phases and the aqueous phase.

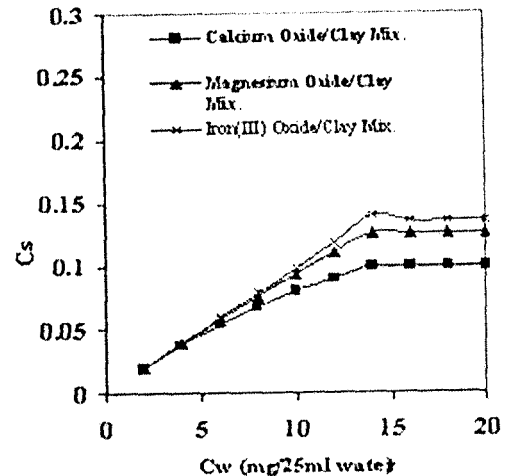


Fig. 21. Distribution ratio (K_d) between Calcium, Magnesium and Iron (III) Oxides/Clay mixtures of 50% Calcium Oxide, 10% Magnesium Oxide and 50% Iron (III) Oxide sorbed phases and the aqueous phase.

Since, strongly adsorbed oil exhibits high K_d values. Sorbed phases according to values obtained in Table 4 can be arranged in the following order: $MgCO_3 > CaCO_3 > CaO > Fe_2O_3 = BaCO_3/Clay Mixture > BaCO_3 > CaCO_3/Clay Mixture \approx Fe_2O_3/Clay Mixture > MgO \approx MgO Clay Mixture \approx CaO/Clay Mixture > MgCO_3/Clay Mixture > Na_2Si_2O_5(OH)_4 > SiO_2$.

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