Usage of Iraqi Surfactant Modified Zeolite for Treatment of Water Produced from Oil Production Processes

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Abstract

This study aimed to remove the oil from the produced water imported from Pai-Hassan field using akashat Iraqi natural zeolite after organic modification with cationic surfactant Hexadecyl Trimethyl Ammonium Bromide (HDTMA) solutions as a numerical complication of critical micelles concentration (CMC) of HDTMA (1CMC, 3CMC, .to 13CMC) solutions. Measuring the Electrical Conductivity (EC) of supernatant, and FT-IR, XRD characterization of solid modified Na/HDTMA zeolite indicates that the optimum HDTMA concentration for zeolite modification is (11 CMC) at 65 C°, and the optimum zeolite weight at constant volume (30 ml) of surfactant solution is 2 g zeolite. Also the removal % of oil from produced water at optimum conditions is 91%.

Keywords: Iraqi Zeolite, Treatment of Water, Oil Production, Surfactant.

Introduction

Produced water is accompanied with the production of oil and gas especially at the fields producing by water drive or water injection. The quantity of these waters is expected to be more complicated problem with an increasing in water cut which is expected to be 3-8 barrels water / produced barrel oil [1]. Co-produced water from the oil and gas industry accounts for a significant waste stream in the United States. Characteristics of produced water include high total dissolved solids content, dissolved organic constituents such as benzene and toluene, an oil and grease component, and chemicals added during the oil production process [2]. The discharge of produced water to the environment is regulated by the Environmental Protection Agency (EPA) in the United States. The EPA mandates that produced water discharge, as overboard water, must contain oil and grease concentration less than 29 ppm and 42 ppm, respectively [3]. While most produced water is disposed via reinjection, some facilities are required to remove organic constituents before the water is discharged. Current treatment options are successful in reducing oil; however, they cannot always meet the levels of current or proposed regulations for discharged water. Therefore, an efficient, cost-effective treatment technology is needed for removal of dissolved constituents such as benzene, toluene, ethyl benzene and xylenes (BTEX). Treatment through sorption onto materials such as surfactant-modified zeolite (SMZ) may be both effective and relatively inexpensive [2]. Organoclay, incorporated into a treatment process shows promise of being a cost effective method of treatment to remove crude oil from brine either as a final treatment prior to brine disposal at sea or as a precursor to desalination. Organoclay also pre-polishes the waste water before further treatment [4]. Adsorption can be carried out using many types of adsorbents. One of these many types of adsorbents is granular activated carbon (GAC) which has been widely accepted by E&P industry for quite a long time for removing hydrocarbons from waste water by adsorption. Organoclay has emerged as a better substitute for this GAC.

In fact, studies show that if a comparison is made between the organoclay and GAC, organoclay has several advantages over the GAC as an adsorbent [5].

The removal process with organoclay can be quantified as seven times more effective as GAC as far as the removal rate is concerned [6].

To follow is a brief outline of some of the advantages of using organoclay over GAC [7, 8]:

1- Organoclay has higher adsorption capacity than GAC and can adsorb 60-70% hydrocarbons by weight.
2- It is very effective in removing insoluble and dispersed hydrocarbons.
3- It does not desorb the adsorbed hydrocarbons.

Zeolites are micro porous crystalline aluminosilicates, composed of TO_4 tetrahedra (T = Si, Al) with O atoms connecting neighboring tetrahedra. For a completely siliceous structure, combination of TO_4 (T = Si) units in this fashion leads to silica (SiO_2), which is an uncharged solid. Upon incorporation of Al into the silica framework, the +3 charge on the Al makes the framework negatively charged, and requires the presence of extra framework cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral. The zeolite composition can be best described as having three components:

S $M^{m+}_{n/m}$	$Si_{1-n}Al_nO_2$	nH_2O
Extra framework cations	framework	sorbed phase

The extra framework cations are ion exchangeable and give rise to the rich ion-exchange chemistry of these materials. The novelty of zeolites stems from their micro porosity and is a result of the topology of the framework. Figure (1) shows the framework projections and the ring sizes for commonly studied frameworks [9, 10].

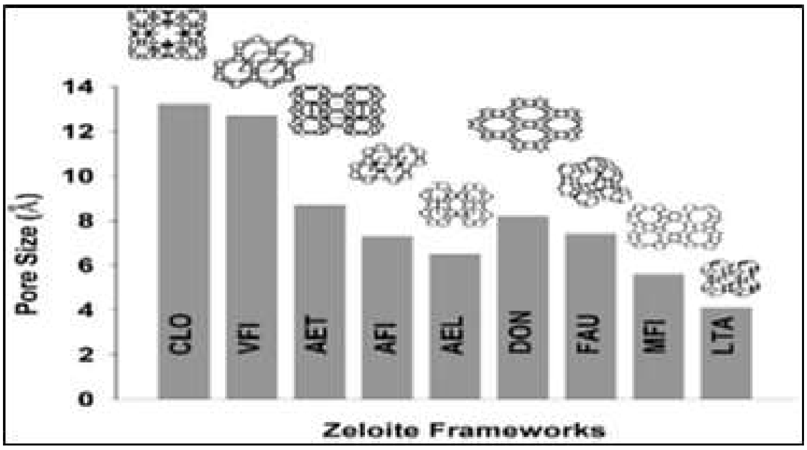

Fig. (1) Comparison of pore sizes of different framework structures

Inexpensive natural zeolites are good potential material for water and wastewater treatment. The potential advantages for application of natural zeolites in water and wastewater treatment are promising. Firstly, a benefit gained by using natural zeolites for water and wastewater treatment is their ability to undergo ion-exchange and adsorption. In addition, natural zeolites can be treated and modified in order to trap contaminants in water and wastewater. Also, natural zeolites exist abundantly; low cost and only low technology systems are required. An additional benefit of using natural zeolites is their regenerative properties [11].

Natural zeolites can be modified by cationic surfactants such as hexadecyl trimethyl ammonium Bromide (HDTMA). HDTMA quaternary amines can be defined as “a tetra substituted ammonium cation with a permanently charged pentavalent nitrogen and a long, straight alkyl chain (C16)”[12].The long hydrocarbon chain imparts a strong degree of hydrophobicity to the surfactant tail while the positively charged ammonium head remains hydrophilic. Counter ions such as bromide or chloride serve to neutralize the cationic effect of the head group a rendering them capable of sorbing anions. Thus, the SMZ has some adsorption capacity for cations, anions, and non-polar organic compounds such as BTEX [2].

As soon as organoclay is introduced into water, its quaternary amine becomes activated and opens out perpendicularly off the clay platelets into the water as shown in figure (2). A Cl^{-1} or Br^{-1} ion is loosely attached to the carbon chain. So, after being replaced by the sodium ion and getting bonded with Cl^{-1} , sodium salt is produced. Now, the hydrophilic end of the amine dissolves into the oil droplet and removes the droplet from water by adsorption [7].

The overall goal of this research was to develop a cost-effective, simple technologies, and practical method of treating co-produced waters from oil-field sources using a treatment scheme that includes sorption of organics by surfactant-modified Iraqi natural zeolite.

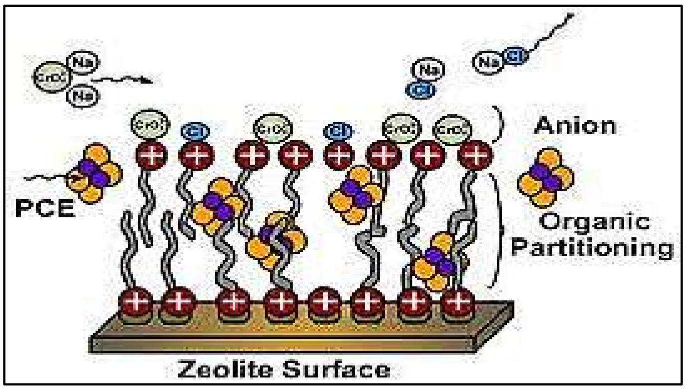

Fig (2)

Materials and methods

Materials

All Chemicals used were of analytical reagent grad unless otherwise is mentioned. The clay used in this study was zeolite, which originated akashat / ar-Rutbah / al-Anbar / Iraq location, obtained from the General Company for akashat phosphate mine – Iraq. The samples were sieved to produce the desired particle size fractions. The samples with a particle size 45µm was then dried in air and stored until use. Hexadecyl trimethyl ammonium Bromide - surfactant with a critical micellization concentration (CMC): (335.34 – 364.5 mg/L) (average = 350 mg/L) (water) [13, 14], was supplied by Sigma-Aldrich - USA. Distilled and deionized water with conductivity value of (1.5 x 10^{-5} S cm^{-1}) was used in all experiments. NaCl (Sigma Aldrich, min. 99.5%). produced water samples imported from Pai- Hassan field at constant pH values.

Apparatus

Philips – pw 9526 digital conductivity meter with glass probe (WTW-LAT1 of K coefficient = 0.973). Sartorius BL 210S balance, pH-meter DW-9421 from Philips instrument, Shimadzu FTIR Spectrometer – 30 000:1/ IRAff.
Shimadzu X-ray Diffractometer P 04 - XRD-6000 Thermo stated shaker bath (Alba Tech.). Test sieves (Retsoh Gmb & Co. KG, Germany).

Materials Characterization

Akashat – Iraqi crude zeolite clay mineral, and Hexadecyl trimethyl ammonium Bromide - surfactant (HDTMA) were characterized by FT –IR spectroscopic analysis (Shimadzu FTIR Spectrometer – 30 000:1/ IRAff), and X-ray powder diffraction (Shimadzu X-ray Diffractometer P 04 - XRD-6000).

Zeolite modification using numerical CMC complication of HDTM

Batch experiments were conducted to modifying zeolite clay mineral using 250 ml round bottomed flask with rubber stopper. To ensure that there is an excess of sodium ion concentration with relation to cation exchange capacity (CEC) 7 g sample of zeolite was contacted with 100ml 1 mol/dm3 NaCl for 24 h. The sodium form of zeolite was washed two times with water. After filtration the solid residue was dried in air. As a next step 1 g of sodium–zeolite and 20.0 ml of an aqueous solution of known (HDTMA) - surfactant concentration were transferred into these round bottomed flasks. The (HDTMA) -surfactant solution (mixture) was set with fixed concentrations (1, 3, 5, 7, 9, 11, and 13 times of CMC). The flasks were allowed to reach equilibrium at 25± 1 ºC, 45± 1 ºC, and 65± 1 ºC in a reciprocating shaker for 24 h. The solution and solid phase were then separated by filtration and the solid residue was dried in air and stored until use.An appropriate aliquot (about 10 mills.) of the supernatant was removed to measure the electrical conductivity (EC) using Philips – pw 9526 digital conductivity meter with glass probe (WTW-LAT1 of K coefficient = 0.973). Also the electrical conductivity (EC) was measured for the numerical complication of (CMC) of (HDTMA) (1CMC, 3CMC, .to 13CMC) solutions before clay modification as shown in table (1).

Table (1) Electrical conductivity (EC) for the numerical complication of (CMC) of (HDTMA) and Zeolite modification supernatant

HDTMA Conc. Times of CMC	HDTMA Conc. mg/L ppm.	EC of HDTMA solutions (m S/cm)	EC of supernatant after modification at 25°C (m S/cm)	EC of supernatant after modification at 45°C (m S/cm)	EC of supernatant after modification at 65°C (m S/cm)
1 x CMC	350	8.45	8.75	12.39	12.53
3 x CMC	1050	21.15	26.80	25.56	18.30
5 x CMC	1750	35.20	43.40	42.10	49.40
7 x CMC	2450	44.90	55.70	56.00	62.80
9 x CMC	3150	65.90	72.20	67.10	71.60
11 x CMC	3850	67.50	72.70	80.90	85.90
13 x CMC	4450	75.10	75.80	92.70	97.30

The dried separated modified Na/HDTMA zeolite samples were characterized by FT –IR spectroscopic analysis (Shimadzu FTIR Spectrometer – 30 000:1/ IRAff), and X-ray powder diffraction (Shimadzu X-ray Diffractometer P 04 - XRD-6000).

Treatment of Pai- Hassan field produced water with different weights of Na- HDTMA (11 & 13 CMC) Zeolite

A samples of 30 ml of produced water imported from Pai- Hassan field were mixed with different weights (1 g, 1.5 g, 2 g, & 2.5 g) of Na- HDTMA (11 & 13 CMC) zeolite, in round bottomed flasks, agitated for 1 hr (250 r.p.m.) using thermo stated shaker bath (Alba Tech.) at room temperature (25±2) °C. Then the samples filtered to measure the oil content, TDS, EC, and pH for the water samples obtained, as shown in tables (2&3).

Table (2) Data of Pai- Hassan field produced water (30 ml) sample of 250 ppm oil content and 7730 µS cm-1 EC after treatment with different weights of Na- HDTMA (11 CMC) Zeolite

Zeolite wt./g.	Oil content ppm. After treatment	Removal % of oil content	TDS mg/L after treatment	EC µS cm^{-1} after treatment	pH after treatment
1.0	45	82	2700	5410	8.0
1.5	30	88	3400	6830	8.4
2.0	22	91	3940	7650	8.8
2.5	22	91	3950	7680	8.9

Table (3) Data of Pai- Hassan field produced water (30 ml) sample of 250 ppm oil content and 7730 µS cm-1 EC after treatment with different weights of Na- HDTMA (13 CMC) Zeolite

Zeolite wt./g.	Oil content ppm. After treatment	Removal % of oil content	TDS mg/L after treatment	EC µS cm^{-1} after treatment	pH after treatment
1.0	42	84.0	3920	5704	7.1
1.5	31	87.6	3310	6782	7.1
2.0	28	88.8	3870	7077	6.8
2.5	28	88.8	3600	7085	7.2

By repeating the same procedure of treatment of Pai- Hassan field produced water with 2 g optimum weights of Na- HDTMA (11 & 13 CMC) Zeolite, and them measuring the oil content, EC, TDS, T.H. (CaCO3), Ca^{+2}, Mg^{+2}, Na^{+}, and pH for the water samples obtained, as shown in table (4).

Table (4) Comparison Data for Pai- Hassan field produced water (30 ml) sample before and after treatment with 2g weights of Na- HDTMA (11 & 13 CMC) Zeolite

Variable name	Produced water sample before treatment	Produced water sample after treatment with 2g. Na- HDTMA (11 CMC) Zeolite	Produced water sample after treatment with 2g. Na- HDTMA (13 CMC) Zeolite
Oil content ppm.	250	22	28
EC µS cm^{-1}	7730	7650	7077
TDS mg/L	6720	3940	3870
T.H. ($CaCO_3$)	1000	32	34
Ca^{+2} (ppm)	405	1.22	1.33
Mg^{+2} (ppm)	996	15.85	17.07
Na^{+} (ppm)	286	1.558	1.617
pH	3.7	8.8	6.8

Results and discussion

Characterization of IRAQI Zeolite

As we can observe in the FT-IR spectrum of crude zeolite figure (3), the bands at 1420 cm^{-1} could be assigned to the presence of carbonates as anions occluded in the internal cavities of the cancrinite zeolite. The bands observed at 3406 cm^{-1} correspond to water molecules occluded inside the cancrinite structure. Finally, the bands appearing in the (1049–605 cm^{-1}) region correspond to symmetric and asymmetric vibrations of the atoms that form the structural units of the zeolite. Those bands are considered as the fingerprint of the zeolite, specially the asymmetric vibrations between (711 and 416 cm^{-1}) [15].

XRD pattern of the crude zeolite sample was recorded at room temperature. Figure (4) gives images of typical cancrinite structure of composition |Na_8

$(CO_3)_{1.2}(H_2O)_2| [Si_6Al_6O_{24}]$. The good crystallinity for cancrinite sample was verified by the presence of the five reflections at 2θ angles of approximately (11°, 23°, 25°, 29°, and 33°).

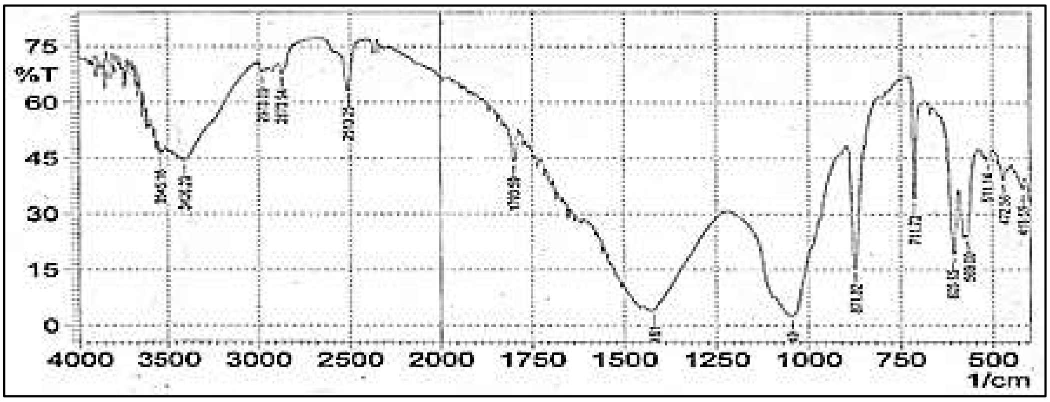

Fig. (3) The FT-IR spectrum of crude zeolite

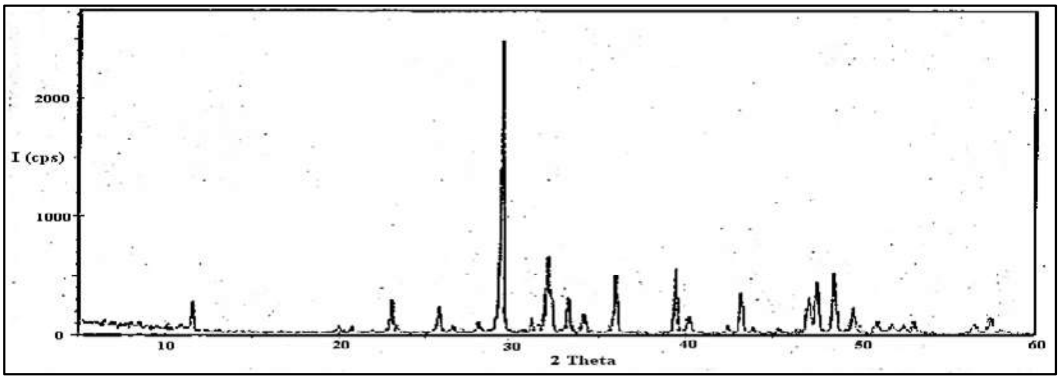

Fig. (4)

Characterization of HDTMA

FT-IR spectrum of HDTMA Figure (5) shows O-H stretching at 3385 cm^{-1} , CH_2 asymmetric stretching vibration at 2931 cm^{-1}, and 2848 cm^{-1}, CH_2 scissoring mode at 1487 cm^{-1}, and 1462 cm^{-1}, and a finger print region at (960 – 719 cm^{-1}). XRD pattern of HDTMA figure (6) shows seven reflections at 2θ angles of approximately (6.5°, 10°, 13.5°, 17°, 20.5°, 24°, 27.5°).

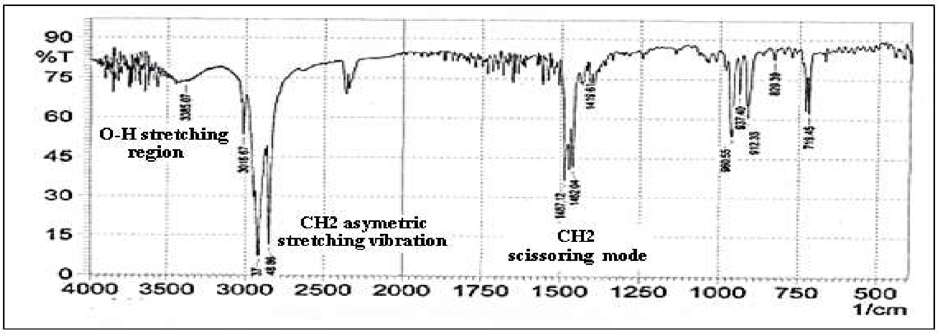

Fig. (5) The FT-IR spectrum of of HDTMA

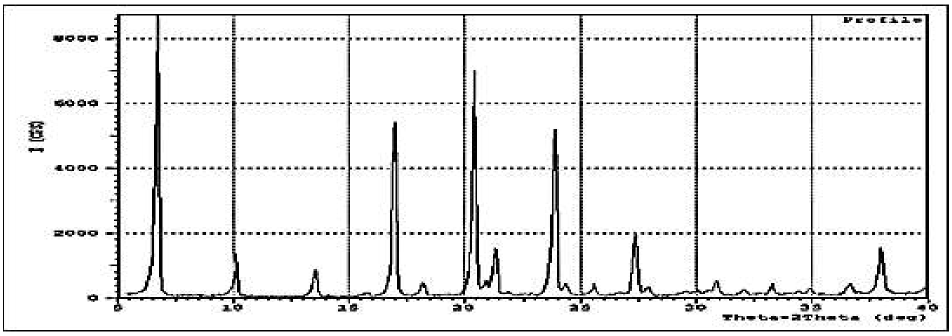

Fig. (6) The x-ray diffraction spectrum of HDTMA

Effect of EC & concentration on zeolite modification extent

Using data in table (1) for Plotting HDTMA solutions conc. mg/L against the EC m S/cm of supernatant after modification at temp. (25°C, 45°C, & 65°C), figure (7) shows that the optimum concentration of HDTMA surfactant was 13 CMC (i.e. 4450 mg / L), and the optimum temperature was 65 C°, due to the highest EC at this concentration and temperature .

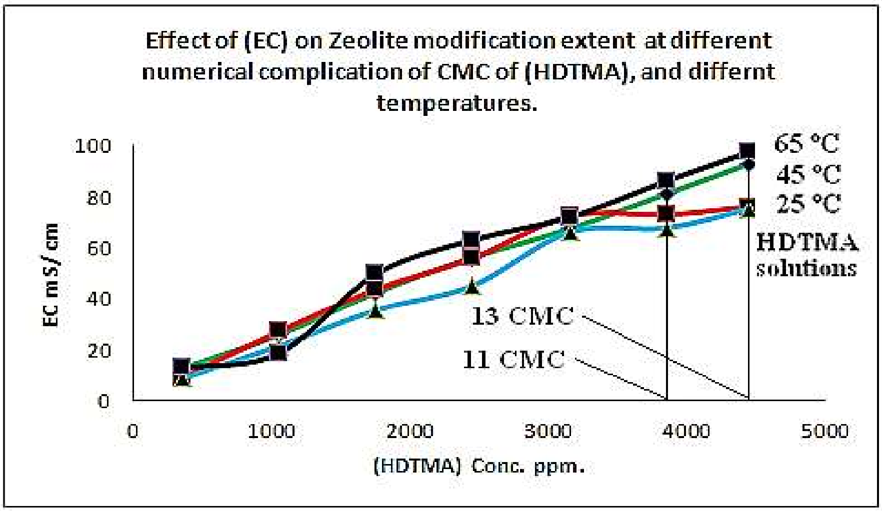

Fig. (7) Effect of EC on zeolite modification extent

The explanation of this is the high release of zeolite cations by the surfactant caionic micelles, and these released inorganic cations make the supernatant solution more conductive. While the organic surfactant cations attached to the cancrinite zeolite cavity pores. To make sure of this the solid modified Na/HDTMA zeolite (11CMC), and (13CMC) was characterized as shown in figures (8-11).

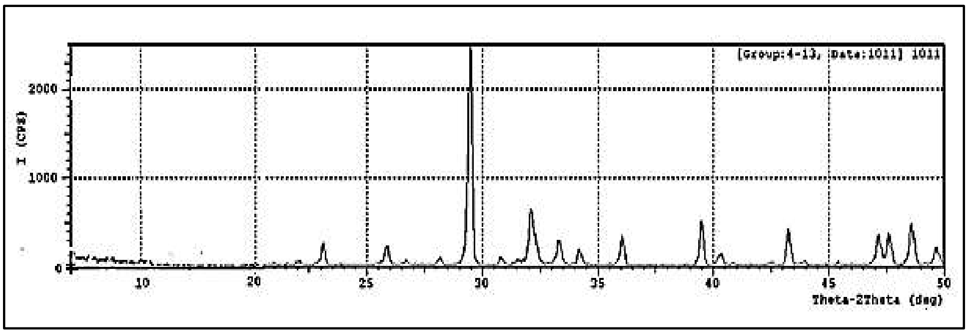

Fig. (8) The x-ray diffraction spectrum of modified Na/HDTMA zeolite (11CMC)

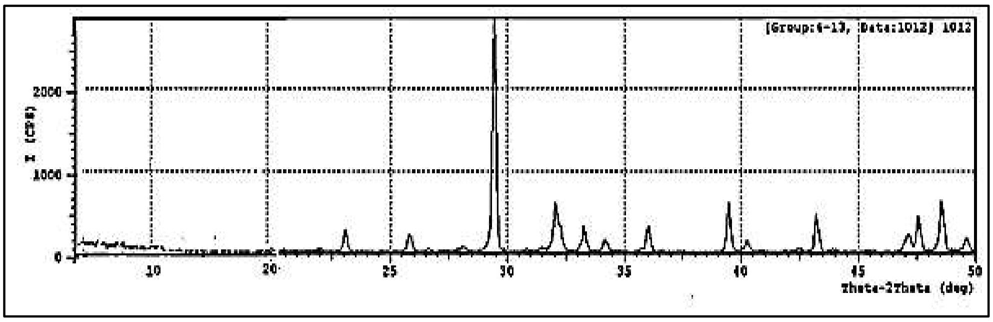

Fig. (9) The x-ray diffraction spectrum of modified Na/HDTMA zeolite (13CMC)

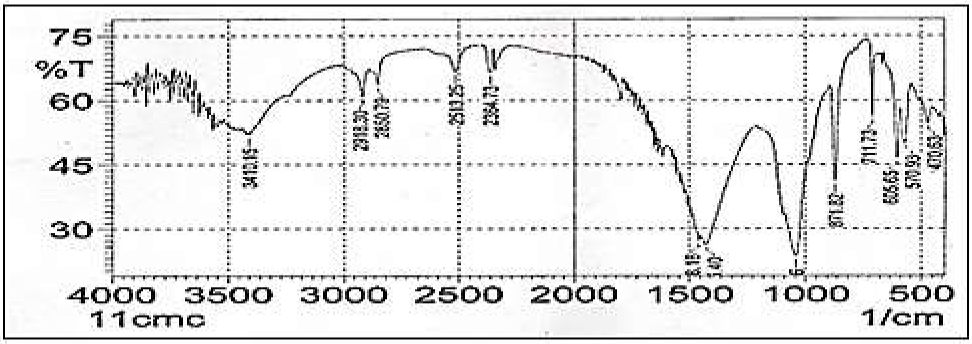

Fig. (10) The FT-IR spectrum of of modified Na/HDTMA zeolite (11CMC)

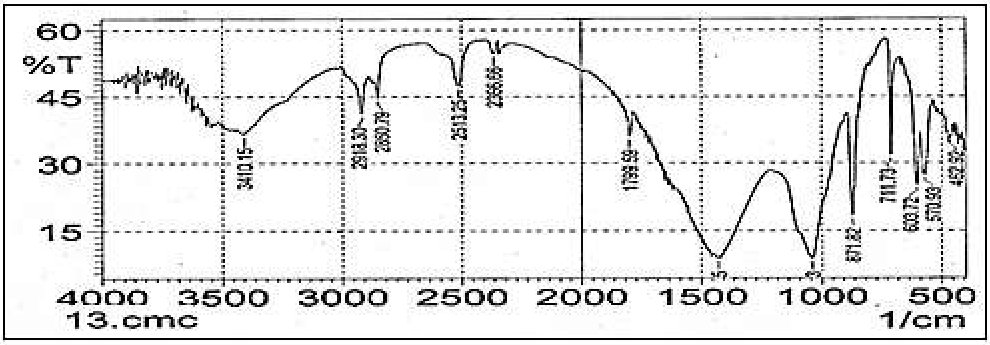

Fig. (11) The FT-IR spectrum of of modified Na/HDTMA zeolite (13CMC)

Taking two optimum concentrations is for Comparison**.** XRD patterns figures (8 &9) indicates that there is no obvious different between them, as a result of convergence between the concentrations. The spectra of Na/ cancrinite, Na/HDTMA– cancrinite, differ only in the sense of peaks intensity, not in their positions. The peak around 10 θ for Na/HDTMA– cancrinite has pronounced lower intensity than peaks for Na/ cancrinite, which results rather from the change in the interaction in the internal structure of the zeolite. The HDTMAC cations in micelles form are probably sorbed within the pores of cancrinite. But FT-IR spectrums figures (10 & 11) showed different values of peak intensities and peaks areas of CH_2 - asymmetric stretching vibration at (2918 cm^{-1}, & 2850 cm^{-1}) as shown in table (5).

Table (5) Comparison Data of organic surfactant CH2 - asymmetric stretching vibration peaks intensities and areas

Modified Zeolite	Peak 2918 cm^{-1} Intensity	Peak 2850 cm^{-1} Intensity	Peak 2918 cm^{-1} Area	Peak 2850 cm^{-1} Area
Na/HDTMA zeolite (11CMC)	60.774	63.72	12.368	19.729
Na/HDTMA zeolite (13CMC)	41.065	44.636	22.585	29.139

It's clear now to decide that the optimum modification concentration is (11CMC), because the intensity of organic surfactant CH2 - asymmetric stretching vibration peaks is higher than that of (13CMC), i.e. the extent of organic modification is higher.

Effect of weights of Na- HDTMA (11&13 CMC) Zeolite on Water Treatment of Pai- Hassan field produced water.

Using data in tables (2&3), for plotting the calculated removal% of oil of produced water samples against zeolite clay weights were shown in figures (12&13), indicates that the optimum weight of Na- HDTMA (11&13 CMC) zeolite is 2g in which oil removal% is high, also the results confirmed that the optimum concentration of modification is (11CMC), due to higher oil removal % (91%) for Na- HDTMA (11CMC) zeolite.

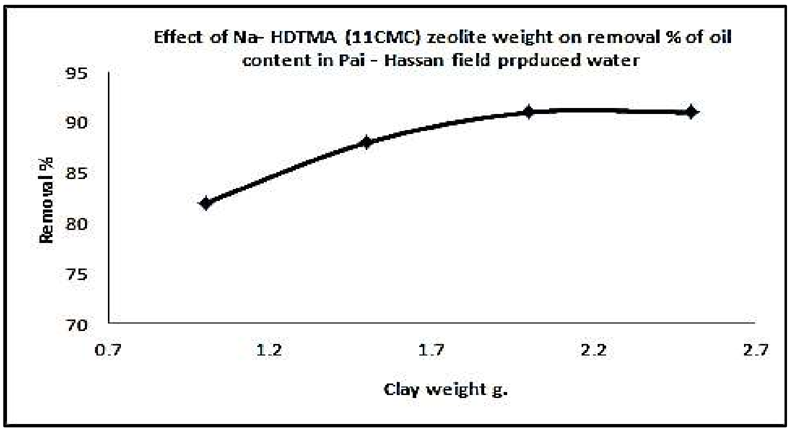

Fig. (12) Effect of Na- HDTMA (11 CMC) Zeolite weight on removal% of oil content in Pai- Hassan field produced water

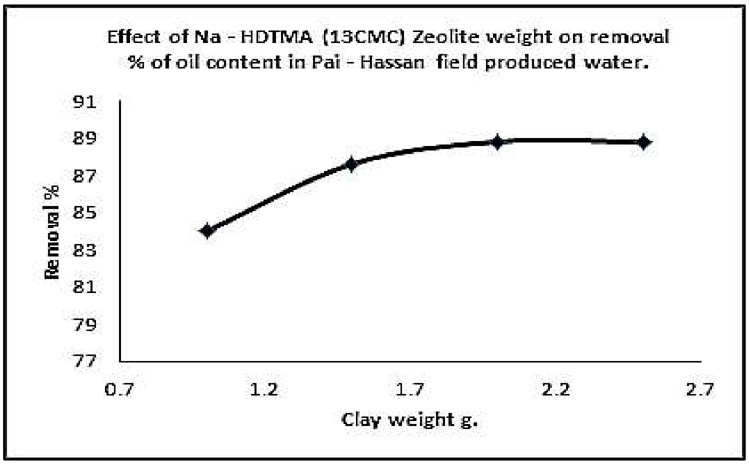

Fig. (13) Effect of Na- HDTMA (13 CMC) zeolite weight on removal% of oil content in Pai-Hassan field produced water

Water Treatment of Pai- Hassan field produced water at optimum weight 2g of Na- HDTMA (11 & 13 CMC) Zeolite

Table (4) results indicate that oil content of produced water decreased to a level lower than the Environmental Protection Agency (EPA) level (29 ppm). Also the T.H. ($CaCO_3$), decreased to low level lower than the WHO, and Iraqi limits of drinking water (500 ppm). Ca^{+2}, Mg^{+2}, and Na^{+1} content decreased to very low values. This indicates that the treatment process succeeded in two things, the first is removing of oil content, and the second is water softening.

Conclusion

Many facts have been discovered in this study; one of these facts is that we can use the EC of supernatant for the zeolite modification vessel as a variable to indicate the extant of modification along the FT-IR and XRD patterns of solid modified zeolite. The other fact is that the removal% of oil from the produced water samples depends on the efficiency of modification process. The last fact is that the modified zeolite clay remove the oil content of produced water and improve the water quality compared to the WHO, and Iraqi limits of drinking water.

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