REMOVAL OF OIL FROM WASTEWATER BY ORGANOCLAY PREPARED FROM IRAQI BENTONITE

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ABSTRACT

The present study deals with the removal of oil from wastewater by organoclay. The organoclay was prepared by combination of Iraqi bentonite with quaternary amine (hexadecyltrimethyl ammonium chloride). The wastewater samples were obtained from the washing unit of fuel oil in the "*South Baghdad Gas Power Plant*". The operating conditions of batch process for removal of oil from wastewater by using the prepared organoclays were studied in details (quantity of organoclay, mixer speed and time of adsorption). Initial concentration of wastewater used in this study was within a maximum range of 230-1512 mg/L. XRD and FTIR diagram of the prepared organoclay showed a considerable differences from those for natural bentonite which indicates the exchange of quaternary amine with Ca^{++} ions at the surface of bentonite. The concentration of oil in the wastewater samples decreased below 10 mg/L after treatment with organoclay. Batch kinetics studies were conducted by using kinetic equations (Lagergren and Ho et al) and batch isotherm studies was conducted by using isotherm models (Freundlich, Langmuir and BET).

الخلاصة

يتناول هذا البحث عملية إزالة الملوثات النفطية من المياه الصناعية باستخدام الطين العضوي. ان الطين العضوي المستخدم في هذا البحث تم تصنيعه عن طريق مزج خام البنتونايت العراقي (Iraqi bentonite) مع الامين الرباعي المسمى هكساديسايل تراي ميثايل امونيوم كلورايد (hexadecyltrimethyl ammonium chloride). إن مخلفات المياه (wastewater) المستخدمة في هذه الدراسة أخذت من وحده غسل زيت الوقود (fuel oil) الموجودة في محطة كهرباء جنوب بغداد الغازية. لقد تم دراسة الظروف التشغيلية لإزالة زيت الوقود (fuel oil) من نموذجين من المياه الصناعية بالتفصيل (كمية الطين العضوي و سرعة الخلاط وزمن الامدصاص). ان التراكيز الأولية للمياه الصناعية المستخدمة في التجارب كانت ضمن حدود 230 الى 1512 مل/لتر. النتائج التي تم الحصول عليها من مخططات الأشعة السينية (XRD) وكذلك مخططات الأشعة تحت الحمراء (FTIR) للطين العضوي المحضر اظهرت اختلاف واضح عن مثيلاتها العائدة للبنتونايت وهذا يشير الى استبدال ايونات الكالسيوم Ca^{++} الموجودة على سطح البنتونايت بايونات الأمين الرباعي الموجبة. النتائج المستخلصة من هذه الدراسة بينت إن تركيز الملوثات النفطية في المياه الصناعية انخفض دون 10 ملغم/لتر (الحدود المسموح بها لتصريف المياه الملوثة بالنفط) بعد معاملتها بالطين العضوي. كذلك تم دراسة حركية عملية الامتزاز (Kinetics)

(adsorption capacity) ودراسة سعة عملية الامتزاز (Lagergren and Ho. et al) باستخدام المعادلات الحركية
.(Freundlich, Langmuir, and BET) باستخدام النماذج الرياضية

KEYWORDS: Oil removal; Wastewater treatment; Organoclays; Bentonite; Adsorption.

INTRODUCTION

Many natural and synthetic media have been used for treating oily waters. These media can be classified as filtering media (sand, coal, and diatomaceous earth), coalescing media (fiberglass, polyesterfelt, amberlite XAD-2, and polypropylene), and adsorption media (activated carbon, peat, attapulgite, bentonite, and organoclays) (Mathavan and Viraraghavan 1989, Zunan et al. 1995, Alther 1996a, Alther 1996b).

Adsorption is very efficient, cost effective and most importantly has the capability of meeting the environmental compliance as far as the discharge standard of the oil content of the wastewater is concerned.(Slejeiko 1981). Activated carbon is a common adsorbent used for the removal of hazardous pollutants from aqueous solutions. However, activated carbon adsorption is a nonselective process (Cadena 1989). Organoclay has emerged as a better substitute for activated carbon. In fact, studies show that if a comparison is made between the organoclay and activated carbon, organoclay has several advantages over the activated carbon as an adsorbent (Alther 2002).

Organoclays are manufactured by modifying bentonite (which is a kind of smectite group clay mineral, is almost made up of 80 wt.% of montmorillonite and contains a crystal lattice with three layers) or other clays with quaternary amines, thus changing the hydrophilic nature of clays to organophilic. Quaternary amine is a type of surfactant that contains a nitrogen ion. The nitrogen end of the quaternary amine (i.e., the hydrophilic end) is positively charged and ion exchanges onto the clay platelet for sodium or calcium (Lagaly1984, Alther 2002, Moazed and Viraraghavan 2005, Janes and Boyd 1991, Kowalska et al. 1994).

Moazed and Viraraghavan (2005) used powdered bentonite organoclay to remove oil from water. The concentrations of oil in oily waters varied from 26 to 381 mg/L. The results indicated that the organoclay can remove up to 100% oil from oil in water emulsions. Consequently, the organoclay could be considered an excellent media for treating oily waters. Carmody et al. (2007) investigated the synthesis of oranoclays by the ion exchange of sodium in Wyoming Na-Montmorillonite with three surfactants octadecyltrimethylammonium bromide (ODTMA), $C_{21}H_{46}NBr$, didecyldimethylammonium bromide (DDDMA),$C_{22}H_{48}BrN$, and di(hydrogenated tallow)dimethylammonium chloride (tallow).The organoclays were tested for hydrocarbon adsorption (diesel, hydraulic oil and engine oil), that are likely to be involved in land-based oil spills. Greater adsorption was obtained if the surfactant contained two or more hydrocarbon long chains.

The aim of the present research is to study the removal of oil from wastewater produced from washing unit of "South Baghdad Gas Power Plant" by using bentonitic organoclay. The organoclay was prepared by modifying Iraqi bentonite with quaternary amine (hexadecyltrimethyl ammonium chloride solution 25% wt./vol.). The operating conditions for oil removal were studied in details. Kinetics and adsorption isotherm were also predicted.

EXPERIMENTAL WORK

MATERIALS

Oily Water

The oily water samples were collected from the washing unit of fuel oil in the South Baghdad Gas Power Plant. Oil concentrations used in this study were within the maximum range of 230-1512 mg/L. The characteristics of oily water are shown in table 1.

Table 1. Characteristics of oily water

characteristics	Value
PH	10.13
Oil and grease, mg/L	549
Biological oxygen demand (BOD), mg/L	156
Chemical oxygen demand (COD), mg/L	120
Chlorides, mg/L	230
Nitrates, mg/L	16.1
Phosphates, mg/L	0.92
Sulphates, mg/L	14
Total dissolved solids, mg/L	775
Total suspended solids, mg/L	509
Electrical conductivity	1446

IRAQI BENTONITE

The bentonite used in this study was calcium bentonite powder from the State Company for Geological Survey and Mining (Iraq). The characteristics of the bentonite are presented in table 2.

HEXADECYLTRIMETHYL AMMONIUM CHLORIDE

This type of surfactant was used to modify the hydrophilic nature of bentonite to organophilic. It is produced by the Indian Company ,Unilab Chemicals and Pharmaceuticals PVT.LTD., as a solution in water with concentration of 24-26% (wt./vol.), pH value for 10% concentration of 2.8-3.2, and density of 0.97-0.98 g / cm^3 at 20 $^\circ$C.

Table 2. Characteristics of bentonite

Characteristics	Value
Partical size, mm	0.075
Cation exchange capacity (CEC), meq/100g	70-87
Chemical (wt% dry basis)	
Silica (SiO_2)	54.26
Alumina (Al_2O_3)	14.87
Ferric oxide (Fe_2O_3)	4.94
Magnesium oxide (MgO)	3.8
Calcium oxide (CaO)	5.53
Sodium oxide (Na_2O)	0.98
Potassium oxide (K_2O)	0.38
Titanium oxide (TiO_2)	0.75
Loss on ignition (L.O.I)	12.8
Mineralogy	momntmorillonite, palygorskite, calcite, feldspar, quartz.

EXPERIMENTAL PROCEDURE

Synthesis of Organoclay

Organoclay was prepared by adding the required quantity of hexadecyltrimethy ammonium chloride solution (25% wt./vol.) to the desired quantity of bentonite (particle size of 0.075 mm) in a stainless steel container and mixed thoroughly by hand. The produced paste was then introduced into a meat grinder and the product was collected in a container. The reacted material (organoclay) is then dried in an electrical oven at 60 °C for 48 hours and then ground by agate mortar followed by screening to particle size of 0.075 mm. Organoclay with ratios of 10, 20, 30, 38 g amine/ 100 g bentonite was prepared in this study to find the best ratio of amine to bentonite that gives the highest oil removal efficiency.

Oil Removal From Wastewater

One liter of oily water was first placed into the glass beaker and a desired quantity of prepared organoclay was then added to the beaker. The materials were mixed using an electrical mixer at adjustable mixer speed for the required time. Then the slurry was filtered using vacuum filtration unit to separate organoclay from treated water. The filtrate was used for oil concentration measurement using partition graphmetric method 5520B (standard method, 1995).

RESULTS AND DISCUSSION

X-ray Diffraction Analysis of Bentonite and Organoclay

Figures 1 and 2 show the interlayer spacings of natural bentonite and organoclay. Tables 3 and 4 represent peak data list of these figures respectively. The organoclay and natural bentonite were previously dried at 60 °C.

The properties of organoclays were investigated by basal x-ray diffraction analysis. The basal spacings of the original clays were changed from 14.256 to 18.470 Å. The organoclay displayed a greater interlayer spacing than the corresponding natural bentonite. This behavior was confirmed by Diaz et al. (2005) and Diaz (1999, 2001).

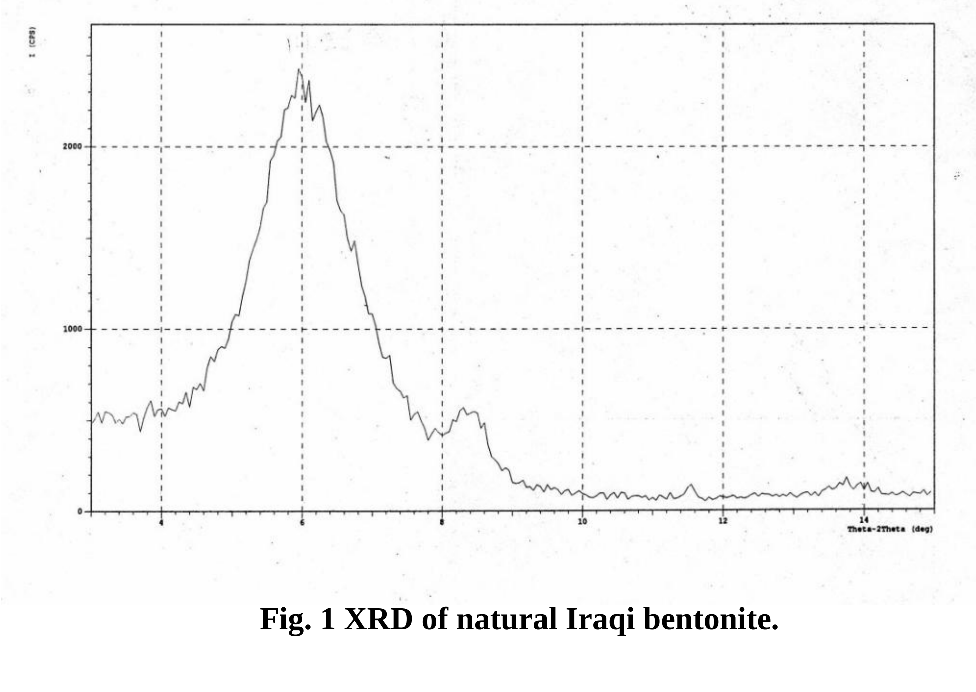

Fig. 1 XRD of natural Iraqi bentonite.

Table 3. Peak data list of natural Iraqi bentonite.

Peak №	2theta(deg)	d (Å)	I/I1	FWHM(deg)	Intensity (counts)	Integrated Int (counts)
1	3.8481	22.94287	4	0.63340	29	781
2	6.1949	14.25574	100	1.64190	782	28207
3	8.6621	10.20007	13	0.60000	98	2072

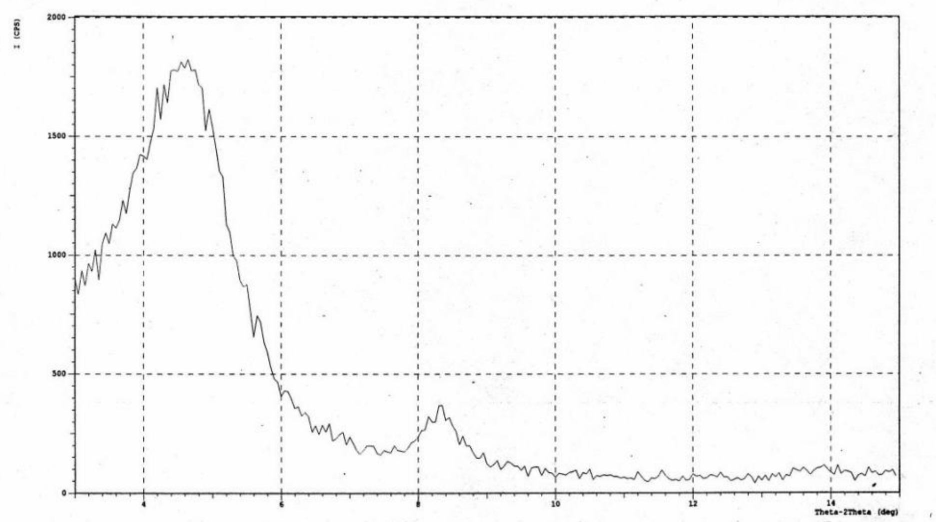

Fig. 2 XRD of prepared organoclay.

Table 4. Peak data list of prepared organoclay.

Peak №	2theta(deg)	d (Å)	I/I1	FWHM(deg)	Intensity (counts)	Integrated Int (counts)
1	4.7808	18.46877	100	1.40150	471	13955
2	8.4699	10.43109	10	0.64880	48	598
3	14.0156	6.31370	4	1.07500	17	506

INFRARED CURVES

The absorption of infrared radiation by clays was recorded over a range of 4000 to 400 cm^{-1} as shown in figures 3 and 4 for natural Iraqi bentonite and prepared organoclay respectively. The natural clay showed characteristics smectitic clay mineral peaks at 470.6, 524.6, 749.62, 918.05, 1033.77, 1635.52, 3417 and 3625.92 cm^{-1}. The natural clay showed no intense peaks corresponding to organic matter at 1464, 2827 and 2909 cm^{-1}. Bala et al. (2000) assigned the 1464 and 2827 cm^{-1} peaks to the CH_2 scissor vibration band and the symmetrical CH_3 stretching absorption band respectively. The 2909 cm^{-1} peak was assigned to CH stretching band.

The organophilic clay also showed the characteristic peaks of clay minerals, in spite of being of low density. This is an indication of the organophilic character of the clay. The organic matter peaks at 1473.51, 2854.45 and 2923.88 cm^{-1} were sharper than those of the natural clay. The CH_3, CH_2 and CH bands confirmed the alkylammonium intercalation in the interlayer galleries of the clay mineral, and the lower intensity of the characteristic clay mineral peaks indicated the organophilic nature of the treated clay.

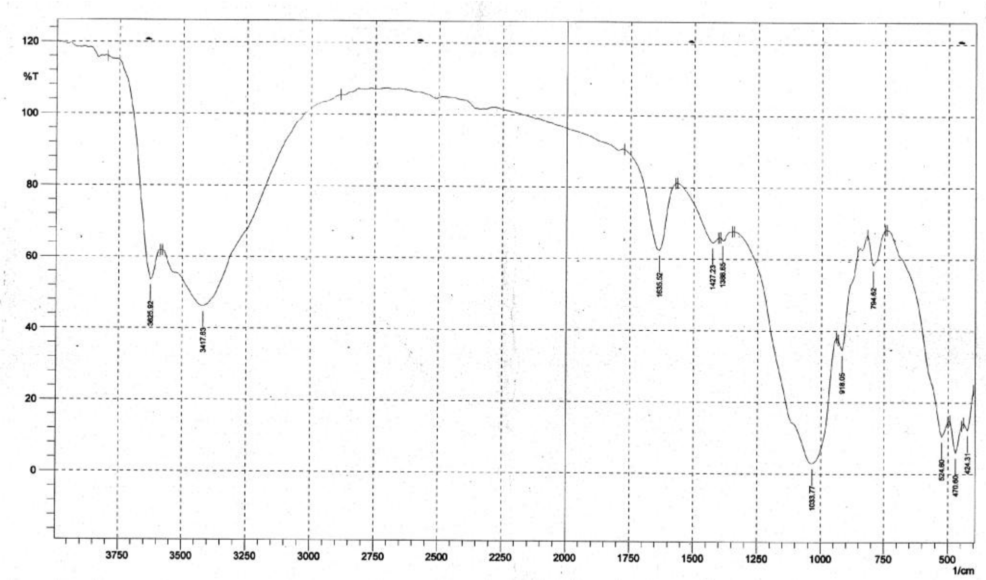

Fig. 3 Infrared curve of natural Iraqi bentonite.

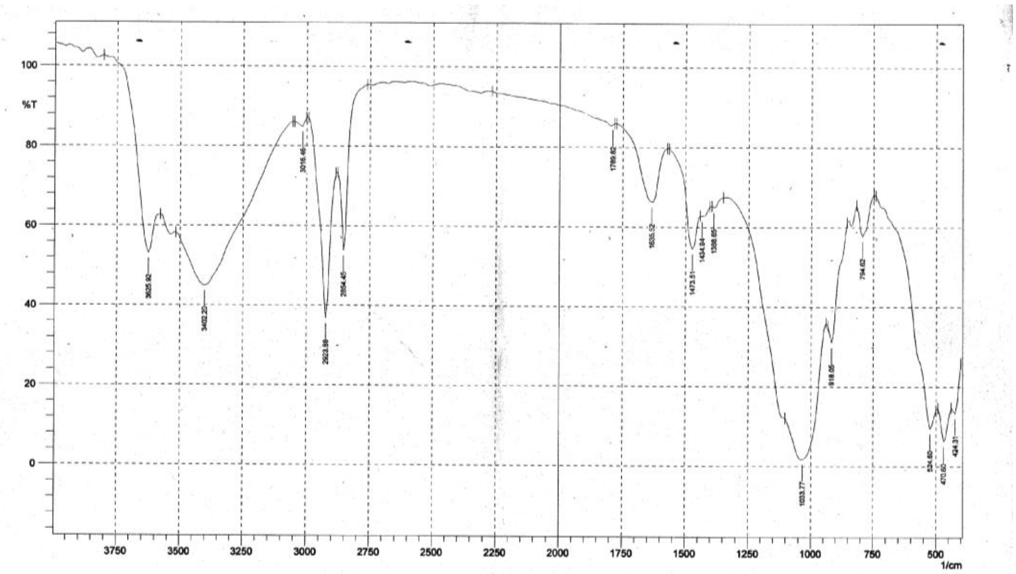

Fig. 4 Infrared curve of prepared organoclay.

EFFECT OF BENTONITE QUANTITY ON OIL REMOVAL

The ability of bentonite to remove oil from wastewater was studied by adding 5, 10, 15 and 20 g of Iraqi bentonite to 1 liter of wastewater with initial oil concentration 871.8 mg/L. Mixer speed used was 450 rpm, and time 1 hour. The results of these experiments is shown in figure 5.

Bentonite appears good capability for oil removal where the concentration of oil decreases rapidly from 871.8 to 298.4 mg/L when 5 g of bentonite is added. Using quantities of bentonite more than 5g, the concentration of oil decreases slowly until it reaches 183.4 mg/L for 15g of bentonite.

Oil concentration was not decreased below 10 mg/L (allowable limits of oil in the discharged effluents), as shown in, figure 5. This is because of the hydration of bentonite which causes that organic compounds with average molecular weights (amu) below 150 are weakly adsorbed or not adsorbed by pure montmorillonites (bentonite) due to their relatively large solubility in water (unless they carry a charge and can enter into an exchange reactions). The interaction forces under these conditions are the same in magnitude as hydration forces, so that competition with water molecules for the solid surface dominates. Soluble compounds with molecular weights above 150 amu, whether or not charged are often adsorbed by montmorillonites due to their reduced solubility in water (Cadena, 1989).

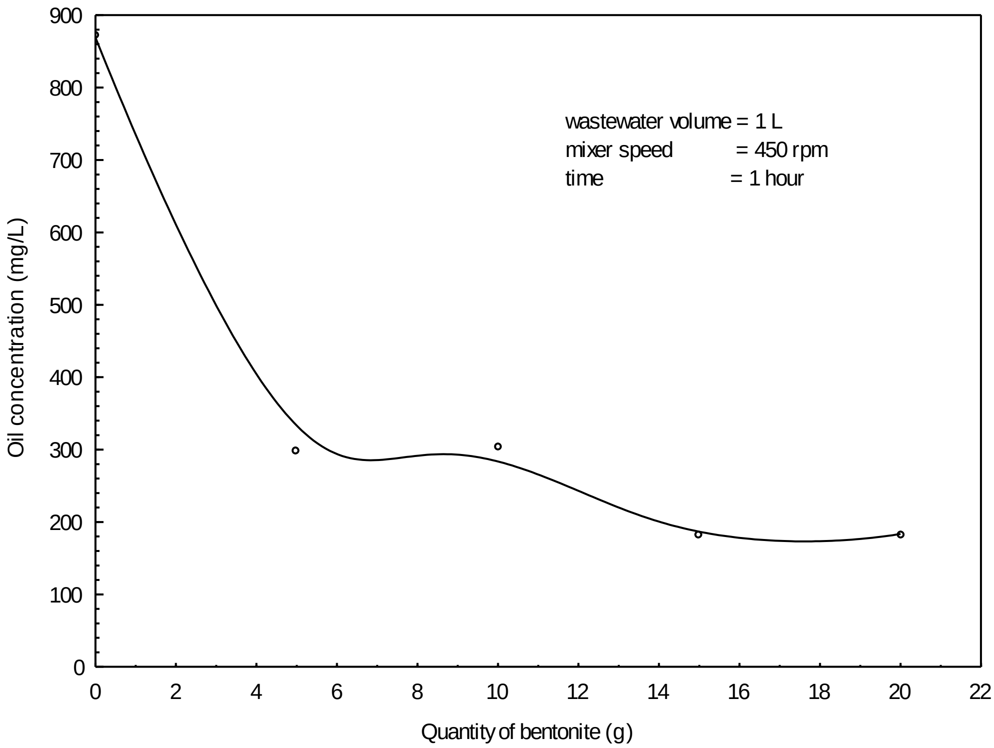

Fig. 5 Effect of bentonite quantity on oil concentration.

EFFECT OF QUANTITY OF ORGANOCLAY ON OIL REMOVAL

The prepared organoclays with quaternary amine weight ratios of 10, 20, 30 and 38 g/100g bentonite were investigated to find the quantity of organoclay required to remove the greatest amount of oil from wastewater. Figure 6 shows the effect of quantity of organoclay (2, 5, 10, 15 and 20g) on the concentration of oil in wastewater for the four organoclays prepared. One liter of wastewater with initial concentration of (1450 – 1512 mg/L), mixer speed 450 rpm, and time 1 hour were used.

As shown in figure 6, the concentration of oil in wastewater samples decreased rapidly as the quantity of organoclay increased until it reaches 10g for amine ratio of 10 and 2g for amine ratio of 20, 30 and 38 g amine/100g bentonite after which the concentration falls gently. The best quantity of organoclays were 20g for amine ratio of 10 g amine/100g bentonite and 15 g for amine ratios of 20, 30, and 38 g amine/100g bentonite respectively, where the lowest concentrations of oil obtained in treated water were 117, 13, 1 and 8.8 mg/L respectively Figure 6 also shows that the lowest oil concentrations of 1 and 8.6 mg/L are obtained for organoclay with amine ratios of 30 and 38 g amine/100g bentonite respectively, which represents oil removal efficiency of 99.93% and 99.4% respectively.

The reason for the rapid decrease of oil concentration especially for organoclays with high amine ratio is due to the organophillic nature of the organoclay. The concentration of oil decreases gently after this rapid decrease because the surface of the organoclay is filled with the oil and much more organoclay must be added to remove extra amount of oil, also the oil concentration difference between the bulk of the liquid and the surface of the organoclay, which represents a driving force for oil adsorption, decreased gradually causing a decrease in the adsorption rate, so another surface layer of organoclay must be added to overcome this problem (Patle 2004).

Mozed and Viraraghavan (2005), used organoclay to remove oil from produced water (a byproduct of oil and gas production) and they reach oil removal efficiency of 97%.

Same results were obtained for initial oil concentration of (255 – 264) mg/L, where best oil concentrations for treated water were 140, 20, 1 and 6 for organoclays with amine ratio of 10, 20, 30 and 38 g amine/100g bentonite respectively. In these experiments mixer speed was 450 rpm and time 1 hour. The results are shown in figure 7. The results from figures 6 and 7 prove that prepared organoclay can be used efficiently for removal of oil at wide range of concentration in wastewater.

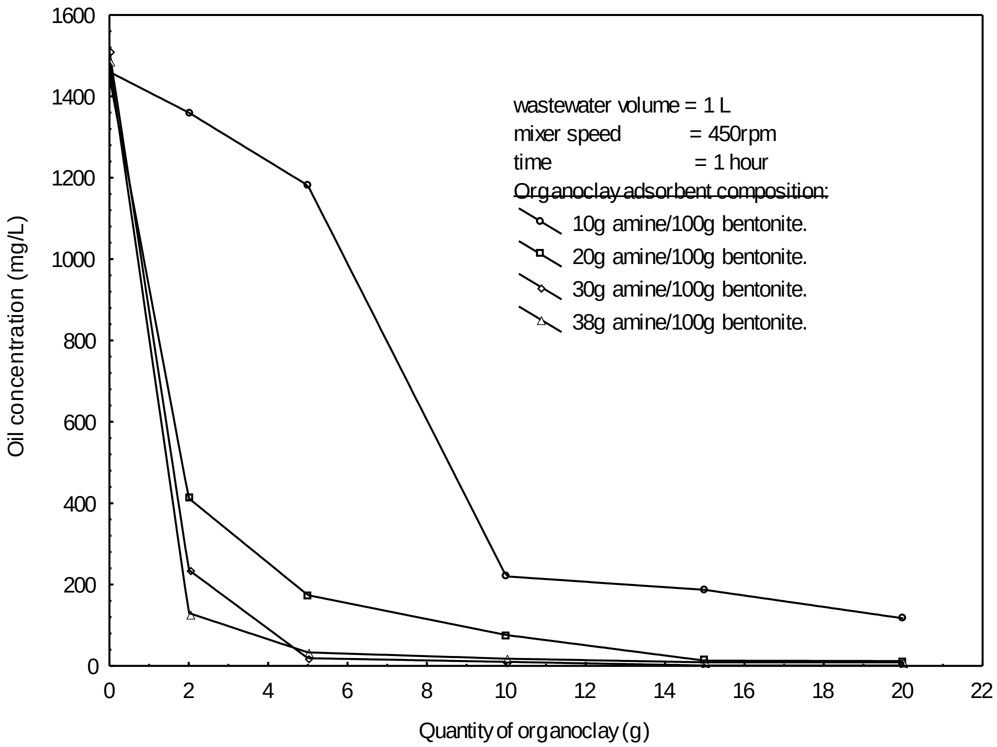

Fig. 6 Effect of organoclay quantity on oil concentration for different weight ratio of amine to bentonite ($C_{\circ}$ = 1450–1512mg/L).

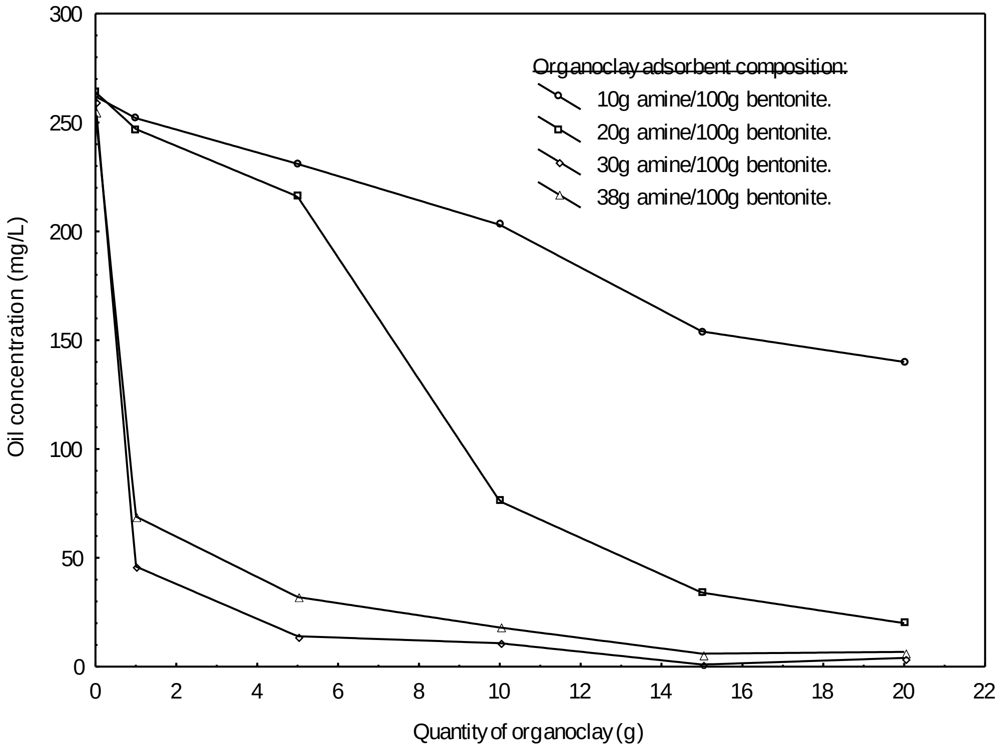

Fig. 7 Effect of organoclay quantity on oil concentration for different weight ratio of amine to bentonite ($C_{\circ}$ = 255–264 mg/L).

EFFECT OF AMINE TO BENTONITE WEIGHT RATIO ON ORGANOCLAY ADSORPTION OF OIL

In order to show the effect of weight ratio of amine to bentonite on oil removal, the equilibrium oil concentrations of treated water were plotted against amine to bentonite weight ratio figure 8. Mixer speed used for these experiments was 450 rpm, time 1 hour, quantity of prepared organoclays 20g for amine ratio 10 g amine/100g bentonite and 15g for amine ratios 20, 30 and 38 g amine/100g bentonite. One liter of wastewater was used with initial concentration of (1450 – 1512) mg/L. It can be seen clearly from figure 8 that the ratio of amine to bentonite has a significant effect on the oil removal efficiency where the concentration of oil decreases from 117 to 8.8mg/L as the amine ratio in organoclay increases from 10 to 38g amine/100g bentonite. The best amine ratio was 30g amine/100g bentonite, where oil concentration decreased to 1 mg/L.

Figure 9 shows the effect of amine ratio for initial concentration of oil of (255 – 264 mg/L). Similar effect is observed from this figure, where the best amine ratio was 30g amine/100g bentonite for which oil concentration decreased to 1 mg/L.

The weight ratio of amine to bentonite was also represented in term of cation exchange capacity (CEC). The cation exchange capacity for bentonite is 80 meq/100g bentonite. Weight ratio of amine to bentonite was calculated from its relation with cation exchange capacity percentage, where 80 meq/100g bentonite represnts 100% CEC. The results cited in table 5 and appropriate equation to satisfy these results is found to be:

$$\textbf{g amine/100g bentonite} = \mathbf{0.256 \times \%\ CEC} \qquad (1)$$

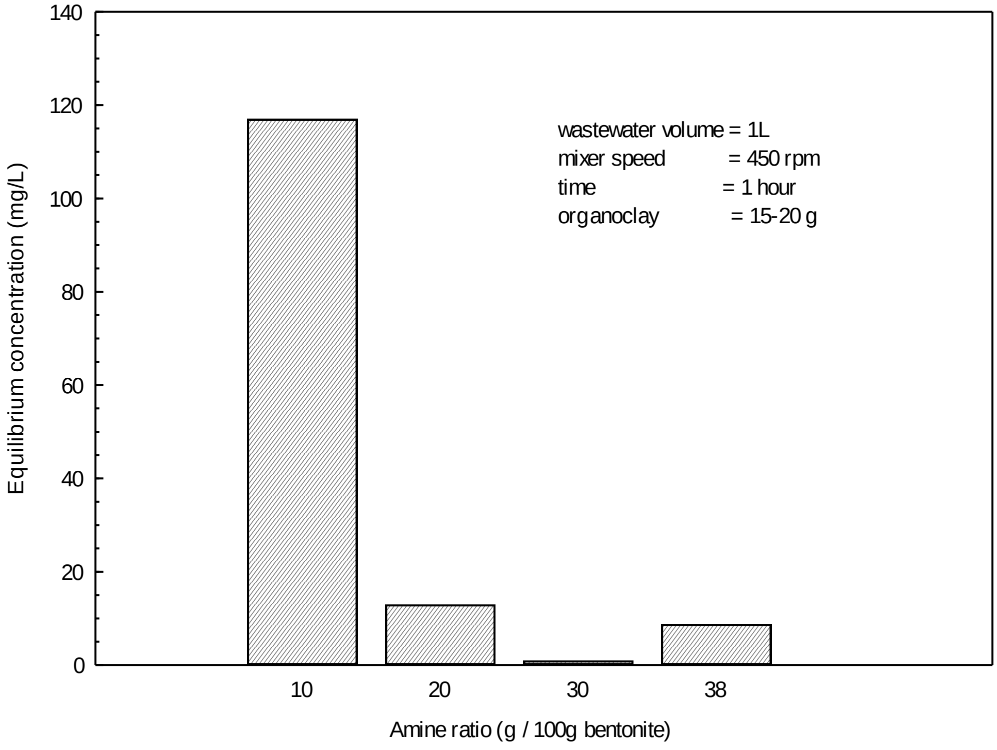

Fig. 8 Effect of amine to bentonite weight ratio on equilibrium concentration ($C_\circ$ = 1450–1512mg/L).

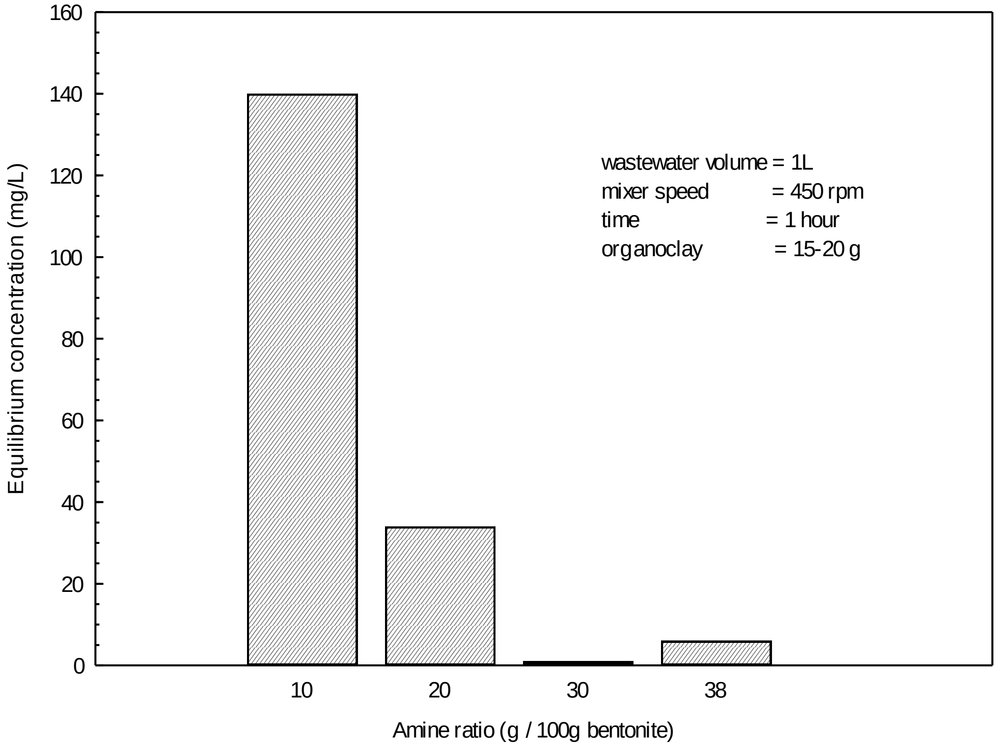

Fig. 9 Effect of amine to bentonite weight ratio on equilibrium concentration ($C_\circ$ = 255–264 mg/L).

Table 5. Amounts of amine used for preparation of bentonite organoclay
(100% CEC equivalent to 25.6 g amine / 100g bentonite; CEC for bentonite = 80 meq/100g bentonite)

%CEC	0	39.1	78.12	117.18	148.4
g amine/100g bentonite	0	10	20	30	38

Figure 10 represents the effect of cation exchange capacity (%CEC) on the adsorption capacity.

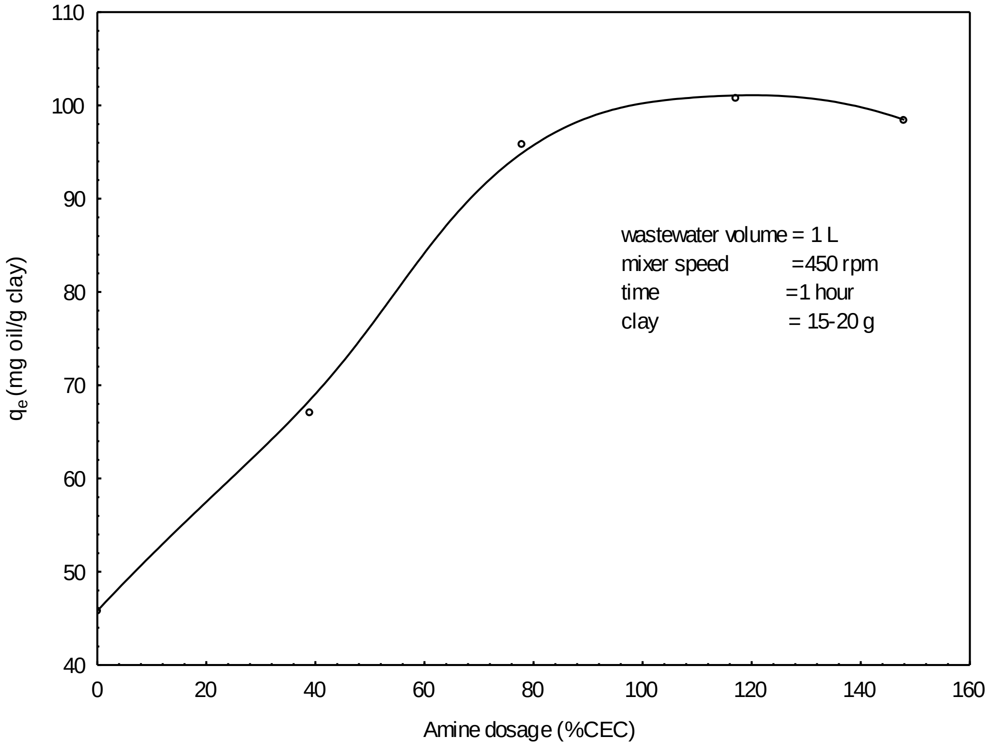

Fig. 10 Effect of amine dosage (%CEC) on adsorption capacity of organoclay ($C_\circ$ = 1450–1512mg/L).

Increasing amine dosage causes the increase of adsorption capacity of organoclay. 30g amine/100g bentonite (117% CEC) shows the maximum oil removal. Oil adsorption increased rapidly in the range from 0 to 78.12% CEC, above which the amine dosage had small effect on adsorption capacity.

EFFECT OF MIXER SPEED

To show the effect of mixer speed on the removal of oil from wastewater by organoclay, four experiments were conducted for the mixing speed 50, 150, 250, and 450 rpm. Initial oil concentration was 1221 mg/L, time 0.5 hour, and 15g organoclay of 30g amine/100g bentonite added to 1 litter of wastewater. The results is shown in figure 11.

Oil concentration decreases as mixer speed increases and the lowest oil concentration (below 8 mg/L) observed for mixer speed higher than 250 rpm. Oil concentration decreases to 3.2 mg/L for mixer speed 450 rpm.

The results of the effect of mixer speed is not surprising, where oil concentration decreases as mixer speed increases due to the decreasing in the resistance to mass transfer for oil from bulk of the wastewater to the surface of organoclay. The resistance to mass transfer is due to the diffusion layer surround each particle of organoclay. Patel (2004) stated that the mass transfer mechanism for oil adsorption by organoclay is a two phase process and can be described as diffusion of oil from the oil-water emulsion to the surface of the organoclay and the adsorption of oil within the pore structure of the organoclay.

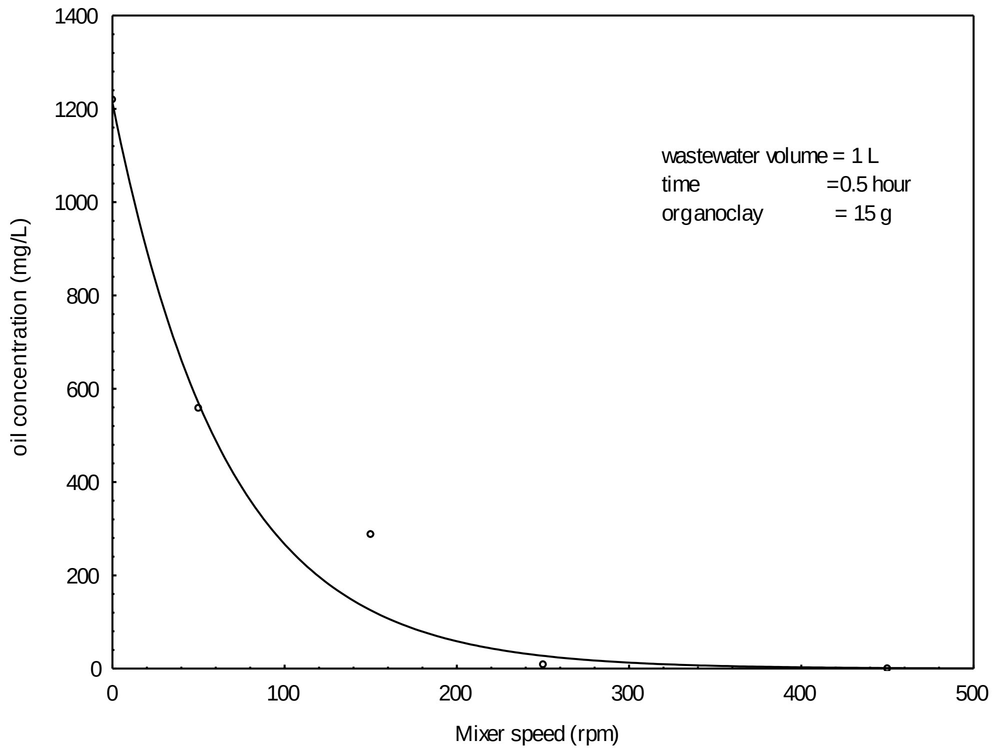

Fig. 11 Effect of mixer speed on oil removal using organoclay.

BATCH KINETICS STUDY

The plots of oil concentration versus time for initial oil concentration 1512 and 230 mg/L are shown in figures 12 and 13, respectively. In these experiments 15g organoclay of 30g amine/100g bentonite was added to 1 liter of wastewater and mixer speed fixed at 450 rpm.

From these plots, the equilibrium time was found to be 30 minutes for both concentrations. Also, it can be seen from these plots that adsorption of oil by organoclay included two phase adsorption fast followed by slow rate adsorption . The elapsed time for the rapid adsorption rate was 10 minutes. The residual oil concentrations of 1.6 and 1.2 mg/L were observed after the rapid adsorption phase for initial concentrations of 1512 and 230 mg/L respectively.

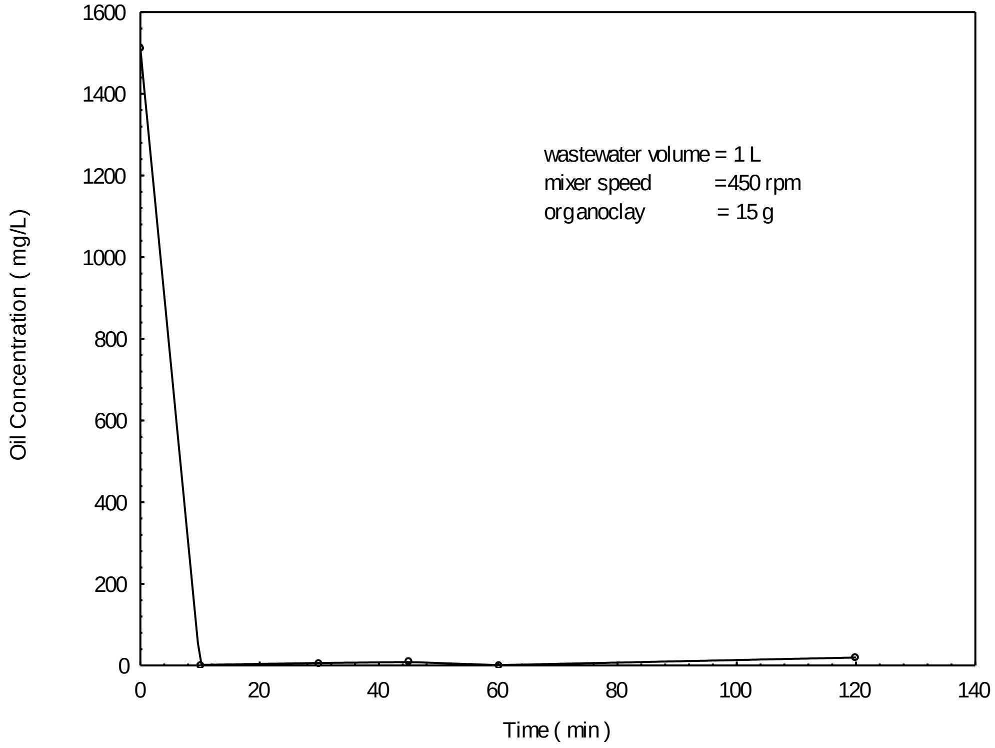

Fig. 12 Equilibrium time for the adsorption of oil by organoclay ($C_\circ$ = 1512mg/L).

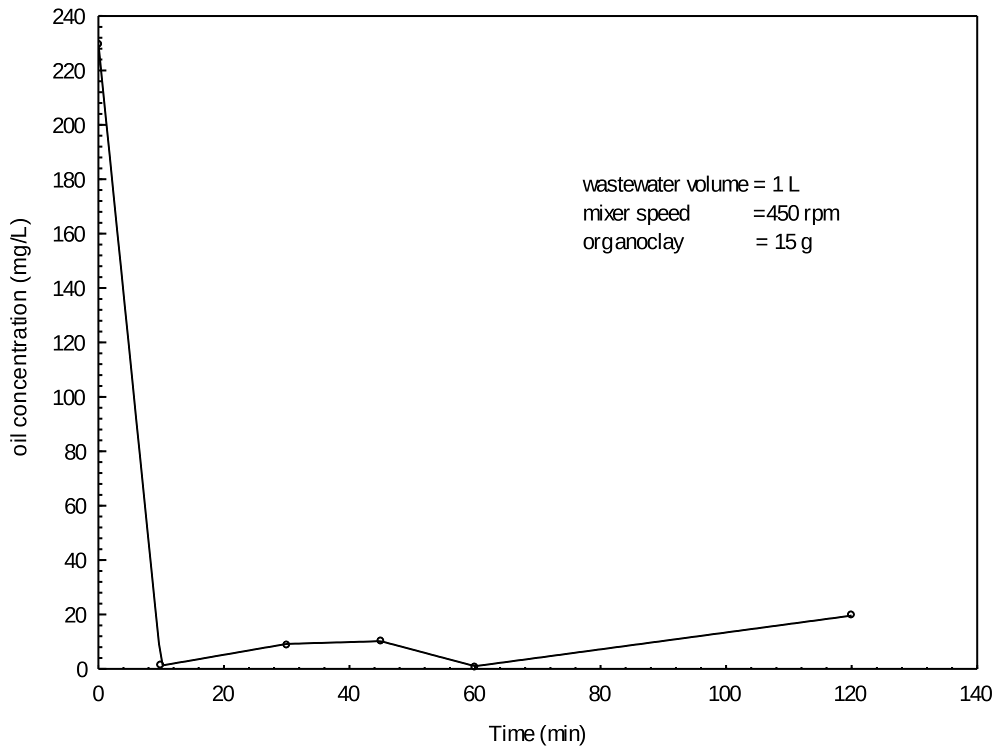

Fig. 13 Equilibrium time for the adsorption of oil by organoclay ($C_\circ$ = 230 mg/L).

Batch kinetic data was fitted to the Lagergren eq. (2) and Ho et al. eq. (3) models (Ho and McKay 1999; Ho et al. 1996) by non-linear regression analysis using software "STATISTICA".

$$q_t = q_e - q_e \exp(-kt) \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{2k'q_e^2} + \frac{t}{q_e} \quad (3)$$

Where:

k = equilibrium rate constant of sorption (1/h);
k' = second-order reaction rate constant for adsorption (g/mg.h);
q_e = amount of metal ion adsorbed at equilibrium (mg/g); and
q_t = amount of metal ion adsorbed (mg/g) at any given time t (h)

Tables 6 and 7 show the Lagergren and Ho et al. models and parameters for the adsorption of oil by organoclay for initial oil concentrations 230 and 1512 mg/L. The Lagergren and Ho et al. models are plotted in figures 14 and 15 for both initial concentrations.

Table 6. Lagergren and Ho et al models for the adsorption of oil by organoclay.

Description	Equation	Correlation coefficient (r)
C_o = 230 mg/L		
Lagergren model	q_t =14.78436-14.78436 exp (-3.9986 t)	0.99713
Ho et al. model	t/q_t =1/[2×21.8776)(14.8126)2]+t/14.8126	0.99678
C_o = 1512 mg/L		
Lagergren model	q_t =100.307-100.307exp (-72.112 t)	0.999939
Ho et al. model	t/q_t =1/[2×17.51504)(100.3683)2]+t/100.3683	0.999930

Table 7. Parameters calculated using Lagergren and Ho et al. model for the adsorption of oil by organoclay

Description	Lagergren model		Ho et al. model	
	k (1/h)	q_e (mg/g)	k' (g/mg.h)	q_e (mg/g)
C_o = 230 mg/L	53.9986	14.78436	21.8776	14.8126
C_o = 1512 mg/L	72.112	100.307	17.51504	100.3683

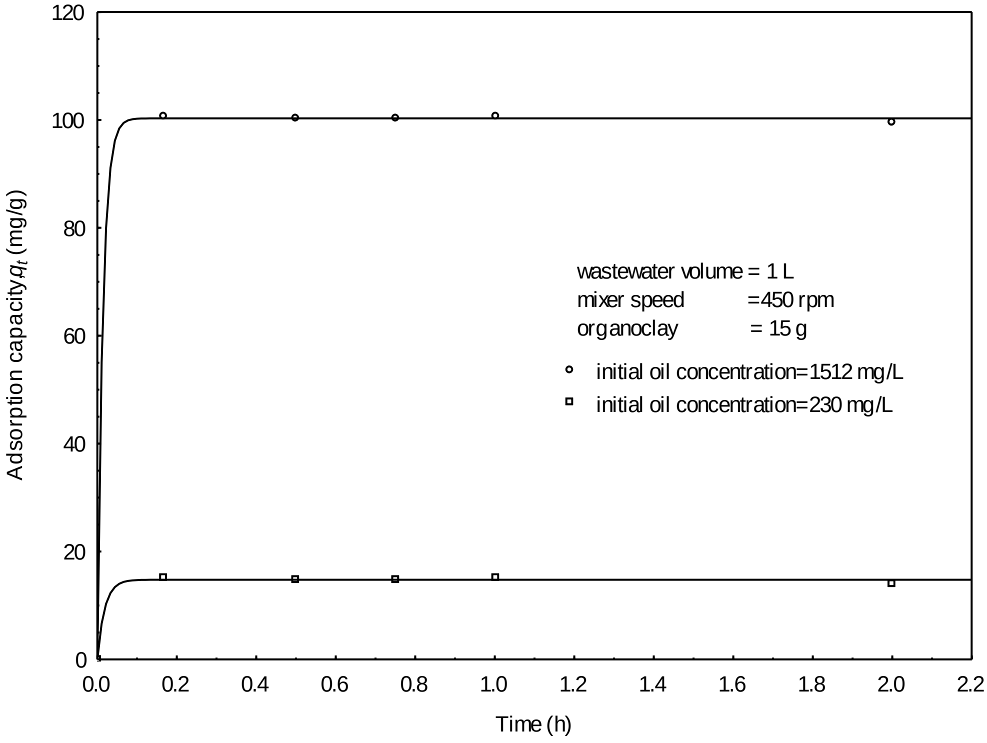

Fig. 14 Lagergren plot for the adsorption kinetics of oil by organoclay

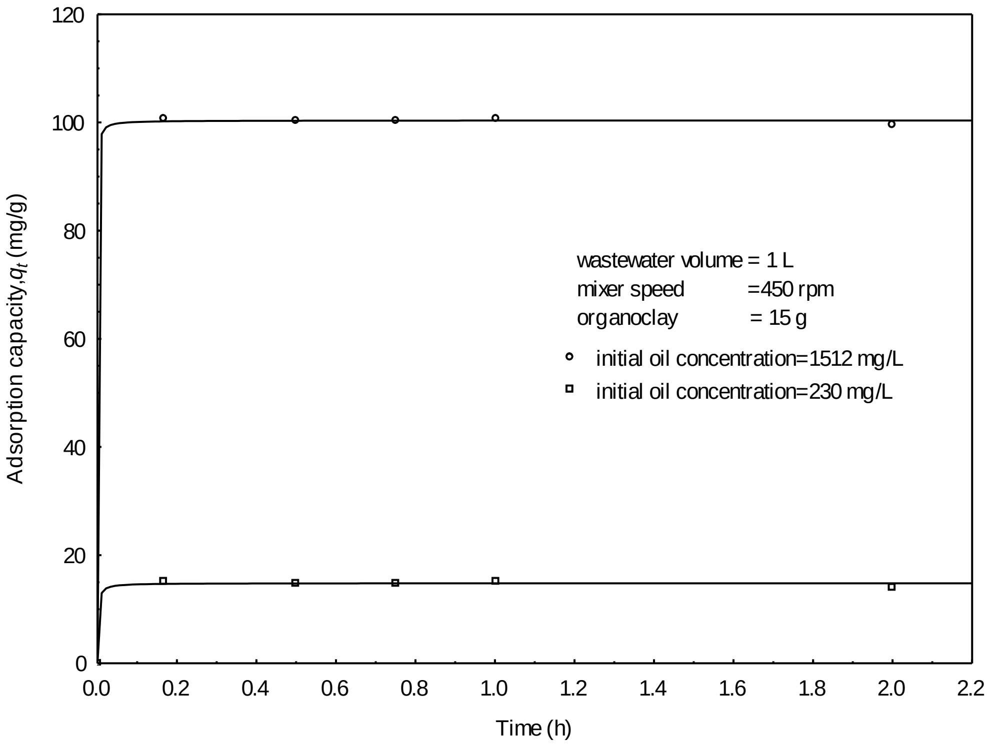

Fig. 15 Ho et al. plot for the adsorption kinetics of oil by organoclay

Based on the correlation coefficient values (r > 99%), it was found that the adsorption kinetics for oily wastewater concentrations of 230 and 1512 mg/L can be will described by lagergren and Ho et al. model as well.

BATCH ISOTHERM STUDIES

Several experiments were performed to study the isotherm of oil adsorption by organoclay. The quantity of organoclays were varied between 1 to 15 g and the concentration of oil in treated water was measured for each experiment. The organoclay used was 30 g amine/100 g bentonite and the mixer speed was 450 rpm, and time 0.5 hour. One liter of wastewater with oil concentrations of 245 and 1512 mg/L were used.

From these experiments the adsorption capacity of organoclay, mg oil adsorbed/ g organoclay (x/m), were calculated and plotted versus oil concentration by using a non – linear isotherm models Freundlich eq. (4), Langmuir eq. (5) and BET eq.(6) (Reynolds and Richards 1996).

$$\frac{x}{m} = kC_e^{\frac{1}{n}} \tag{4}$$

$$\frac{x}{m} = \frac{abC_e}{1+aC_e} \tag{5}$$

$$\frac{x}{m} = \frac{ACX_m}{(C_s - C)[1+(A-1)\frac{C}{C_s}]} \tag{6}$$

Where:

x = mass of solute adsorbed to the solid (mg);
m = mass of adsorbent used (g);
k = Freundlich equilibrium constant indicative of adsorptive capacity;
n = Freundlich constant indicative of adsorption intensity;
C_e = concentration of solute in solution in equilibrium (mg/L);
a = Langmuir constant; the amount of solute adsorbed per unit weight of an adsorbent in forming a complete monolayer (L/mg);
b = Langmuir constant (mg/g);
A = a constant describing energy interaction between the solute and the adsorbent surface;
X_m= amount of solute adsorbed in forming a complete monolayer (M/M);
C = concentration of solute in solution at equilibrium (M/L_n^3) in BET model; and
C_s = saturation concentration of solute in solution (M/L_n^3).

The non–linear estimation was performed using the "STATISTCA" and shown in figures 16, 17 and 18. The details of the regression equations obtained for the Langmuir, the Freundlich and the BET isotherms for the adsorption of oil from different oily waters by the organoclay are presented in tables 8 and 9.

From the statistical analysis (high values of the correlation coefficients) it was found that generally the adsorption of oil by organoclay could be well described by the all three isotherm models (Freundlich, Langmuir and BET isotherm). The correlation coefficients were in the range of 92-94% for initial oil concentration 245 mg/L, while it is in the range of 91- 92% for initial oil concentration 1512 mg/L.

Maximum adsorption capacity 641.8 mg oil/g organoclay was found for initial oil concentration 1512 mg/L which represents 64.18% of the weight organoclay. Alther (1995, 1996b, 2002) reaches oil adsorption capacity up to 70% of the organoclay weight, and he stated that organoclays are capable of removing emulsified oils from water by up to about 100 percent.

Table 8. Regression equations of various isotherm models for oil adsorption by organoclay.

Description	Equation of regression	r
C_o = 245 mg/L		
Freundlich	$x/m = 1.3842\ C_e(1/0.808)$	0.93981
Langmuir	$x/m = (0.00127\times2624.677\ C_e)/(1+0.00127C_e)$	0.92509
BET	$x/m=(0.7478\times856.3933C_e)/(C_s-C_e)\times[1+(0.7478-1)\ C_e/C_s]$	0.94310
C_o = 1512 mg/L		
Freundlich	$x/m = 68.23774\ C_e(1/2.41173)$	0.91648
Langmuir	$x/m = (0.03597\times658.377C_e)/(1+0.03597C_e)$	0.90869
BET	$x/m=(68.53088\times560.8312C_e)/(C_s-C_e)\times[1+(68.53088-1)C_e/C_s]$	0.91583

The values of parameters in the isotherm models applied to oily waters are presented in table 9.

Table 9. Values of isotherm constants for bentonite organoclay

Description	Freundlich		Langmuir		BET	
	k	n	a	b	A	X_m
C_o = 245 mg/L	1.3842	0.808	0.00127	2624.677	0.7478	856.3933
C_o = 1512 mg/L	68.2377	2.41173	0.03597	658.377	68.53668	560.8312

Depending on the isotherm figures, the strategy of choice of the adsorption capacity for the organoclay is that maximum adsorption capacity must be selected to get minimum oil concentration for the treated water. The weight of organoclay used for oil removal is calculated from the selected adsorption capacity at the desired final oil concentration of the treated water. Also isotherm equations are used with known initial and final oil concentration to calculate x/m from which the weight of oganoclay can be determined. These calculations can be used successfully in the scale up of adsorption unit (design of batch adsorption unat).

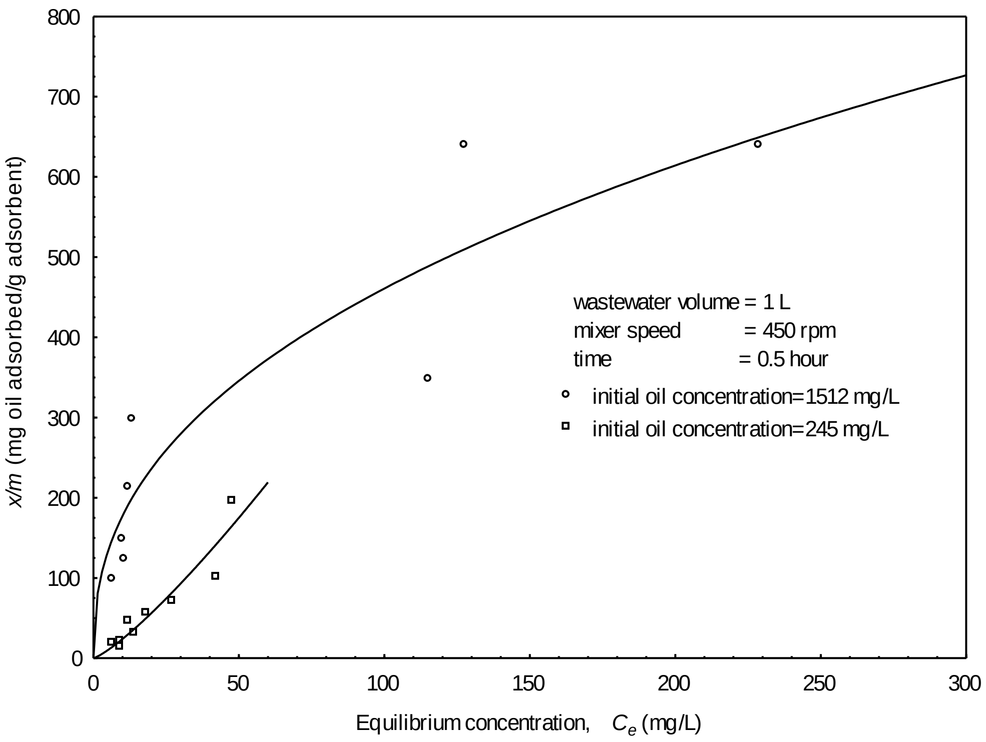

Fig. 16 Freundlich isotherm for the adsorption of oil by organoclay

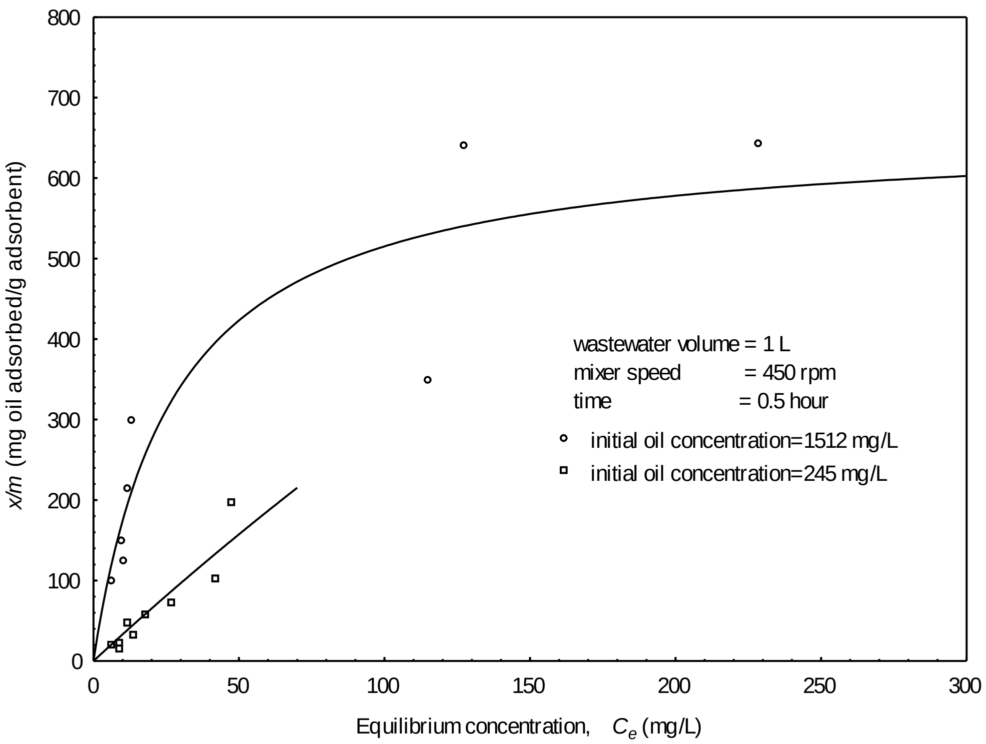

Fig. 17 Langmuir isotherm for the adsorption of oil by organoclay

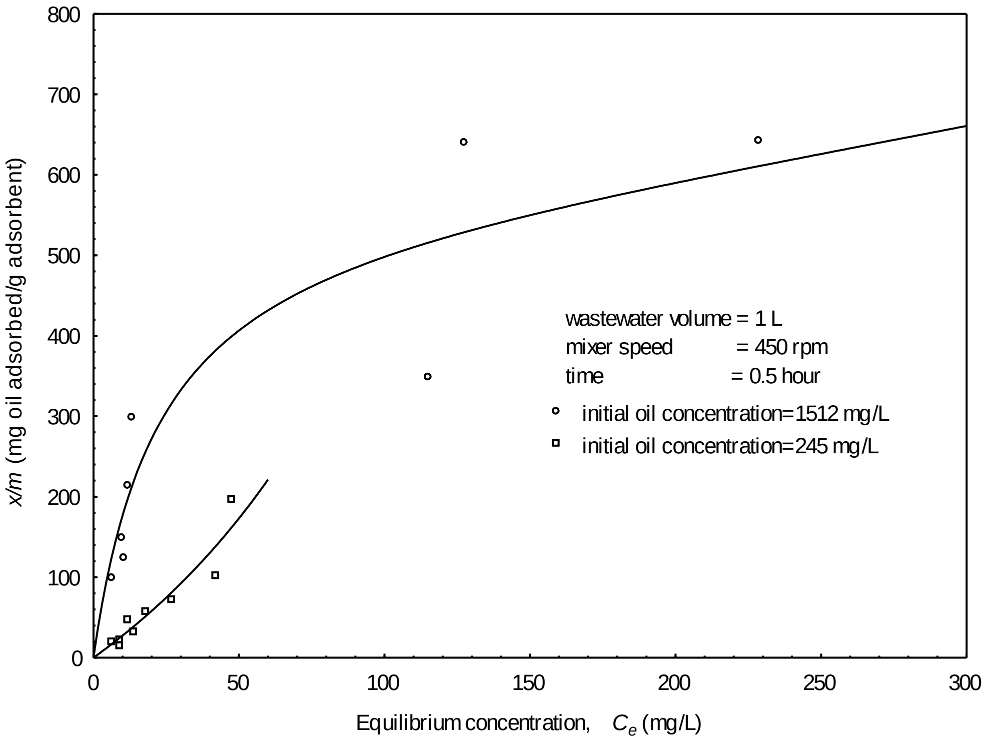

Fig. 18 BET isotherm for the adsorption of oil by organoclay

CONCLUSIONS

- Iraqi Bentonite has a good capability for oil removal where decreasing the oil concentration in waste water from 871 to 183.2 mg/L using maximum 20g/L of bentonite. But the oil concentration can not be achieved to decrease below the recommended limit for oily wastewater discharge (10 mg/L).
- Spectrophotometer measurements (XRD and FTIR) gave good approximation for the exchange of the quaternary amine (hexadecyltrimethyl ammonium HDTMA+ cation) in specify place of ca^{++} at the surface of bentonite to obtain organoclay.
- The quantity of quaternary amine that used in preparation of organoclay has very appreciable effect on the removal of oil from wastewater. As the weight ratio of quaternary amine in the organoclay increases then the oil removal increases. 15g/L of organoclay with amine ratio of 30g amine/ 100g bentonite is recommended to remove oil from wastewater
- Mixer speed has a considerable effect on the removal of oil from wastewater. Oil concentration falls from 1221 mg/L to 3.2mg/L when mixer speed increased from 0 to 450 rpm respectively for operating time of 0.5 hour.
- Batch kinetic studies showed that equilibrium time was reached within 0.5 hour of contact between the organoclay and wastewater.
- Results clearly followed that both pseudo first order (Lagergren) and pseudo second order (Ho et al.) models provided realistic descriptions of the kinetics of adsorption of fuel oil by organoclay. The correlation coefficients (r) obtained from “STATISICA PROGRAM” for the two models exceed 99%.

- The isotherm models (Freundlich, Langmuir and BET) gave excellent fitting for the adsorption capacity of organoclay versus equilibrium concentration of oil . The correlation coefficients (r) obtained from "SATISTICA PROGRAM" for these models were in the range of 90.87- 91.65% and 92.51- 94.31% for oil concentrations of 1512 and 245 mg /L respectively.
- Organoclay prepared from Iraqi bentonite is very effective in removing oil from wastewater. The best results obtained for the removal of oil from wastewater with concentration of 1512mg/L are 15g of prepared organoclay having 30g amine /100g bentonite added to 1 liter of wastewater for 0.5 hour and using mixing speed of 450 rpm to reduce the concentration of oil below 10mg/L which is the standard limit for discharge oily wastewater.

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