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Studying the Treatability of Different Types of Nanoparticles for Oil Content Removal from Oily Wastewater Produced from Refinery Process

Saja Mohsen Alardhi,[a] Forat Yasir AlJaberi,[b,*] Laith Majeed AlSaedi[c]

[a] *Nanotechnology Advanced Material Research Center, University of Technology, Iraq*

[*b] *Chemical Engineering Department, College of Engineering, Al-Muthanna University, Al-Muthanna, Iraq*

[c] *Missan Oil Company*

Abstract

Huge amount of oily wastewater is annually discharged from several activities such as oil refineries, chemical and petrochemical industries. Several methods are employed for the treatment of oily wastewater including physical, chemical, and biological techniques in order to minimize the harmful impacts before being reused. The present study compares the treatability among three different types of nanoparticles NPs (MCM-41, MWCNT and $BaFe_2O_4$) to remove oil content from real oily wastewater discharged from refinery process under the effect of the operational variables which are the dose of the effective NPs (0.025-0.10 g), agitation speed (100-250 rpm), and the contact time (5-120 min) using batch-scale. RSM design method and Minitab program were performed to design the experiments and to estimate the mathematical correlations and the optimum values of the operational variables. Various devices were employed to test the properties of nanoparticles such as X-ray diffraction, SEM and FTIR. The results revealed that the (MCM-41) type possesses the higher treatability in comparison to other types. Moreover, the Langmuir isotherm gives a better fit than the Freundlich isotherm model. The optimum values of the operational parameters obtained were 0.063g, 162rpm and 120min for the dosage of MCM-41 NPs, agitation speed and the contact time respectively. The oil content removal efficiency at these conditions of the optimum values was 98.3% as observed which proofs the treatability of MCM-41 NPs in case of real oily wastewater.

Keywords: Refinery wastewater; Oil content; Wastewater treatment; Nanoparticles; RSM design; Adsorption; Adsorption isotherm models.

1. Introduction

Petroleum refineries are consisting of various processes such as distillation, hydro-treating, desalting and cooling systems that depend on the type of crude oil refined and the required products. Each refinery process consumes large amount of water, that may reach about 80 million cubic meter every day in comparison to other industrial activities in a given region [1,2]; Oil pollution may arise either accidentally or operationally whenever the oil is produced, transported, stored and treated, or when it is used on land or at sea [3], hence, huge amount of wastewater is discharged annually which are different in their properties depending on the process specification and its arrangement. Oily wastewaters are classified as a great crisis affecting the aquatic systems and therefore it is extremely important to find efficient and suitable methods to treat these oily water [4,5].

Petroleum- polluted wastewaters include several kinds of organic and inorganic contaminants with diverging levels of pollution, Petroleum wastewater is depicted by an extent of contaminants containing organics, such as dispersed oil, oil and grease and heavy oil (viscosity larger than 100 mPas), polycyclic aromatic hydrocarbons (PAH), phenols, and inorganics such as ammonia and heavy metals [6]. In 2014, more than 17500 m^3 of wastewater every day that contains numerous kinds of organic and

*Corresponding author e-mail: furat_yasir@yahoo.com.; (Dr. Forat Yasir AlJaberi).
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inorganic pollutants are released from Iraqi industrial activities [7].

Oil in water can be classified as free, dispersed, emulsified and dissolved oil. The first two kinds can be removed from wastewater by modest physical processes. However, emulsified and/or dissolved oil are more complicated to be separated. Vintage oily wastewater handling processes comprise separation by gravity and skimming, air flotation, de-emulsification, coagulation and flocculation. These techniques have different drawbacks such as low efficiency, high operation costs, corrosion and recontamination problems [8]. The adsorption technique as an economical and excellent approach for the removal of organic pollutants has drawn much research awareness in many environmental fields [4,9].

Nano-materials have private mechanical, electrical, chemical, optical and magnetic properties of ferrites and several other features that permit them to possess efficient adsorption characterizations for some contaminants such as heavy metals and organic pollutants. The matchless physical and chemical attributes result from its high surface-to-volume ratio comparing with micro or bulk-sized [10, 11] which are called as the "material of the 21st century"[12]. Carbon nanotubes (CNTs) that are represented by Single Walled carbon nanotubes (SWCNT) and Multi walled carbon nanotubes (MWCNT) become a suitable for several applications, with exceptional features display extraordinary adsorption properties towards different organic and inorganic compounds. which used in different types, such as particles, wires and tubes, have been widely used to adsorb CCl4, SO2, diethyl 4 nitrophenyl phosphate, heavy metals and COD reduction[13]. Furthermore, The intrinsic properties of BaFe2O4 nanoparticles, such as high magnetic saturation and coercively, high chemical and mechanical resistance, and high curie temperature, have indicated that it as a good candidate for microwave devices, radar-absorbent materials, permanent magnets, drug deliveries, photo catalytic catalysts, credit cards, etc.[14].

The most popular metal oxides used as adsorbents are iron oxides (Fe_xO_y), silicon (Si), titanium (Ti) and tungsten (W). They are at most used for adsorption of heavy metals and radionuclides [15, 16]. MCM–41, one of the members of M41S reported by scientists at the Mobil Research & Development Corporation in 1992, is a hexagonal and ordered mesoporous silica material, with uniform mesopores. Since the discovery of MCM–41, researchers have taken an interest in its synthesis and application because of its large internal surface, high thermal and hydrothermal stability, possibility of controlling the pore dimension, and potential acidity [17].

The present study was divided into two parts, the first one compared the removal efficiency of oil content from real oily wastewater among three types of nanomaterial; Mobil Composition of Matter No. 41 (MCM-41), Multi-Walled Carbon Nanotubes (MWCNTs), and Barium Nanoferrite (BaFe2O4). While the second part had been employed the effective type of nanomaterials to study the impact of the operational variables; the dosage, agitation speed and contact time on the process of treating 84.9 ppm of oil content from Al-Dora refinery wastewater. Response surface methodology (RSM) and statistical program software (Minitab-17) were performed to design the experiments and evaluate the required mathematical correlations as well as the graphical analysis.

2. Experimental Section

Response surface methodology (RSM) is defined as an useful collection of a statistical technique for analyzing problems where several independent variables impact dependent responses [18,19]. A rotatable central composite design (CCD) as a type of response surface methodology (RSM) was utilized to evaluate the mathematical correlation of oil content removal efficiency from real oily wastewater which is related to the operational parameters shown in Table 1. This correlation of the required response could be obtained using Eq. 1[18,20]:

$$Y = B_0 + \sum_{i=1}^{q} B_i X_i + \sum_{i=1}^{q} B_{ii} X_i^2 + \sum_{i}\sum_{j} B_{ij} X_i X_j + \varepsilon \tag{1}$$

where:
X_1, **X_2**, to **X_q**: the operational parameters that are continuous and a controllable with negligible **ε** error.
B_o, **B_i**, to **B_{ij}**: the regression coefficients.
ε: a random error (or residual) which refers to the amount of variation in Y.

Table 1
Operational parameters

Parameters	Ranges
X_1: Dosage (g)	0.025-0.10
X_2: agitation speed (rpm)	100-250
X_3: Contact time (min)	5-120

2.1. Chemicals

Tetraethyl orthosilicate (TEOS, 98%), sodium hydroxide (NaOH), cetyltrimethyl ammonium bromide (CTAB, 99%), and ethanol (EtOH, 99%) were purchased from Sigma Aldrich. Where the preparation of NPs types had been done according to the general methods in the literature.

2.2. Instruments

X-ray diffraction analysis of MCM-41 was carried out using a diffraction unit [Type: Shimadzu-6000, Origin: Japan]. X-Ray diffractometer (XRD) with 2Θ range from 0° to 10° with scan rate 2 (deg/min) and Cu-kα (λ = 1.541) as radiation source was applied. While the morphology analysis of MCM-41 was performed using SEM instrument [Type: VEGA 3 LM, Origin: Germany].

Moreover, FT-IR analysis was carried out for the prepared sample of mesoporous material using FT-IR instrument [Type: Bruker –Tensor 27, Origin: Germany] which had done at Nanotechnology Advanced Material Research Center, University of Technology. The oil content presented in the treated water samples was analyzed by Ocma-350 oil analyzer [Horiba LTD, Origin: Japan]. The electrical shaker [Type: BS-21] was supplied by Heidolph Origin, Germany.

2.3. Oil removal procedure

Batch adsorption tests were performed by adding the desired amounts of MCM- 41(0.025-0.10g) to 100mL of oily wastewater (**89.4 ppm**).Then, the mixture had settled in an electrical shaker[Type: BS-21, Heidolph Origin: Germany] set at (100-250) rpm where the contact time is (5-120 min). After the end of each run, the spent MCM- 41 was centrifuging and filtered, and then the filtrate was collected for residual oil content analysis. The amount adsorbed per gram of MCM-41 (mg/g)or the adsorption capacity (q),was achieved using the following Eq.2[19] :

$$q_e = \frac{(C_i - C_f)\,V}{M} \tag{2}$$

Where q_e : adsorption capacity at equilibrium of adsorbent (mg/g), C_i and C_f (mg/ L)are the initial and final concentrations, respectively, V (L)is the solution volume, and M (g)is the amount of adsorbents used.

The removal ratio was calculated from the Eq.3[21]:

$$\%Removal = \frac{C_i - C_e}{C_i} \times 100 \tag{3}$$

Where C_e: concentration of adsorbate at the equilibrium (mg/L)

3. Results and discussion

3.1. Analysis of NPs

Three types of NPs, i.e. adsorbents, were performed in this study (MCM-41, MWCNTs and $BaFe_2O_4$) in order to their treatability of removing oil content from real refinery wastewater which had collected from Al-Dora Refinery with 89.4 ppm of oil content. Based on the oil content removal efficiency by using these adsorbents, it was found that the MCM-41 possesses the best removal percentage of the oil content (98.3%) in comparison to other two types of NPs as revealed in Table 2, therefore, it was chosen to complete the rest of the experiments under the effect of the designed operational variables.

Table 2
Oil content removal efficiency from 89.4 ppm refinery wastewater by using three types of NPs (adsorbents).

Adsorbents (NPs)	Oil content (ppm)	Removal efficiency(%)
MCM-41	1.5	98.3
MWCNTs	15.6	82.5
$BaFe_2O_4$	3.8	95.7

As revealed in Table 3, the results proved that the MCM-41 NPs has a higher treatability of real oily wastewater in comparison to the other two kinds of nanoparticles. Therefore, the following items will concern about using this kind of NPs to remove pollutants from wastewater under the effect of the operational variables.

3.2. Characterization of MCM-41 NPs

The characterization of MCM-41 NPs had been studied by XRD, SEM and FTIR. Fig.1. shows the crystal structure, structural identity, and phase composition of MCM-41 where the small-angle XRD pattern explains characteristic diffraction peaks for this material. The mesoporosity, as well as the existence of a periodic hexagonal long range order of the channel, were characterized as an indication of the strong diffraction peak for 100 plane at 2.80. Moreover, the d-spacing value is 37.8A° for the XRD peak which agreed with [22].

Moreover, the SEM image of MCM-41 shown in Fig. 2 clearly illustrates the well-ordered hexagonal array structure. Closer investigation on the surface of the MCM-41 revealed the presence of mesoporous uniform size channels with a sphere shape and smooth surfaces in the range of 5–100 nm in diameter. A narrow pore distribution can also be observed from the micrographs.

While the result of FTIR spectra of MCM-41 is clearly explained in Fig. 3 that the strong absorption band for this material centered at 1024 cm^{-1} was attributed to the asymmetric stretching of Si–O–Si groups. Furthermore, the broad and weak band at 960 cm^{-1} were indexed to the symmetric stretching vibration of Si–OH moieties presented in the pore channels. The broad peak around 3417 to 3221 cm^{-1} is for Si–OH also. O–H bending peaks presented at 1639 cm^{-1}. The absorption band at 460 cm^{-1} was corresponding to the bending vibration of Si–O–Si. The absorption band at 1483 cm^{-1} which assigned to C-H stretching vibration of the alkyl group, it was clearly observed in the spectrum of MCM-41.

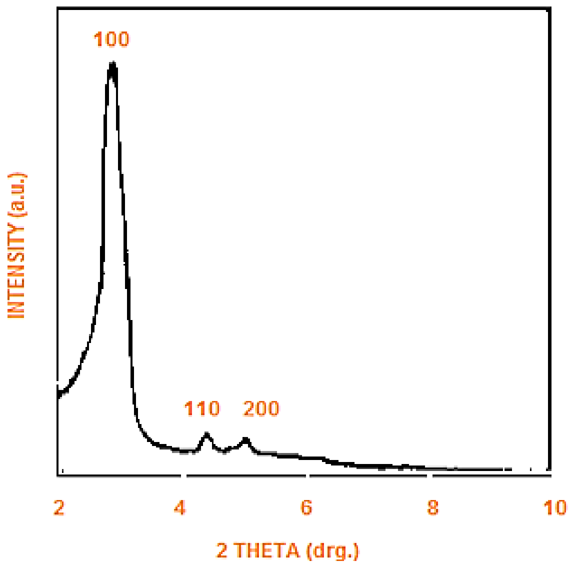


Fig. 1. Powder XRD pattern of the synthesized MCM-41 NPs

In practice, MCM-41 nanomaterials are ordered as mesoporous materials where in recent years, MCM-41 has been performed as an adsorbent in the treatment of wastewater because of its many significant features such as the presence of a tunable channel with a diameter in the range of 2.0–10.0 nm and arrays of homogeneous nonintersecting hexagonal channels. MCM-41 possesses high surface areas of approximately 1000 m^2/g with 80% porosity of their total volume. Further, MCM-41 exhibit tremendous thermal, hydrothermal, and hydrolytic stabilities [23].

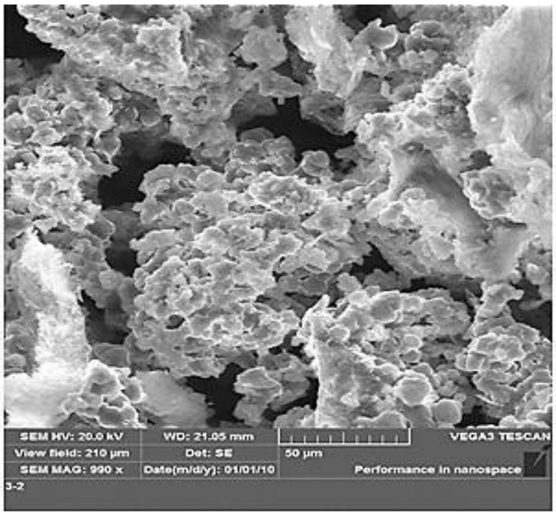


Fig. 2. Scanning electron microscopic (SEM) images of MCM-41 specimen

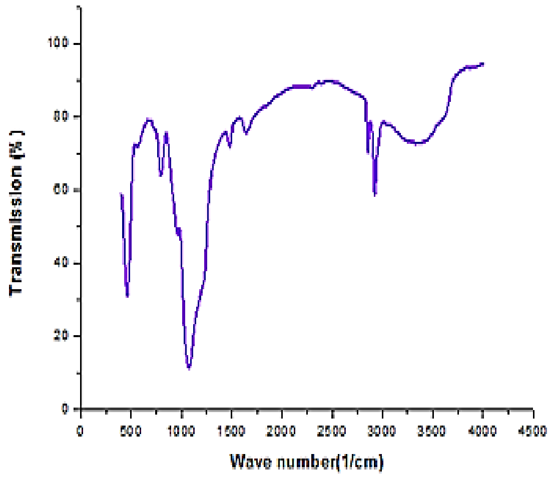


Fig. 3. FT-IR spectra for prepared MCM-41

3.3. Adsorption Isotherm Models

There are several types of sorption isotherms used to investigate the behavior of the adsorption process via the treatment of any kind of wastewater using this type of technique. The most models used for studying the adsorption behavior through the treatment process were the Langmuir and Freundlich isotherm models which are describing the interaction between the adsorbent and the contaminant in an obvious manner [4]. The Langmuir linearization form is shown in Eq. 4 as follows [24]:

$$\frac{C_{eq}}{q_e} = \frac{1}{q_m} C_{eq} + \frac{1}{K_L q_m} \quad (4)$$

where:

q_m: Langmuir constant relating to adsorption capacity (mg/g)

K_L: Energy of adsorption (L/mg)

The constants q_m and K_L could be specified from the slope and the interception of the linear plot of C_{eq}/q_e versus C_{eq}.

However, the R_L parameter shows that the isotherm is either favorable (R_L<1), unfavorable (R_L>1), irreversible (R_L=0), or linear (R_L=1). This parameter is defined as follows [25]:

$$R_L = \frac{1}{1+K_L C_0} \quad (5)$$

where C_0 is the highest initial dye concentration (mg/L).

The Freundlich linear form is given by Eq. 6 as follows:

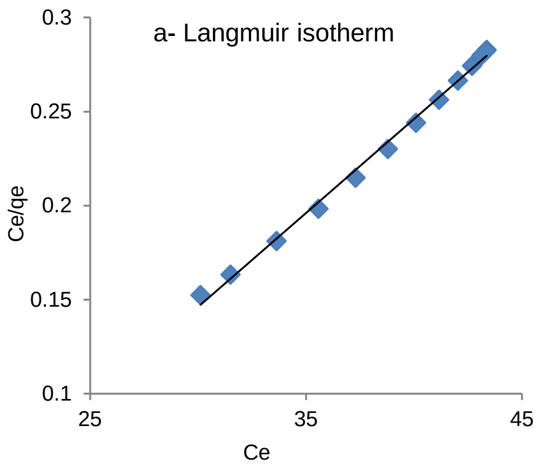
$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_{eq} \quad (6)$$

where:

n: Adsorption intensity; K_f : Adsorption capacity, respectively, of the sorbent.

The values of Freundlich constants can be obtained from the plot of experimental data of ln q_e versus ln C_{eq}.

At mean values of the operational variables and different values of the contact time, the isotherm models of Langmuir and Freundlich are shown in Fig. 4 and Table 3 as follow. The results show that Langmuir isotherm gives a better fit in comparison to the Freundlich isotherm model for the treatment of oily wastewater using MCM-41 nanotubes material.



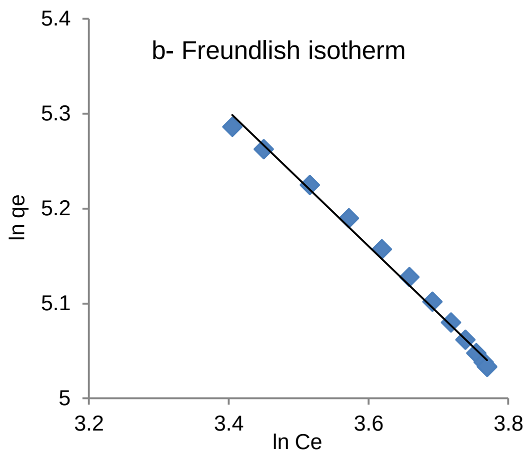


Fig.4. (a) Langmuir and (b) Freundlich models for different values of the contact time (89.4ppm, 0.06g NPs, 175rpm)

Table 3
Langmuir and Freundlich models and their constants for different values of the contact time and (89.4ppm, 0.06g NPs, 175rpm)

Parameters	Langmuir	Freundlich
correlation	y = 0.01x - 0.1537	y = -0.7088x + 7.7123
n	----	1.411
q_{max}	100	----
K_f	----	2236
K_L	0.065	----
R^2	0.996	0.993
R_L	0.0147	----
Case	favorable	Physical adsorption

3.4. Removal of oil content

The real and coded values of the operational parameters are listed in Table 4. Moreover, Table 5 shows the obtained results of oil content removal efficiency response (**Y**$_{OCRE}$) for each of the designed experiments. The regression coefficient (R^2) is (0.9048), so the number of iterations is terminated.

Table 4
Real and coded operational variables

Real parameter (Xi)	Coded parameters				
	-1.732	-1	0	1	1.732
X_1: Dosage (g)	0.025	0.04	0.06	0.08	0.1
X_2: Agitation speed (rpm)	100	130	175	220	250
X_3: Contact time (min)	5	30	62	96	120

Table 5
Obtained results of oil content removal efficiency

Run No.	X_1: Dosage (g)	X_2: Agitation speed (rpm)	X_3: Contact time (min)	Y_{OCRE} %
1	0.04	130	30	67.23
2	0.08	130	30	42.51
3	0.04	220	30	62.19
4	0.08	220	30	48.99
5	0.04	130	96	57.94
6	0.08	130	96	56.38
7	0.04	220	96	54.59
8	0.08	220	96	54.14
9	0.025	175	62	51.57
10	0.10	175	62	24.83
11	0.06	100	62	53.02
12	0.06	250	62	42.06
13	0.06	175	5	51.23
14	0.06	175	120	62.53
15	0.06	175	62	32.55
16	0.06	175	62	46.98
17	0.06	175	62	39.60
18	0.06	175	62	44.07
19	0.06	175	62	41.83

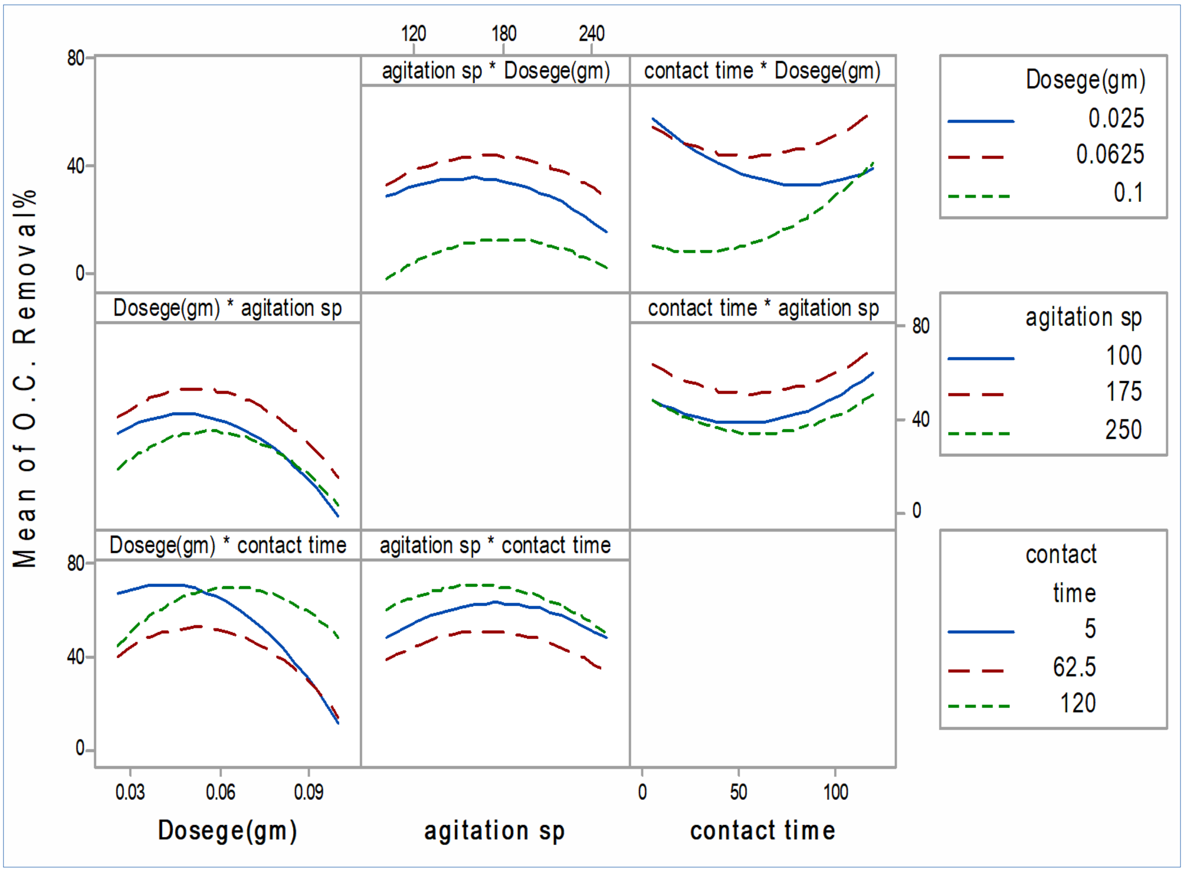


Fig. 5. Interaction plot among variables for oil content removal efficiency response

The empirical mathematical correlation of oil content removal efficiency related to the operational variables is shown in Eq. 7 where the high value of the regression coefficient shows the statistical significant of this model:

$$Y_{OCER}\ \% = -13.8 + 1007\, x_1 + 0.820\, x_2 - 0.857\, x_3 - 16681\, x_1^2 - 0.00265\, x_2^2 + 0.0048\, x_3^2 + 1.76\, x_1 x_2 + 6.80\, x_1 x_3 - 0.0006\, x_2 x_3 \; : \mathbf{R^2 = 90.48\%} \quad \mathbf{(7)}$$

The maximum interactions among the operational variables are shown clearly in Fig. 5 which revealed the effect of each of the variables individually on the oil content efficiency response when the other two variables were taken at their mean values.

Fig. 5 reveals, in general, the activity of nano-material presented at low value until reaches the optimum amount then decreases as long as the dosage amount increases. The same behavior noted for the impact of raising the speed of agitation, oil content removal raises as agitation speed increased but when it reached to the mean value it tends to minimize at the high value of agitation speed. Whereas the behavior of this response differs with time in comparison with the previous two variables, the applicability of oil content removal decreased as the contact time increases until reaches the mean value of the designed range of contact time then it was sharply raised.

The contour plots in Figs. 6 and 7 explain obviously the behavior of this response via the variation of two variables while the third one had fixed at the mean value.

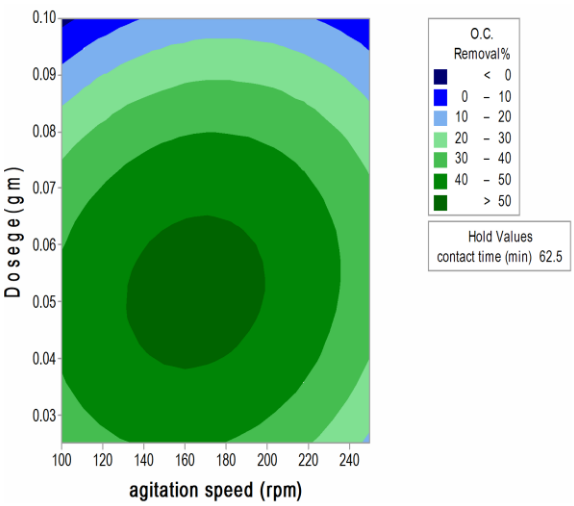


Fig. 6. Contour plot of oil content removal vs. dosage; agitation speed ; mean value of contact time.

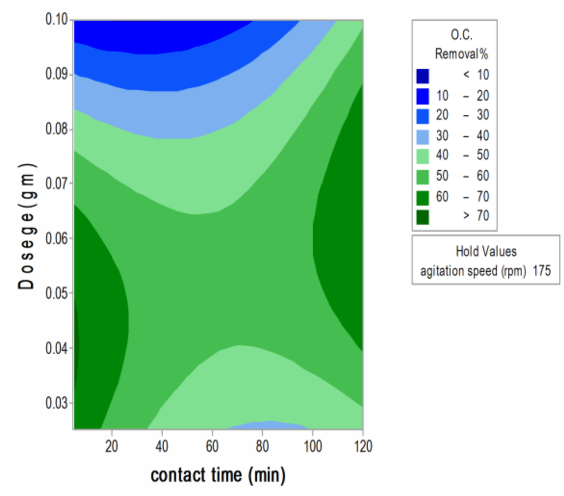


Fig. 7. Contour plot of oil content removal vs. dosage; contact time; mean value of agitation speed

As noted, when the contact time equals 62.5min, the highest removal of oil content occurs approximately at the range (0.04-0.06g) of dosage and the agitation speed ranged (135-200rpm). While the maximum value of this response was achieved at 175rpm of agitation speed when the values of dosage and contact times ranged (0.04-0.09g) and (100-120min) of dosage and contact time respectively.

3.5. Effects of the operational variables

Each of the studied variables in the present study affects the behavior of the oil content removal efficiency via the treatment of refinery wastewater while other variables had taken at their mean values.

3.5.1. Effect of dosage

Fig.8 shows the effect of MCM-41 NPs dosage (**x_1**) on the behavior of the oil content removal efficiency when the values of the agitation speed and the time of treatment were taken at their mean value. As noted, clearly, removal efficiency increases as the dosage of NPs increased until the mean value of this NPs then tend to minimizes till reaches the end of the experiment because the NPs is saturated due to the phenomenon of physical adsorption according to Freundlich isotherm model that had obtained before. Eq. 8 relates the response of oil content removal efficiency to the value of NPs dosage.

$$\textit{O.C. removal } \% = 1913\, x_1 - 16917\, x_1^2 \; : R^2 = 95.4\% \quad \mathbf{(8)}$$

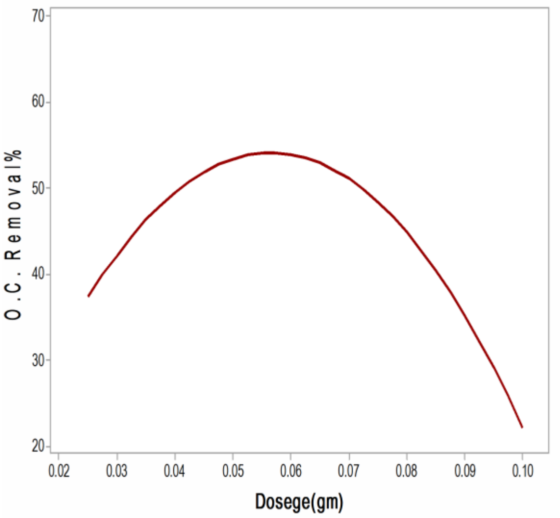


Fig. 8. Oil content removal vs. dosage; agitation: 175rpm; contact time:62min

3.5.2. Effect of agitation speed

The impact of the agitation speed (**x_2**) on the behavior of oil content removal efficiency is shown in Fig. 9.

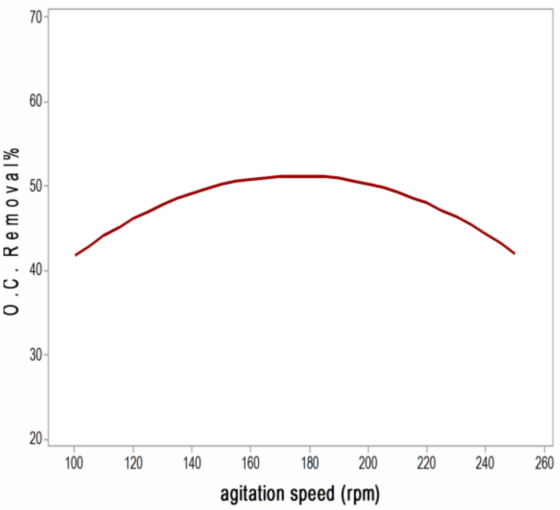


Fig. 9. Oil content removal vs. agitation speed; contact time: 62min; dosage: 0.06g

The increase and decreasing of this response are not sharp, but it approximately maximized at the mean value of the agitation speed. At low and moderate values of agitation speed, the pollutant adsorbed efficiently toward the NPs adsorbent in comparison to what occurred at the high speed of agitation because the adsorption process was not completed since the pollutant keep moving rapidly and randomly in the treated wastewater and the NPs could not adsorb it. Therefore, agitation speed should be designed at the optimum value in order to achieve the highest value of oil content removal efficiency. The mathematical correlation of this response that related to the blending speed in the condition of mean values of MCM-41 NPs dosage and contact time is shown in Eq. 9.

$$\textit{O.C. removal \%} = 0.584\, x_2 - 0.002\, x_2^2 \quad : R^2 = 94.9\% \qquad \textbf{(9)}$$

3.5.3. Effect of contact time

The influence of the contact time (**x_3**) on the behavior of oil content removal efficiency is obviously noted in Fig. 10 where it raises sharply along the time of experiment till reaches 90min approximately the tend to minimize along the rest of experiments' treatment time.

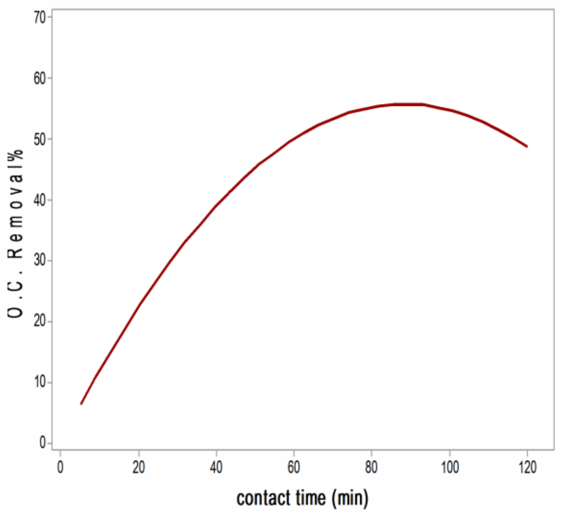


Fig. 10. Oil content removal vs. contact time; dosage: 0.06g; agitation speed: 175rpm

Since the values of NPs dosage and agitation speed are taken at their mean values, the interpretation of this behavior tend to saturation manner of active sites of the adsorbent in spite of the time of the experiment was not finished yet, therefore, the excess time of the experiment will not be beneficial because the adsorption process was completed. The oil content removal efficiency related to the contact time by a mathematical correlation as revealed in Eq. 10.

$$\textit{O.C. removal \%} = 1.261\, x_3 - 0.007\, x_3^2 \quad : R^2 = 87\% \qquad \textbf{(10)}$$

3.6. Optimization of the operating parameters

Fig. 11 shows the results of the D-optimization measurement where the composite desirability (D) equals 1 which give the optimum values of the operational variables that may give the best performance of oily wastewater treatment process via the employment of efficient nanoparticles materials. The optimum values for the dosage of NPs, agitation speed and contact time were obtained as 0.063 g, 162 rpm and 120 min respectively.

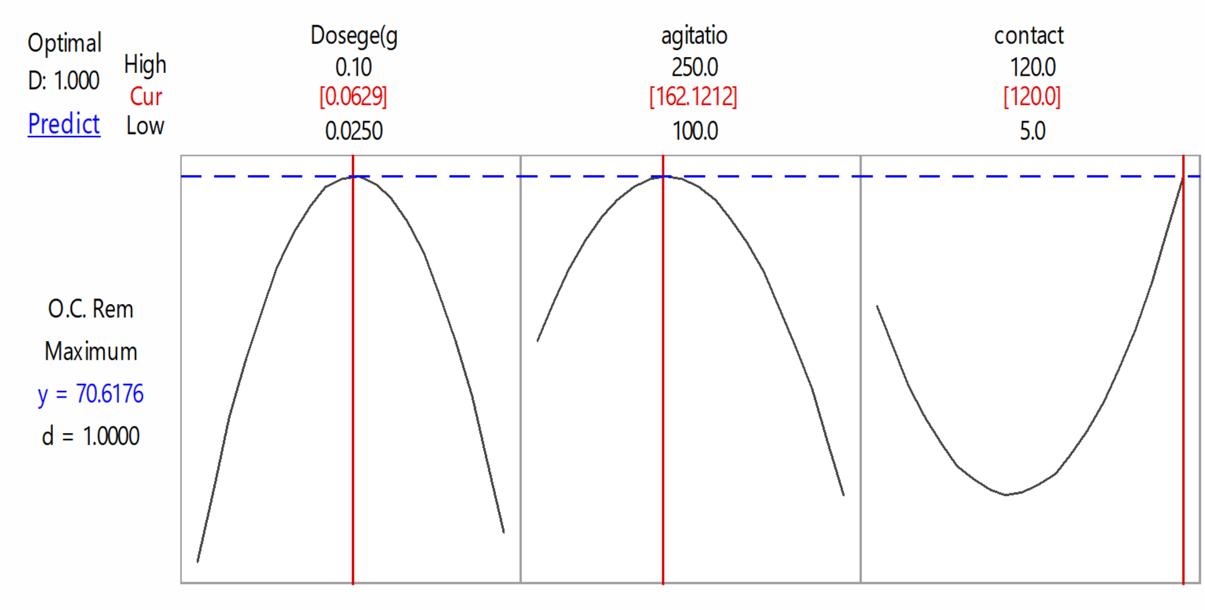


Fig. 11. Optimization plot for oil content removal efficiency

3.7. Comparative study

The comparison between the MCM-41 with other adsorbents which reported in the literature is shown in Table 6. The unique features of the high inner surface area, controllable size of the pore and desirable unity has considerable interested in materials science, chemistry, physics and other related areas. It can be noted from Table .5 that MCM-41 is a good adsorbent for oil removal from wastewater.

Table 6. Maximum oil Removal Efficiency (%) by various adsorbents

No.	Adsorbents	Maximum Removal Efficiency (%)	Reference
1	La@CS-GEL	91	[26]
2	Raw sugarcane bagasse	63.4	[27]
3	Rice hull	97	[28]
4	MCM-41	98.3	This study

La@CS-GEL: lanthanum embedded chitosan/gelatin

4. Conclusion

Oily wastewater is one of the most concerned pollution sources that must be treated using efficient methods to overcome the problems of toxic and refractory characteristics. The present study employed the technique of using NPs as adsorbent materials in order to remove oil content from real oily wastewater. Three types of NPs materials were compared in their efficiency for that proposes where MCM-41 NPs had found as the effective adsorbent among other types under the influence of the operational variables. It can be concluded that MCM-41 NPs shows promising adsorption capacity for oil removal Where the Characterization of MCM-41 was carried out which revealed the presence of various functional groups on the adsorbent surface and that the surface of the adsorbent was rough and suitable for adsorption. The operating parameters for the maximum sorption were (0.063 g) sorbent dose, (162 rpm) blending speed and (120 min) contact time. Removal of oil from real water samples was attained at normal pH. The experiments of this study, as well as the mathematical correlations, were found using RSM experimental method as well as Minitab-17 program. The isotherm model of Langmuir gives a better fit than the Freundlich isotherm model. It can therefore be concluded that that MCM-41 NPs offers promise as an economically viable alternative for sequestering of the oil removal from the aqueous solution. The work can be extended for the removal of other type of organic contaminates from effluents as well.

5. Conflicts of interest

There are no conflicts to declare.

6. Formatting of funding source

Self funding

7. Symbols:

MCM-41 Mobil Composition of Matter No. 41
MWCNTs Multi-Walled Carbon Nanotubes
$BaFe_2O_4$ Barium Nanoferrite
O.C. removal Oil contact removal
Y_{OCRE} (%) Oil content removal efficiency
x_1 Dosage of NPs (g)
x_2 Agitation speed (rpm)
x_3 Contact time (min)
R^2 Regression coefficient

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