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GAS CONDENSATE DESULFURIZATION BY OXIDATION METHOD IN THE PRESENCE OF NANOCLAY AND CHITOSAN ADSORBENT: AN EXPERIMENTAL STUDY

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ABSTRACT

Oxidative desulfurization process for gas condensate using a mixture of hydrogen peroxide and formic acid have been investigated. Oxidation under optimal conditions accompanied extraction operation using acetonitrile and finally adsorption was performed on clay, nanoclay and novel adsorbent of chitosan – nanoclay. By use of oxidation process on feedstock with the initial sulfur amount of 2500 ppm optimum parameters for reaching the minimum sulfur content were derived. Effects of operating parameters such as temperature, the amount of formic acid used as catalyst for oxidation and process time were investigated and the best operating conditions for oxidation were determined by designing the relevant experiments. Adsorption isotherms modeling and also kinetic models has been studied. The best conditions for oxidation were determined as follows: Acid-to-feed ratio =1, Reaction temperature= 50°C, Reaction time= 45 min. After about 30 minutes of adsorption process, the adsorbent was saturated and the increase in contact time had no effect on the removal of sulfur compounds. Adsorption isotherms modeling of common Langmuir and Freundlich models showed that both nanoclay and nanoclay-chitosan adsorbent followed Freundlich's model for adsorption. Studies of three common kinetic models : pseudo-first-order, pseudo- second-order, and intra-particle diffusion model indicated that the kinetics of this adsorption was of the pseudo second order type. This effective way of combination the Oxidation in optimum condition with this sorbent should be used as novel technology of desulfurization in order to achieve the gas condensate with minimum sulfur.

1. INTRODUCTION

Energy production is one of the most important issues in the world. Economic Fossil fuels are the world's largest source of energy. With stricter environmental considerations, much attention has

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been paid to clean fuel and reducing sulfur compounds in fuels and hydrocarbons. The US EPA has released a new regulation requiring the use of low-sulfur fuels. This regulation requires that the sulfur content to be limited to 15 ppm for diesel and 30ppm for gasoline fuels [1,2].

Due to the structure of gas condensate in terms of existing hydrocarbons, it can be considered as one of the main sources of gasoline supply. These condensates are very valuable and used as refineries feed to produce petrol for kerosene and gasoline. There are many studies on the desulfurization of heavier hydrocarbons in comparison to studies on lighter hydrocarbons such as gas condensate [3,4] . In addition to environmental restrictions and regulations, sulfur compounds easily react with metals which raises two important technical issues: the first problem is the corrosion of equipment and pipelines, and the second one is the reaction of these compounds with catalysts (often metal or metal oxide) causing catalyst poisoning [5]. So the separation and removal of these compounds from hydrocarbons is ineviTable. Thus, most of methods for reducing or eliminating such compounds have been developed very fast. The widely used method is hydrodesulfurization (HDS) method, which is carried out at high temperature and pressure in the presence of hydrogen.

HDS process is highly efficient for removing thiols, sulfides, disulfides and some thiophene derivatives but has limitations to remove some compounds, such as benzothiophene and di-benzotyophene. In addition, in order to improve the efficiency of this process, it is necessary to increase the temperature and pressure to a high level for which to be reached, costly catalysts, bigger reactors and a great deal of time are required. So tendencies to finding some alternative and inexpensive ways to remove sulfur compounds have been increased.Number of processes have been proposed to remove the above compounds, including the adsorption process, oxidation, extraction and biological desulfurization [6]. Oxidative desulfurization has been considered as a new and effective alternative method.

During ODS process sulfur compounds in feedstock are oxidized and the corresponding sulfoxides and then sulfones are produced. These compositions have a high polarization and can be removed by extraction, adsorbent or distillation method at the later step [7,29]. Various oxidizing agents, such as H_2O_2, t-butyl hypochlorite, ozone and t-butyl hydroperoxide, are currently used in Oxidative desulfurization processes. Since there is no need of using hydrogen, then ODS could be considered as a proper alternative method for HDS. Investment and operating cost of hydrogen providing will be eliminated in ODS process[8].

The adsorption desulfurization process is one of the most advanced methods available because of its ease of use, affordability, cost-effectiveness and recoverability which mostly can be followed after ODS[9,10, 28]. This process occurs when a high surface area for sulfur compounds is provided by a porous non-reactive substrate on an active adsorbent [11]. The main challenge for this method for liquid hydrocarbon fuels is the selectivity for separating low-polar sulfur compounds from non-polar liquid phase [12, 26,27]. Several studies have been carried out on the adsorption of various sulfur compounds such as benzothiophene and di-benzotyphene from liquid fuels using a variety of active carbons [13,14,15,16,17]. Other adsorbents such as zeolite, Cu+, Ag+ and nickel zeolite have been investigated. These adsorbents are used in ambient temperature and pressure conditions [17,18,19]. Montmorillonite as a clay nanoparticle, which is the most important phase in bentonite, with dimensions of about 10 angstroms and due to its unique properties such as inflammation in polar environments, high specific surface area, surface electrical properties and cation exchange capacity, have been used in various applications in the industry and also as filler and adsorbent. Chitin is the most abundant amino polysaccharide and it is estimated that produced annually in about equal amounts to cellulose [20]. The importance of this natural biopolymer is not only due to its inexpensive production resources and use of waste material in its production, but also because of its high potential for use in a variety of fields due to improvements in the field of chitin chemistry [21] .

One of the most important derivatives of chitin is chitosan, which is obtained by the acetylation of the Acetamide group by an alkaline solution. Chitin and chitosan are commercially valuable due to their high nitrogen content (6.89%) and unique properties such as non-toxicity. Also the possibility of surface adsorption have made them valuable natural materials[22,23]. Moreover, chitosan easily dissolve in acidic solvents and forms a hydrogel in aqueous media. Because of these conditions and inaccessible binding sites, its strength should be improved for practical applications as adsorbent. Several attempts such as crosslinking or coating with bentonite has been done to adjust the chitosan by which the mass transfer is facilitated and in order to enhance its adsorption capacity, the active sites are exposed [21].

This study aims to remove sulfur compounds from the gas condensate using the oxidation by H2O2 in presence of formic acid and accompanied the optimum oxidation conditions by extraction and adsorption on nanoclay and chitosan.

2. EXPERIMENTAL SECTION

2.1 MATERIAL AND METHOD

The research steps include: performing oxidation, extraction and adsorption processes, studying surface morphology and adsorbent size, optimizing experimental conditions, assessing isotherms of adsorption, reviewing the kinetics of adsorption.

2.2 CHEMICAL AND ADSORBENTS

All chemicals used in this study, including formic acid 99% , hydrogen peroxide with a purity content of 30%, hydro-chloric acid fuming 37% and NaOH pellets were obtained from a European company. Clay and nanoclay were supplied from Kava sanat co. and Chitosan were purchased from Chitoteck Company. The studied condensate at the highest sulfur content of 2500 ppm was obtained from one of the South Pars oil fields. Horiba 2800 -SLFA fluorescence ray-X used to determine the sulfur amount according to the US Standard (D-ASTM4294).

2.3 OXIDATION STAGE

This stage covered the effects of important parameters of ODS in gas condensate feed. Several parameters such as oxidation time, temperature and the effect of catalyst quantity have been investigated. The analysis were extracted by Minitab17.

2.4 EXTRACTION STAGE

An applied conventional method for extraction is liquid-liquid extraction. This process is on basis of polar molecules dissolving in polar solvents. As the oxidized components are more polar than original sulfur components, the oxidized components could be extracted by polar solvents.

2.5 ADSORPTION EXPERIMENTS

Before starting the adsorption experiments, the adsorbents were placed in an oven at 110 ° C for 2 hours to dry completely. 10 g of these adsorbents with 50 cc of hydrocarbon sample was poured and stirred at different time periods. Then, the solid phase was separated by filtering the. The procedure for synthesis of mix adsorbent of chitosan and nanoclay was extracted from the study of Ming-Chun Lu., et al [2,21]. About 5g chitosan was mixed with 300ml of 5% (v/v) HCL and stirred for 2h at 300rpm. Then 100g of nanoclay was slowly added into the solution and stirred for another 3h. Adding drops of 1N NaOH was continued to reach a neutralized level and the washing was done several times then dried at 65C^0 for twenty-four hours and finally sieved.

2.6 MODELING OF ADSORPTION ISOTHERMS

Isotherms are the simple mathematical relations that have been obtained either theoretically or experimentally and indicate the relationship between the amounts of adsorbed substance at constant temperature and equilibrium concentration. Two commonly used adsorption isotherms of Langmuir and the Freundlich used for examining adsorption data.

The Langmuir equation is presented in the bellow form and as can be seen in Eq(2), is a linear equation.

$$q_e = q_{max} K_L C_e/(1 + K_L C_e) \tag{1}$$

$$C_e/q_e = (1/q_{max} K_L) + (C_e/q_{max}) \tag{2}$$

In above equations, q_e denotes the equilibrium level of adsorption (mg/g), C_e has the equilibrium level of adsorbent in solution (mg/l), q_{max} represents the highest amount of adsorbent monolayer capacity (mg/L), and K_L is the constant of the Langmuir equation (L/mg) [24]. By drawing the linearization diagram including $1/q_e$ vs. $1/C_e$ the relevant constants are obtained.

The Freundlich equation is expressed in the form of Equation (3):

$$q_e = K_F \ C_e^{1/n} \tag{3}$$

In this equation, K_f represents the adsorption capacity. The Freundlich is a linear isotherm that can be seen in Equation (4) [25]. Plotting Ln q_e and Ln C_e is used to estimate relevant constant.

$$\ln \ q_e = \ln \ K_F \ + \ 1/n \ \ln \ C_e \tag{4}$$

2.7 MODELING OF THE REACTION KINETICS

The reaction kinetics or chemical kinetics are used for studying the rate of chemical processes, these studies indicate the rate at which the adsorption process occurs and the amount of time it takes to reach equilibrium. Kinetic equations of pseudo-first-order, pseudo-second-order, and Intra-particle diffusion were studied. The pseudo-first-order is Equation (5)

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{5}$$

where q_t represents the adsorbed level at time t and q_e denotes the level of equilibrium, moreover, k_1 stands for a constant representing the pseudo-first-order kinetic. By considering the q_t as Equation (6) and integrating this equation, final form of pseudo-first-order equation will obtained as Equation (7) [23].

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{6}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

The pseudo-second-order rate equation has the form of Equation (8):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

By integrating the above equation and applying the initial conditions will be as Equation (9):

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t}t \qquad (9),$$

where k_2 is the pseudo- second order kinetic constant [24].

Intra-particle diffusion model explains the adsorption processes as Equation (10)

$$q_e = k_3 t^{1/2} + c \tag{10}$$

In the Equation (10), k_3 is the constant of reaction.

3. RESULTS AND DISCUSSION

3.1 OXIDATION EXPERIMENTS

Oxidation experiments are conducted within a batch system of a glass reactor. 50 cc of gas condensate and 20 cc of hydrogen peroxide was poured into the reactor and the temperature increased by placing it in the hot water bath. By placing a magnetic stirrer under the hot water bath, the solution is stirred concurrent with warming. After assuring that the solution is warmed up and magnetic stirrer is working properly, the formic acid added as a catalyst to the solution. reaction time was studied from 30 to 60 minutes.

Experiment design has been done for the oxidation experiments by considering the factors of temperature, time and the feed ratio (ration of gas condensate and formic acid) as are presented in Table 1.

Table 1: Oxidation experiments level definition.

Factor	Low Block (-1)	High Block (+1)
Formic acid ration to Hydrocarbon feed	0.8	1.2
Temp (°C)	40	60
time (min)	30	60

In order to optimize the experiments and reduce the number of them as well as time and cost-saving, a three-factor factorial design was designed with the assumption that the process was linear for block 1 and with three midpoints for the curvature criteria, which is represented in Table 2.

Regarding the data of variance analysis as in Figure 1, it is shown that the curvature criteria (with a significant level of 5%) is equal to zero and indicates that the assumed linear model is invalid and a non-linear design must be considered.

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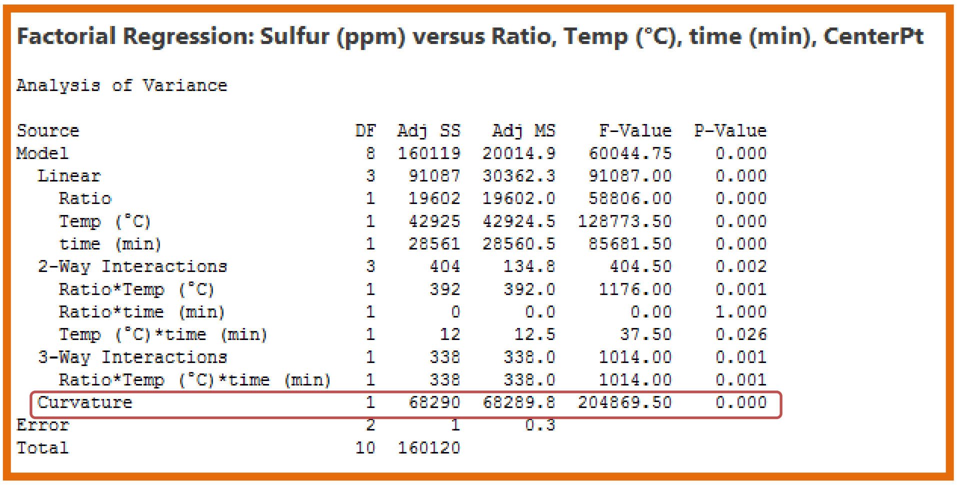
Table 2: Three-factor factorial design

RunOrder	Blocks	Feed Flow (cc)	Ratio	Temp (°C)	time (min)	Sulfur (ppm)
1	1	50	1.2	40	60	950
2	1	50	0.8	40	30	1180
3	1	50	1.2	60	30	937
4	1	50	0.8	60	30	1009
5	1	50	1.2	60	60	802
6	1	50	1	50	45	808
7	1	50	1	50	45	809
8	1	50	1.2	40	30	1054
9	1	50	0.8	60	60	900
10	1	50	0.8	40	60	1050
11	1	50	1	50	45	808



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Factorial Regression: Sulfur (ppm) versus Ratio, Temp (°C), time (min), CenterPt

Analysis of Variance

Source                           DF  Adj SS   Adj MS    F-Value  P-Value
Model                             8  160119  20014.9   60044.75    0.000
  Linear                          3   91087  30362.3   91087.00    0.000
    Ratio                         1   19602  19602.0   58806.00    0.000
    Temp (°C)                     1   42925  42924.5  128773.50    0.000
    time (min)                    1   28561  28560.5   85681.50    0.000
  2-Way Interactions              3     404    134.8     404.50    0.002
    Ratio*Temp (°C)               1     392    392.0    1176.00    0.001
    Ratio*time (min)              1       0      0.0       0.00    1.000
    Temp (°C)*time (min)          1      12     12.5      37.50    0.026
  3-Way Interactions              1     338    338.0    1014.00    0.001
    Ratio*Temp (°C)*time (min)    1     338    338.0    1014.00    0.001
  Curvature                       1   68290  68289.8  204869.50    0.000
Error                             2       1      0.3
Total                            10  160120
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Figure 1: Data of variance analysis.

As it was realized the model is nonlinear, in the second step, the response surface of the Box-Behnken design with three main factors of feed ratio, temperature and time were designed according to Table 3 with repetition in two blocks.

Table 3: Response Surface Design

RunOrder	Blocks	Feed Flow (cc)	Ratio	Temp (°C)	Time (min)	Sulfur (ppm)
1	1	50	1.2	60	45	805
2	1	50	1	40	60	950
3	1	50	1.2	50	30	930
4	1	50	1	50	45	808
5	1	50	1	60	60	809
6	1	50	1	40	30	1086
7	1	50	0.8	50	60	896
8	1	50	1	50	45	809
9	1	50	0.8	60	45	898
10	1	50	0.8	40	45	1051
11	1	50	0.8	50	30	1010
12	1	50	1.2	40	45	948
13	1	50	1	50	45	808
14	1	50	1.2	50	60	802
15	1	50	1	60	30	941
16	2	100	1	40	30	1097
17	2	100	0.8	40	45	1060
18	2	100	0.8	50	60	906
19	2	100	1	40	60	958
20	2	100	0.8	60	45	906
21	2	100	1	50	45	820
22	2	100	1.2	50	60	818
23	2	100	1.2	60	45	820
24	2	100	1.2	40	45	961
25	2	100	1	60	30	947
26	2	100	1	50	45	818
27	2	100	1.2	50	30	942
28	2	100	1	60	60	818
29	2	100	1	50	45	819
30	2	100	0.8	50	30	1020

As a similar way of the first step, the experiments were performed after designing and the amount of residual sulfur in the solution was measured and recorded as a response. The results of the variance analysis for the effect of each factor on the amount of residual sulfur are presented in Table 4.

Table 4: Analysis of variance

Factors	Mean squares (MS)	Sum Of Squares (ss)	Degrees of Freedom (DOF)	F-Values	P-Values
Ratio	32490.1	32490	1	1685.45	<0.001
Temp	85118.1	85118	1	4415.58	<0.001
time	64516.0	64516	1	3346.83	<0.001
Ratio×Ratio	12476.7	12477	1	647.24	<0.001
Temp×Temp	43052	43052	1	2233.36	<0.001
time×time	27234.7	27235	1	1412.83	<0.001
Ratio×Temp	66.1	66	1	3.43	0.080
Ratio×time	72	72	1	3.74	0.068
Temp×time	24.5	24	1	1.27	0.274
Blocks	842.7	843	1	43.72	<0.001
Error	19.3	366	19	-	-
Total	-	256222	29	-	-
Model	25585.6	255856	10	1327.28	-

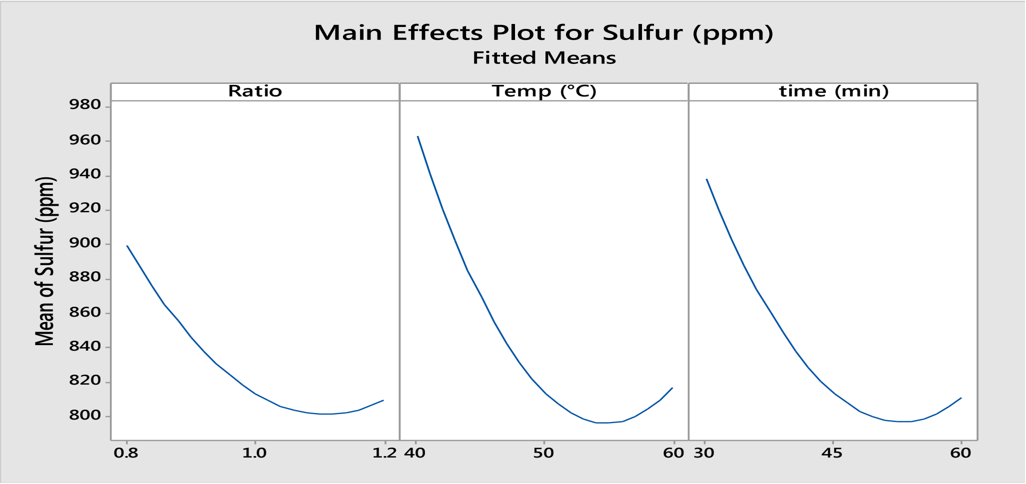

Figure 2: Effects of main factors on the Sulfur amount.

Since the significant p-values for linear and square parameters are equal to zero, variance analysis for effect of each factor indicates that the response change value (residual sulfur content) depends on the first and second exponents of the value of all three factors. Also, according to the F-value, the high amount of which indicates its greater effect showed that temperature has the most significant effect on amount of sulfur. For example, the effect of temperature changes on sulfur removal is approximately 2.5 times the effect of changes in feed ratios. As it has been shown in Figure 2, the sharp slip of the temperature plot also indicated this matter. The interaction of the factors has the least effect on the output and can be eliminated from the model. The plots for factors interaction is showed in Figure 3.

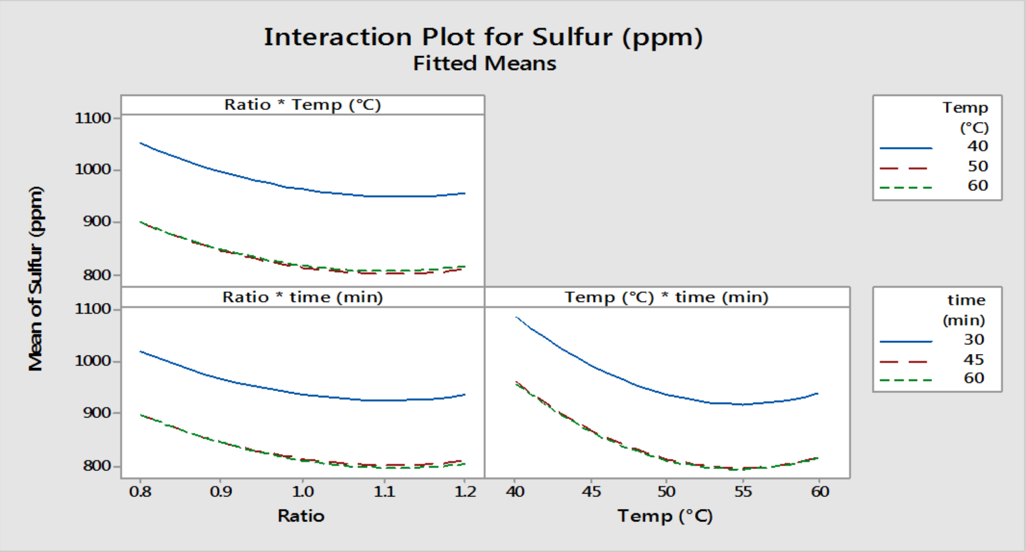

Figure 3: Interaction of main factors on the Sulfur amount

According to the selected model, the following operating conditions have been obtained as the optimum operating point: Acid to feed ratio = 1, Reaction temperature = 50°C, Reaction time = 45 min.

3.2 EXTRACTION EXPERIMENT

After the oxidation reaction, extraction was done in an extractor. Oxidized gas condensate and a suiTable amount of aqueous solvents (acetonitrile and water) were poured into the extractor and it was agitated for 10-15 minutes at ambient temperature. A decanter has been used to separate the organic phase from extracting solvent.

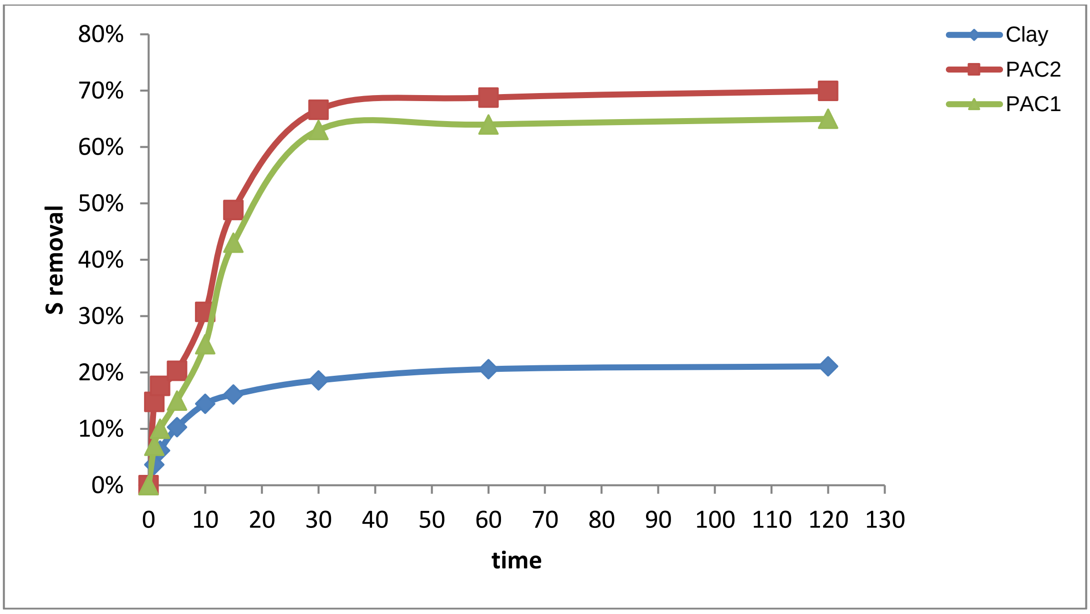

Figure 4: Sulfur Removal with clay, nanoclay (PAC1), (c) nanoclay & chitosan (PAC2).

3.3 STUDYING THE CONTACT TIME OF THE ADSORBENTS

The adsorption activity is performed with three types of adsorbents include clay, nanoclay (PAC1), and the mixture of nanoclay and chitosan (PAC2) for eight samples with the same concentration 602 ppm at different time periods (1, 2, 5, 10, 15, 30, 60, 120 min). By setting the value of V =0.05 liters and W= 10 g in Equation (1), different values of equilibrium concentrations were obtained.

According to the results in Figure 4, after 30 minutes of the start of adsorption, the adsorbent is almost saturated.

3.4 ADSORPTION ISOTHERMS

At this step after the oxidation, 50 cc of solutions with different initial concentrations were prepared, 5 g of absorbent added to each one and mixed in the same way for 60 minutes. Due to low efficiency of normal clay as adsorbent, the studies were done only for PAC1 and PAC2. Langmuir and Freundlich isotherms are investigated and the calculated correlation coefficients for both isotherm models are given in Table 5.

Table 5: Adsorption Isotherm Parameters

	PAC1	
	Langmuir isotherm model	
$q_{max}(mg\ \ g^{-1})$	$K_L(L\ \ mg^{-1})$	R^2
34.722	0.005	0.789
	Freundlich isotherm model	
$K_F\ (mg\ \ g^{-1})\ (L\ \ mg^{-1})\ ^{1/n}$	n	R^2
0.030	1.118	0.997
	PAC2	
	Langmuir isotherm model	
$q_{max}(mg\ \ g^{-1})$	$K_L(L\ \ mg^{-1})$	R^2
45.87	0.005	0.908
	Freundlich isotherm model	
$K_F\ (mg\ \ g^{-1})\ (L\ \ mg^{-1})\ ^{1/n}$	n	R^2
0.043	1.134	0.998

Regarding the values of R^2 in Table (5), the Freundlich model obtained stronger correlation coefficients, which means a better description of the adsorption process. But R^2 values obtained from the Langmuir model are also high, and cannot be easily ignored, and it can be concluded that homogeneous adsorption is not necessarily the only effective method.

3.5 ADSORPTION KINETICS

By setting the value of C_0= 602ppm, V= 50 cc and w= 10 g, plotting Ln(qe-qt) and t/qt vs. time and the q_t vs. squared time value, pseudo-first ,pseudo-second-order and intra-particle diffusion model for the adsorption of sulfur has been fitted and obtained correlation coefficients.

In Table 6, both pseudo-first and pseudo-second-order kinetic constants and correlation coefficients (R^2) and intra-particle diffusion fit for the adsorption of sulfur is shown. The results showed high speed during the first twenty minutes and then it was at low speed until its equilibrium level. The higher correction coefficient for the pseudo-second order model implies that it leads the process of adsorption.

Table 6: Comparison of Kinetics models

	PAC1	
kinetic model	k(rate constant)	R^2 (correlation coefficient)
pseudo-second-order	k1 =0.046(min-1)	0.923
Pseudo-second-order	k2 =0.045(g.mg-1.min-1)	0.976
Intra-particle diffusion	k3 =0.198(mg.g-1.min-1/2)	0.804
	PAC2	
kinetic model	k(rate constant)	R^2 (correlation coefficient)
pseudo-second-order	k1 =0.050(min-1)	0.940
Pseudo-second-order	k2 =0.064(g.mg-1.min-1)	0.987
Intra-particle diffusion	k3 =0.201(mg.g-1.min-1/2)	0.810

3.6 SCANNING ELECTRON MICROSCOPE (SEM)

SEM images of nanoclay, chitosan, nanoclay- chitosan mixture before and after adsorption are presented in Figure 5.

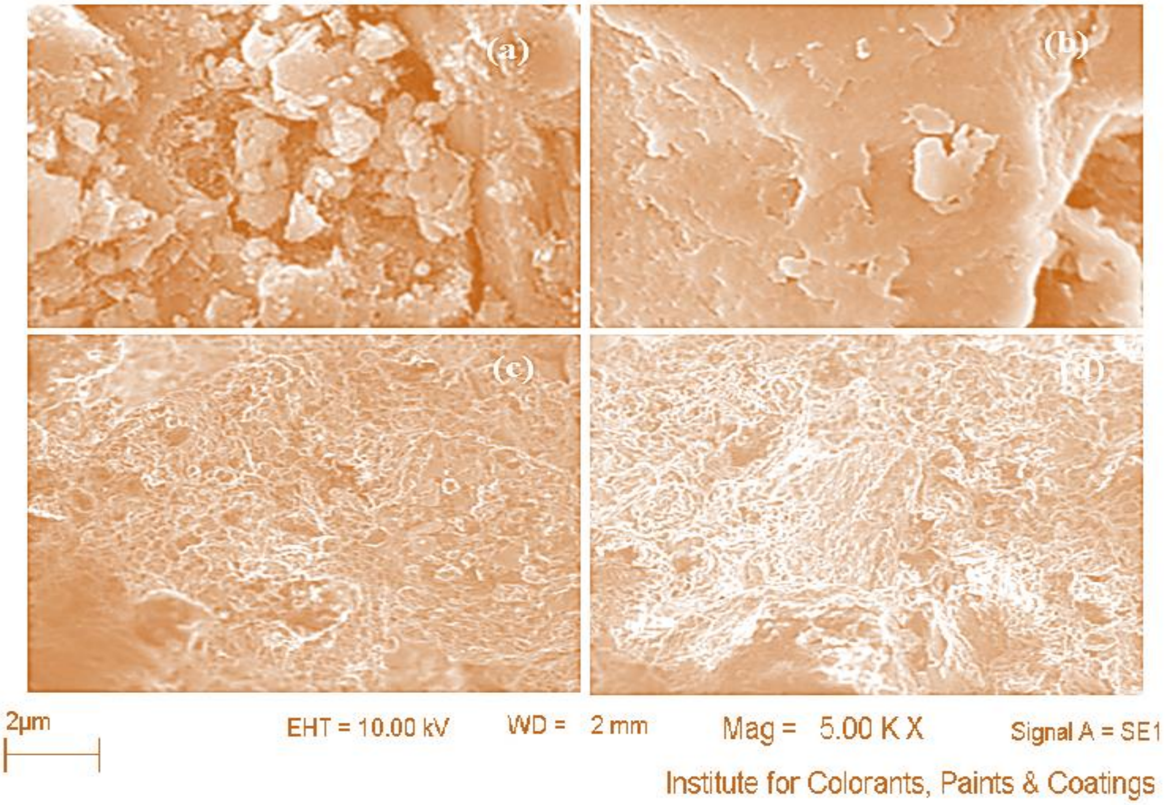

Figure 5: Scanning Electron Micrographs of (a) Nanoclay, (b) Chitosan, (c) Nonoclay & Chitosan before adsorption, (d) Nonoclay & Chitosan after adsorption.

4. CONCLUSION

In this study, for the oxidation section, temperature changes have the most effect on increasing the sulfur removal and the best conditions for oxidation are as follows: Acid-to-feed ratio=1, reaction time=45 min, reaction temperature= 50°C.

The adsorption of ordinary clay for sulfur compounds was very low and over the analyzed time period (120 min), the removal of sulfur compounds was up to 20% and increasing the time from 20 minutes to 120 minutes had no effect on the adsorption process. The adsorption on nanoclay showed good results, and over the time period, the sulfur removal rate was up to 65%. The nanoclay-chitosan mixture produced a better adsorbent and by using this sorbent, the removal of sulfur compounds increased by 70%. The results indicated that adsorption was initially faster and after about 30 minutes of adsorption process, adsorbent was saturated and the increase in contact time period had no significant effect on removal of sulfur compounds. Modeling of adsorption isotherms of Langmuir and Freundlich models described that both nanoclay and chitosan-nanoclay adsorbents had the highest correction coefficient for Freundlich model. The kinetic adsorption data for three commonly used synthetic models of pseudo-first-order, pseudo-second-order, and intra-particle diffusion model, indicated that adsorption of sulfur on these adsorbents follows the pseudo-second-order model. Thus this effective way of combining the ODS with this sorbent should be used to enhance the technology of desulfurization in order to achieve the gas condensate with minimum sulfur.

4. AVAILABILITY OF DATA AND MATERIAL

Information used or generated from this study is available upon request to the corresponding author.

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