Treatment of oily wastewater by using polysulfide polymer

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ABSTRACT

The discharge of water from oil fields is become one of the most significant environmental concerns associated with the oil sector. This study features a low-density polysulfide polymer prepared by Sulfur and used sunflower oils react directly. Because both sulfur and cooking oils are hydrophobic, the polymer can easily extract hydrocarbons like crude oil and diesel fuel from saltwater. Sulfur is a petroleum industry by-product, and leftover sunflower oil may be utilized as a raw material. 150 g food-grade used sunflower oil, 150 g sulfur, and 700 g finely powdered sodium chloride were used in an experiment to make polysulfide. The reaction temperature was adjusted at 180°C. The resulting polymer (a soft rubber) is friable; therefore, it was ground down using a mechanical grinder and screened for particles between 0.5 and 3 mm. The polymer was repeatedly rinsed with DI water to eliminate the sodium chloride porogen. The polymer was filtered through a sieve (0.5 mm) and pressed with a piece of flat plastic to remove surplus water after the final wash. The polymer was then dried in a sieve by putting it in a drying oven (UNB400, Germany) for 24 hours at 42 degrees Celsius. Kinetics of adsorption was examined with pseudo−first order, pseudo−second order and intra particle diffusion models. The experimental results show good fitting with pseudo−second order model for south oil adsorption on polysulfide polymer. Adsorption of north and south oils onto the prepared polysulfide polymer was done experimentally using batch apparatus with controlled conditions of temperature and stirring. Effects of temperature and initial oil concentration for the adsorption process were examined for the ranges (20−40 °C and (10−90) (g/l), respectively. The experimental data follows the Freundlich isotherm model with coefficient of variance (R2) equals, according to the study of adsorption equilibrium isotherms (0.99). According to the findings of the study, the greatest g/l of south oil removal equals 93 percent at the lowest temperature of 20 degrees Celsius.

1. Introduction

Various pollutants are emerging in our environment. One of the pollutants that can cause an environmental problem is the present of oil and grease inside water system[1] and [2]. When petroleum wastewater is introduced into the aquatic environment at high concentrations, it becomes toxic to aquatic organisms and damages other ecosystems in the body of water Abdul Hamid et al. [3].Oily wastewater discharge into natural water streams has risen as a result of industrial growth and human activities. Crude oil spills, power plants, extraction of crude oil, stations, petrochemical plants, and domestic trash such as spent cooking oil and lubricant from vehicle spills are all sources of oily wastewater. Crude oil transportation is another source of oil spills in surface water Singh et al. [4]. Oil and grease may be removed from wastewater using a variety of procedures, which are chosen depending on the effluent’s qualities and condition. Some of the most common methods for treating oily wastewater include gravity, floating, chemical and biological treatment, and dissolved air flotation. These solutions, on the other hand, came at a great price and required constant upkeep. Another option is de-emulsification, although it’s not frequently utilized due to its low removal efficiency and expensive [3].

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Various research has been done in order to determine the best methods for removing oil from water. Oil removal procedures include adsorption, flotation, coalescences, membrane filtration, biological treatment, electrocoagulation, coagulation, and flocculation. Each approach has its own set of benefits and drawbacks. One of the most popular ways for eliminating pollutants is adsorption, which is one of the methods described above. The advantages of employing adsorption techniques, according to earlier studies, include high oil removal efficiency, cheap cost, and low processing cost [3].

2. Experimental work

All chemicals that were used with in experiment are of high purity and analytical grades, except for the oil that was supplied from Al Shanafiya Refinery in Al-Diwaniyah province.

Table 1. Shows the properties of south oil.

| Properties          | South crude oil |
|---------------------|-----------------|
| API                 | 29.3            |
| Salt                | 133.2           |
| SP . GR             | 0.87997         |
| W & S               | 0.075           |
| Source              | Shenafia refinery |

2.1 polysulfide polymer preparation apparatus

As shown in Fig. 1, the 4.7L stainless steel cylindrical reaction vessel with 20 cm internal diameter was placed on a thermostated hot plate, to restrict heat loss from the reaction vessel to the environment, a covering of glass wool was placed on top of it. To collect and discharge reaction gases to a safe location, the whole reaction equipment was constructed under a fume hood. An H-frame platform was used to secure an overhead electrically powered mechanical stirrer (LS-50D, KOREA). An impeller made of stainless steel (15 cm square blade) was positioned in the reaction vessel's middle to get the necessary power for actively mixing the reaction mixture. Tie cables were used to hold the reactor to the H-frame support.

The temperature probe and the large glass funnel were fastened to avoid contact with the reaction vessel's whirling impeller, which was three millimeters from the bottom.

After filtering the samples of each run, the COD value was calculated to assess the process' performance. All of the trials were repeated three times and only the average values were taken.
2.3 polysulfide polymer preparation procedure

In the reaction vessel, 150 g of food-grade used cooking oil was added. The oil was heated to 170 °C and the overhead stirrer was turned on at 100 rpm. The temperature of the oil was immediately measured using a temperature probe and a digital recorder. (150.0 grams) Sulfur was then introduced via the funnel at a pace that kept the temperature of the reaction mixture above 155 °C. The sulfur was added over the course of about 10 minutes. A red bottom layer is formed by molten sulfur and sulfur pre-polymers from ring-opening polymerization, whereas a light top layer is formed by the oil. The two phases begin to interact positively at this scale. At this size, the two phases begin to react, resulting in an opaque mixture over the course of the sulfur addition. The sodium chloride porogen was added once the reaction liquid was opaque and two separate layers were no longer visible. As a result, sodium chloride (700g, finely powdered in a blender) was poured via the funnel at a pace that kept the temperature of the reaction mixture above 155 °C. At compensate for the internal temperature drop, the reaction temperature was adjusted to 180°C when the sodium chloride was added. The whole amount of sodium chloride was added over the course of 20 minutes. The reaction mixture was often an orange, opaque, and somewhat free flowing slurry when the salt was added. The mixture thickens and darkens to a brown tint when it is heated at 180°C. When the viscosity reaches a threshold where the overhead stirrer reports a torque of 40 aN•cm, the reaction is stopped. This alteration happened 15 minutes after the sodium chloride addition was completed. Some gases (H2S) may be produced at this step of the process, hence working under a fume hood is required. Because overheating or extended heating at 180°C causes further gas evolution, the reaction was stopped as soon as the stirrer torque reached 40aN •cm. To halt the reaction, disconnect the stirrer and hotplate from the power source, cut the cable connections, remove the hot plate, and set the reaction vessel on a trivet to prevent additional heating. The resulting polymer (a soft rubber) is friable, allowing the impeller to be easily removed with a spatula. With a big spatula, the polymer was broken into large bits and removed from the reaction tank. After that, the polymer was ground with a mechanical grinder and screened for particles between 0.5 and 3 mm. The screening analysis equipment used to sift the polymer particles is shown in Fig. 3.

To remove the sodium chloride porogen, the polymer was repeatedly washed with DI water. A 200rpm overhead stirrer was used to agitate the mixture for 30 minutes. The polymer was then extracted using a sieve machine (Fritch, Germany) and washed three times in the same manner. The polymer was then dried in the sieve by placing it in a drying oven at 42 degrees Celsius for 24 hours. Worthington et al. (Worthington et al., 2018). Fig. 3 depicts the procedures for making polymer.

3. Results and discussion

3.1. Equilibrium of Adsorption

Isothermal information analysis with the application of characteristic isothermal modeling is a major development in determining the appropriate model that can be used for design purposes. As a result, the relationship of equilibrium data that uses either a theoretical or experimental formula to understand and predict the degree of adsorption, in choosing the most extreme adsorption limit for a given adsorbent [9],[10],[11],[12],[13]and [14].

Figure 4 represent the equilibrium adsorption isotherms curves for the south oil on the surface of the prepared polysulfide adsorbent. These curves were plotted for the range of concentration (0-60) g/l at various temperatures (20, 25, 30, 35, and 40 °C). It could be recognized from these figure that there is a proportional relationship between the concentration of oils in the solution and its concentration in the adsorbed phase. This is clearly shown from the shape curves of isotherms that are of classical adsorption type. This means that any increasing of concentration of oil in the solution increases the concentration of oil on the surface of the adsorbent. But this proportionality becomes less notable at high concentrations of oils in the solution because the adsorbent reaches its maximum capacity. The values of maximum capacities for the prepared polysulfide are shown in Table (2).

| Temp. c | Ce (g/l) | qe (g/g) |
|---------|----------|----------|
| 20      | 0.12     | 1.65     |
| 25      | 0.2      | 1.56     |
| 30      | 0.3      | 1.47     |
| 35      | 0.4      | 1.4      |
| 40      | 0.5      | 1.32     |
It could be recognized from these figures that there is a proportional relationship between the concentration of oils in the solution and its concentration in the adsorbed phase. This is clearly shown from the shape of isotherms curves that are of classical adsorption type. This means that any increasing of concentration of oil in the solution increases the concentration of oil on the surface of the absorbent. But this proportionality becomes less notable at high concentrations of oils in the solution because the absorbent reaches its maximum capacity.

3.2 Effect of temperature

The temperature range for the adsorption process was chosen from 20°C up to 40°C in viewing to the expected values for the industrial process. It was clearly observed from these figures that an increase of temperature causes a decrease in the adsorption capacity for the two oils. This result agrees with previous study which was done by (Yagub et al). Figure 4 shows the effect of temperature on the removal percentage of oils. These figures indicate that the increasing of temperature leads to a decreasing of the removal percentage of the two oils. Where, the removal percentage of south oil decreased from 93% to 75% with the same increasing of temperature. This behavior is in agreement with the study done by Worthington et al.[15]. They explained that the adsorption forces between the absorbed molecules and the active sites become weak when the temperature increases, which leads to a decrease in the removal percentage of oil.

3.3 Formulation of adsorption equilibrium

The experimental adsorption data of south crude oil onto prepared polysulfide polymer were correlated using Langmuir and Freundlich adsorption isotherm models. These equations were chosen in this work because they are the most well-known equations for the adsorption of a pollutant in aqueous solution onto a solid adsorbent (Dada et al., 2012). Langmuir adsorption isotherm represents the adsorption of solute that limits to a single monolayer of solute molecules on the solid adsorbent. This is based on the Langmuir theory of adsorption which assumes the surface of the solid adsorbent as a homogeneous surface. However, Langmuir adsorption isotherm equation could be represented mathematically as (Wang et al., 2010):

\[ qe = Qm b + cE/(1 + b ce) \]  \hspace{1cm} (1)

Where:

- \( qe \): Equilibrium concentration of the oil in the solid phase (g/g).
- \( Qm \): Langmuir maximum uptake of the oil (g/g).
- \( b \): Constant of the Langmuir adsorption (L/g).

Freundlich adsorption isotherm represents the adsorption of solute as a multilayer of molecules onto the heterogeneous surface of solid absorbent. Freundlich adsorption isotherm equation could be represented mathematically as (Dada et al., 2012):

\[ qe = kf ce^{1/n} \]  \hspace{1cm} (2)

Where:

- \( kf \): Constant of Freundlich isotherm .
- \( n \): intensity of adsorption.

Langmuir and Freundlich adsorption isotherm equations were expressed in linear forms and respectively as follow:

\[ ce/qe = 1/(Qm b) + 1/Qm * Ce \]  \hspace{1cm} (3)

\[ \log qe = \log kf + 1/n \log Ce \]  \hspace{1cm} (4)

The experimental data for adsorption of south crude oil on the prepared polysulfide were correlated with the linearized form of Langmuir and Freundlich adsorption equations and shown in Figs. (5-6). It was clearly observed from these figures that the experimental data corresponding the Freundlich isotherm very well. This result indicates that the adsorption of south oil and north oil onto the polysulfide polymer was occurred on heterogeneous surface and multilayered.
This congruence with Freundlich isotherm could be clearly evident by recognizing the values of confidence level (R²). Table 3 shows the comparison between the Langmuir and Freundlich isotherms for south oils equilibrium adsorption data.

Table 3. Isotherm parameters for south oil at temperature range (20–40) °C.

| Temp °C | Langmuir model | Freundlich model |
|--------|----------------|------------------|
|        | Qm (g/g) | P (1/g) | R² | Kf | n | R² |
| 20     | 1.6000  | 0.060  | 0.8160 | 0.5680 | 1.129 | 0.9868 |
| 25     | 1.5500  | 0.066  | 0.8691 | 0.4650 | 1.715 | 0.9701 |
| 30     | 1.4959  | 0.050  | 0.9287 | 0.3540 | 0.974 | 0.9696 |
| 35     | 1.4080  | 0.047  | 0.9201 | 0.2980 | 1.169 | 0.9754 |
| 40     | 1.3000  | 0.042  | 0.8115 | 0.1904 | 0.914 | 0.9729 |

3.4 Kinetic of Adsorption

The quantity of south oil adsorbed on the produced polysulfide as a function of time for the temperature range (20–40) °C is shown in Fig. 7. The amount of oil adsorbed grows fast in the first sixty minutes, as seen by these data. After that, until the equilibrium state is reached, there is no substantial variation in the quantity adsorbed.

These figures show that the rate of adsorption of oil on the polysulfide polymer (slope of curves) is high at initial period and approaches zero at later times. This is due to the decreasing of adsorption driving force which is the oil concentration in solution minus its concentration on the surface of adsorbent.

Pseudo–first order, pseudo–second order and intra particle diffusion kinetics adsorption models were used to correlate the experimental adsorption data of the present study. These kinetics models could be expressed mathematically as (Onal, 2007):

First order:

\[
\frac{dq_t}{dt} = k_1 \ast (q_e - q_t)
\]  

Second order:

\[
\frac{dq_t}{dt} = k_2 \ast (q_e - q_t)^2
\]  

Intra particle model:

\[
\frac{dq_t}{dt} = \frac{1}{2} k_{int} \ast t^{-0.5}
\]

Where:
- \(q_t\): Adsorption capacity at time \(t\) (g/g).
- \(k_1\): The rate constant of pseudo - first order kinetic model (L/min).
- \(k_2\): The rate constant of pseudo-second order kinetic model (g/g. min).
- \(k_{int}\): The intra particle diffusion rate constant ((g/g. min\(^{1/2}\)).

The previous mentioned adsorption kinetic models were integrated to obtain the following formulas:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \ast t
\]  

\[
\frac{t}{q_t} = \frac{1}{k_2 q_t^2} + \frac{1}{q_e} \ast t
\]

\[
q_t = k_{int} \ast t^{0.5} + C
\]

Where \(C\) is constant.

Figures 8 and 9 shows the kinetics experimental data fitting with linearized form of pseudo–first order, pseudo–second order and intra particle diffusion kinetics models for south oil and north oil adsorption on polysulfide polymer. It was clearly observed from these figures that the pseudo–first order and intra particle diffusion kinetics models not corresponding with the experimental rate of adsorption data. It also could be recognized that the second–order kinetic model represents the experimental rate of adsorption data well.
Table 4. Pseudo first order and second order parameters of the adsorption Process in south oils at different temperatures.

| Temp (℃) | First order | Second order |
|----------|-------------|--------------|
|          | qₑ cal. (g/g) | K₁ (1/min) | R² | qₑ cal. (g/g) | K₂ (1/min) | R² |
| 20       | 0.351       | 0.175       | 0.735 | 1.65 | 0.187 | 0.999 |
| 25       | 0.239       | 0.017       | 0.730 | 1.56 | 0.340 | 0.996 |
| 30       | 0.196       | 0.017       | 0.707 | 1.47 | 0.230 | 0.999 |
| 35       | 0.185       | 0.018       | 0.716 | 1.40 | 0.196 | 0.999 |
| 40       | 0.108       | 0.017       | 0.706 | 1.32 | 0.159 | 0.999 |

3.5 Effect of initial concentration

Figure 10. Removal percentage of south oil for different initial concentration at 20 ℃ and contact time 4 hrs.

Figure 11. Removal percentage of south oil for different initial concentration at 25 ℃ and contact time 4 hrs.

Figure 12. Removal percentage of south oil for different initial concentration at 30 ℃ and contact time 4 hrs.

Figure 13. Removal percentage of south oil for different initial concentration at 35 ℃ and contact time 4 hrs.

Figure 14. Removal percentage of south oil for different initial concentration at 40 ℃ and contact time 4 hrs.

It was clearly shown from these figures that an increasing of the initial concentration of the two oils in the solution associated with a decreasing of the removal percentage. However, the increase of initial concentration enhances the adsorption capacity but diminishes the removal percentage of oil. This clearly observed from Figs. (10−14), where the removal percentage at 20 ℃ decreased from 93% to 69.32% for south oil corresponding to an increase of initial concentration from 10 to 90 (g/l). This behavior agrees with study done by (Foo & Hameed, 2010). This behavior may be explained as follows. In most cases of low concentrations of oils in solution, the ratio of the initial number of oil molecules to the available surface area is low. Hence, the partial adsorption is independent on the concentrations while at high concentrations of oils in solution, the available adsorption sites become less as a result of reaching the saturation state.

4. Conclusions

The present study shows that the polysulfide polymer gives high ability in removal of south crude oil from aqueous solution. This work concludes on a variety of important points:

1. FTIR spectra has showed the chemical structure of polysulfide polymer, the result expresses different functional groups (C-H, C=O and C-S) distributed on the surface that indicate the success of the preparation process.
2. The equilibrium adsorption isotherm that was applied on the experimental data showed that the Freundlich isotherm fitted well the experimental adsorption data with confidence level 0.99.
3. Polysulfide polymer was very effective in removing oils, where the maximum percentages removal south oil equals to 93%.
4. Kinetics of adsorption give an idea about the rate of adsorption for north oil and south oil, it was clearly observed that the pseudo-second order model corresponded with the experimental data with confidence level equals to 0.999.

5. Recommendations

1-Studying other parameters effecting on the adsorption capacity such as dosage, pH and contact time.
2- Choosing another type of cooking oil in prepared polysulfide polymer.

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