Treatment Oilfield Produced Water using Coagulation/Flocculation Process (case study: Alahdab Oilfield)

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ABSTRACT
Produced water is a large amount of water wasted throughout the crude oil extraction process, it's a mixture of the well's deposition water and the water of oil wells extraction water. Produced water contains oil, suspended solids and dissolves solid. This study tested produced water collected from Alahdab oilfield/middle oil company for oil content and suspended solid contamination using chemical precipitation and coagulation-flocculation for reinjection and environmental considerations. Coagulation/flocculation is a common method used as primary purification to oily wastewater treatment due to its usability, performance, and low cost. Coagulant experimental was completed by a jar test device, additives of ferric sulfate and aluminium sulfate were in a range about (10 - 40) ppm, as well as polyelectrolyte-(polyacrylamide) as an additional flocculent in the range (1.5-3) ppm. The results show that ferric sulfate was more efficient at removing turbidity than aluminium sulfate under the same conditions, with the best removal of turbidity at dose concentration 30 ppm of Ferric sulfate and a flocculent dose concentration of 2.5 ppm of polyacrylamide, also with oil content decreasing from 396.71 ppm to 53.56 ppm.

KEYWORDS: Oilfield; Coagulation; Turbidity; Oil Content; Produced water.

INTRODUCTION
Produced water is a large volume byproduct of oil production; during the process of oil extraction. Water is transported to the surface from groundwater formations. Around 17 million cubic meters of water are produced daily About 40% of the daily water production (Lin et al., 2020). Produced water is typically very salty, with dissolved and suspended solids, hydrocarbon residues, a variety of organic species, heavy metals, and chemicals used in the industrial production and treatment processes (Jiménez et al., 2018). The chemical and physical characteristics of water vary widely according to the type of hydrocarbons produced, the geological specification, and the area's location from which the water is extracted (Igunnu 2014). Differing oil fields, oil refineries, oil industries, petrochemical plants, and oil terminals are produced to wash storage tanks (Shi et al., 2014). Produced water is extremely complex, it contains thousands of various compounds that differ between the well and throughout the lifetime of the well (Bakke et al., 2013). Treatment of these effluents is needed before disposal, and it can improve oil/water separation, oil recovery, Improving water quality, water reuse, and safety of downstream facilities, and regulating environmental permits (Khalid 2014; Mohammed et al., 2007).

Most common methods for treatment of produced water are sedimentation, flotation, coagulation and flocculation, centrifugal separation, adsorption, ultra-filtration and reverse

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osmosis, these methods can either be used separately or combined (Mohammed et al., 2007; Shahriari et al., 2019). In general, coagulation/flocculation is a two-phased process designed to extract stable particles by creating larger aggregates that are separable in the following separation stage from the aqueous phase. The preliminary stage is the coagulation process in which destabilization is caused by either a decrease in repulsive forces between particles or by precipitate the agglomeration (Hogg 2005). Coagulation is one of the effective ways of removing oil. Dispersed fine-oil particles can be extracted from water by precipitation and converting into large agglomerated flocks (Puszkarewicz 2008).

The following stage of the compound process is flocculation, which involves accumulating coagulated particles and/or precursors deposited into flocs. Coagulation and flocculation are two separate processes that take place in order to resolve the forces that keep suspended particles from colliding and forming flocs (Karbassi & Pazoki 2015).

This method is preferred for the initial purification operations due to the ease of operation, low cost, and high performance, and its uses of less energy than alternative treatments (Altaher et al., 2011).

Coagulation can be classified into two types based on their application: ferric salts and aluminium salts (alu). Precipitate particles that have been positively charged could lay on contaminated particles (hetero-coagulation), again allowing charge neutralization (Sahu & Chaudhari, 2013). Many researchers have studied the processes of coagulation/flocculation in wastewater treatment. Providing an overall description of coagulation-flocculation process and its applications in water and wastewater treatment. Suggestion to use silica in the form polysilicates for this purpose. The range of additives has expanded, including organic compounds, such as anionic, cationic or non-ionic polyelectrolytes, leading to new composite coagulants. Overall, it is evident that the tendency in the coagulation field is the production of modified composite coagulants, which they are becoming more and more complicated, regarding their composition, but also more effective, when compared with the traditionally applied reagents, was done by (Tzoupanos & Zouboulis 2008). The environmentally correct coagulants was used as a viable alternative and has demonstrated advantages over the use of chemical coagulants, they used Moriinga oliefera Lame seeds as a coagulant for oilfield produced water treatment in coagulation/flocculation process, was investigated by (Santana et al., 2010). Improving of coagulation/flocculation process of wastewater from the industries of petroleum and petrochemicals, was investigated by (Altaher et al., 2011). Considered the use of Aluminium chloride polychloride rather than ferric chloride in the treatment of petroleum industries wastewater by (Farajnezhad & Gharbani 2012). The coagulation potential of FCe (FeCl3-induced crude extraction) obtained from P. oveata seeds to remove turbidity from wastewater, was investigated by (Ramavandi 2014). The effectiveness of the coagulation/flocculation process in extracting suspended solid, coatings, oils and greases from biodiesel wastewater, was examined by (Daud et al., 2015). Three coagulants, Zetag 8140, Klaraid IC1176, Klaraid PC1195 and Klaraid CDP1326 were used as flocculants. The results indicated that klaraid CDP1326 turbidity removal more efficiently than others coagulants under same conditions, and the highest turbidity removal, was obtained by (Mousa & Hadi 2016). coagulation/flocculation process have a best value in pre-treating wastewater with biodiesel, this was founded by (Daud et al., 2016). Ferric sulfate and klaraid CDP1326 were used as the coagulant materials and polyelectrolyte (polyacrylamide) was used as the flocculent. The results showed that ferric sulfate had a higher capacity than klaraid CDP1326 to adsorb suspended solids and oil from produced water, was done by (Mousa & Al-Hasan 2017). Coagulation/flocculation process can reduce the content of oil and turbidity from oily wastewater by using various coagulants, was investigated by (Mohammed & Abbas 2017; Mohammed & Shakir 2018).
The objective of the study is to use the coagulation and flocculation process to extract suspended solids and oil from produced water. The study investigates the potential of two coagulant materials (Ferric Sulfate and Aluminum Sulfate) and the polyelectrolyte polyacrylamide flocculent material. Using coagulation-flocculation method for treatment of produced water prior to reinjection into reservoir (oil well) with permissible limit concentrations parameter.

MATERIALS AND METHODS

The following materials were used in the present research:

The following chemicals are two coagulants and Flocculant products used in the study:

Aluminum sulfate (Al2(SO4)3.16 H2O): is a powerful coagulant with a high cationic charge and molecular weight (M.wt =630.38 gm/mol, India (pure)).

Ferric sulfate hydrate(Fe2(SO4)3.7H2O): is a powerful coagulant with a high cationic charge and molecular weight (399.88 gm/mol, India (Extra pure)).

The polyelectrolyte Flocculent (C3H5NO)n: is an organic polymer formed from acrylamide subunits with high molecular weight polyacrylamide and bulk density (600 kg/m3), (France, purity 99%).

The Produced Water samples utilized in this research were supplied from Midland Oil company - Alahdab Oil Field in Waist, Iraq.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Oil content</th>
<th>Turbidity</th>
<th>pH</th>
<th>Oxygen dissolved in water</th>
<th>Specific Gravity</th>
<th>Viscosity</th>
<th>TDS</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values</td>
<td>396.71 mg/l</td>
<td>242 NTU</td>
<td>6.77</td>
<td>0.09 mg/l</td>
<td>1.042 g/ml</td>
<td>1.270 mPa.s</td>
<td>105216 mg/l</td>
<td>164400 μs/cm</td>
</tr>
</tbody>
</table>
After using the test jar device, pipette water is ejected from the beaker into the tube of the sample, ensuring that the sample does not contain any air bubbles. Put the sample into the tube and read the turbidity vale using a calibrated turbidity meter. Repeat the same procedure for other beakers.

The amount of oil content in the produced water was measured by using UV-VIS Spectrophotometer (Thermo GENESYST 10UV, USA) at the maximum absorption wavelength (291 nm). (0.5) grams of NaCl salt have been added in the separating funnel to (100) ml of produced water in order to break the emulsion of the oil. Then add (10) ml of carbon tetrachloride (CCl4), followed by shaking of vigor for (2) minutes. After, (20) minutes the solution will separate in two layers, the organic layer (lower layer) used to measure the absorbance value, later concentration of oil content was calculated using a calibration curve.

Oil removal efficiency in produced water was measured by apply the, equation below.

\[
\text{Oil removal efficiency} = \left(1 - \frac{C_t}{C_i}\right) \times 100, \%
\]

Where Ci: untreated Oil concentration; Ct: treated Oil concentration in (ppm).

**RESULT AND DISCUSSION**

Several experiments were carried out to determine the efficient coagulant capable of reducing turbidity in the produced water to the allowable level. The turbidity values differ with the concentration of colloidal in the produced water, which can be used to detect the presence of residue oil content in the produced water (Sawain et al., 2009). The produced water's turbidity value is (242) NTU, two substances of coagulation used to reduce turbidity to the permitted value such as (Aluminium sulfate & Ferric sulfate). The performance of the coagulant is well known to change between produced water and others (Altaher et al., 2011). Figs. (2 and 3) show a comparison of ferric sulfate and aluminium sulfate at 10 and 20 ppm, with different polyacrylamide doses in the range (1.5 - 3) ppm.
The main objective of this step was to confirm a maximum performance point for coagulant suspensions. As a result, concentrations were well-known and tested, and a good percentage of turbidity emulsion was achieved by ferric sulfate at the same concentration of two coagulants. Comparison of the efficiency of two coagulants in oil content removal from produced water using the same dosage as shown in Figs (4 and 5). Coagulants are considered to be more effective in reducing the suspended solids and oil contents of effluent. The difference in oil removal efficiency between ferric sulfate and aluminum sulfate can be seen in the figures (4 and 5) below. As a result, it was discovered that ferric sulfate has high efficiency than aluminum sulfate in reducing turbidity and oil content under the same conditions, since the Fe+3 iron ion has more affinity than the trivalent aluminum ion Al+3 will be more attracted to the negatively charged surfaces and will suppress the negative surface charge network, which means it will suppress the zeta potential. Therefore, ferric
hydroxide is less soluble than aluminum hydroxide, which precipitates over a wider pH range. It was found that the turbidity and oil removal efficiency of iron sulfate is better than that of aluminum sulfate (Hadi et al., 2020).

![Graph showing oil removal efficiency by using ferric sulfate and aluminum sulfate.](image)

**Fig. 4** Oil removal efficiency by using ferric sulfate and aluminum sulfate.

![Graph showing oil removal efficiency by using ferric sulfate and aluminum sulfate.](image)

**Fig. 5** Oil removal efficiency by using ferric sulfate and aluminum sulfate.

The dose is an important parameter in determining the best conditions for efficacy of coagulant and flocculent treatment. Typically, inadequate quantity or overdose leads to poor coagulation/flocculation processes. As a result of the importance mentioned previously, finding the optimal dose of coagulant and flocculant is considered one of the priorities in order to reduce the costs of excessive doses used in treatment in addition to achieving optimal performance of treatment (Almojjly et al., 2018; Sawain et al., 2009). Two different types of coagulants (ferrous sulfate, aluminum sulfate) in the same dose (10-40 ppm) and different doses of flocculant in the range (1.5-3 ppm) of polyacrylamide were used, to find which one is better than the other and to evaluate the effect of Coagulation and flocculation doses on the turbidity of the produced water, as shown in Figs. (6 and 7). The amount of coagulant used tends to contain an effect on the removal of turbidity, as shown in Fig.6. A dose of ferric
sulfate (30 ppm) removes more turbidity reach to (20.8) NTU than the lower dose of ferric sulfate (10 ppm) which is remove turbidity up to (45.6) NTU by applying a dose of flocculant of 2.5 ppm of polyacrylamide at pH= 6.77; 25 °C as shown in Fig.7. While, the dose of aluminum sulfate (30 ppm) removes more turbidity up to (24.24) NTU than the lower dose of coagulant (10) ppm; achieved turbidity removal up to (52.14) NTU and dose of flocculant (2.5) ppm at pH= 6.77; 25 °C. It’s possible that the low coagulant dosage was just sufficient to supply charge neutralization in order for coagulation to occur. these values with the areas of the recommended coagulation dose by (Mousa & Al-Hasan 2017).

![Fig 6. Turbidity removal by using different doses of ferric sulfate.](image1)

![Fig. 7. Turbidity removal by using different doses of aluminum sulfate.](image2)

Figures 6 and 7 indicate that these combinations of coagulants combined with flocculants have increased turbidity removal by increasing their doses, except for (30) ppm of coagulants doses and (3) ppm of polyacrylamide for two types of coagulant. In the case of ferric sulfate and aluminum sulfate, the removal of turbidity increased gradually to 25.6 and 32.20 NTU, respectively. The charge of density may be used to illuminate this singularity. These coagulants have a high charge density when compared with others coagulants. In addition, the
polymer’s adsorption increases when the density of the polymer charge increased. Therefore, means that particles are rapidly destabilized. In other words, a coagulant with a higher density charge requires less dose of coagulant to destabilize the particles, which can be described as aluminum sulfate and ferric sulfate (Duan & Gregory 2003). The oil removal efficiency and turbidity are both increased when 40 mg/l ferric sulfate is added, when coagulation dose increased the residual turbidity decreased until it reaches the lowest value at the maximum dose of coagulation dose, after this point, it enlarges due to the increased positive charge generated by the higher coagulant dose (Farajnezhad & Gharbani 2012; Mousa & Hadi 2016).

The optimal coagulant or flocculent dose is well determined as a higher or lower value without any change in oil removal efficiency, when coagulant or flocculant is added further (Amuda & Amoo 2007). The amount of flocculant used ranged from 1.5 to 3 ppm, while the dose of ferric sulfate remained constant between 10 and 40 ppm. An inorganic coagulant is often based upon cations like multivalent cations (Fe$^{+3}$–Fe$^{+2}$). The positive charge of the particles interacts with the negatively charged water molecules produced to help the charge accumulate together (Hassan et al., 2009). For other instances, polyacrylamide was added to improve coagulation efficiency (e.g. in lower coagulant doses) to assess an optimum dose of polyacrylamide and measure the oil removal efficiency (Sawain et al., 2009). Figure 8 indicates that specific ferric sulfate has a strong ability to minimize oil removal in produced water. For example, when 30ppm ferric sulfate and 2.5ppm polyacrylamide were added, oil removal increased to 86.498%, and when the flocculent dose was increased to 3ppm, oil removal increased to 91.42 percent while turbidity increased to 25.6 NTU.

![Fig. 8. Oil removal efficiency by using ferric sulfate and polyacrylamide dosages.](image)

Figure 9 shows the effects of aluminum sulfate using as a coagulant, which showed by using 30ppm aluminum sulfate with 2.5 ppm of polyacrylamide, oil removal efficiency increase up to 83.7%, and when raising the flocculent dose to 3 ppm, oil removal efficiency increase to 88.62%, while the turbidity increase to 32.2 NTU, as shown in the previous Figs. (8 & 9) show that when the doses of coagulation and flocculation increases, the oil removal efficiency is increased (Puszkarewicz 2008). Accordingly, the amount of coagulant and flocculent indicate that depends upon the degree of produced water turbidity; therefore it is necessary to find the optimum dose in order to reduce dosage costs while obtaining the best performance in produced water treatment (Duan & Gregory 2003).
CONCLUSION

The coagulation and flocculation processes used in produced water treatment effectively separate oil and suspended solids content. Ferric sulfate and aluminum sulfate are used as coagulants in coagulation/flocculation treatment; the best dosages were found by using Jar test equally to (30 ppm) respectively. The coagulant powder of ferric sulfate seems more effective than aluminum sulfate when used as the primary coagulant. The optimum removal efficiencies (Ferric sulfate, aluminum sulfate with Polyacrylamides) are 86.496% and 83.7%, respectively (30 ppm) ferric sulfate, aluminum sulfate and (2.5 ppm) of polyacrylamide, pH = 6.77 at room temperature). For maximum oil removal effectiveness, the best combination of coagulant doses is equal to (40, 3) ppm for ferric sulfate and aluminum sulfate, each combined with polyacrylamide.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.
REFERENCES


