Treatment of produced water mixed with polymer from petroleum production

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Abstract. In the petroleum industry, polymer flooding is one of the main methods in enhanced oil recovery (EOR) that applies a water-soluble polymer such as partially hydrolyzed polyacrylamide (HPAM) to increase oil production. It is added to the flooding water to improve the oil movement. During the process, water is produced as a by-product along with oil and gas production. Moreover, produced water with polymer is more difficult to treat than that from conventional water-flooding process because it is complex and highly contaminated wastewater. The proper technology is required to treat this kind of wastewater and reuse it for oil production. Furthermore, the small to fine particles in the produced are needed to be removed because these particles can plug the reservoir in the oilfield. One of the main treatment processes is to apply the coagulant to agglomerate the fine particles and remove them before injection the water into the reservoir. Therefore, the objective of this study is to treat the produced water mixed with HPAM from petroleum production by using coagulants like polyaluminium chloride (PAC) and to investigate the effect of parameters such as coagulant dosage and polymer concentration on the treatment of produced water. The results are compared the performance with the conventional coagulant, potassium aluminum sulfate (potassium alum). The operating parameters of this study are coagulant dosage ranging from 300 to 900 mg/L and HPAM concentrations from 500 to 2,000 mg/L. In addition, the turbidity, as well as total suspended solids (TSS) are also studied. The results indicated that with an increase in HPAM concentration, the TSS and turbidity increase gradually under the same conditions. The results show that with 900 mg/L of coagulants, TSS and turbidity can be removed up to 89% and 94% with PAC and 39% and 27% with potassium alum, respectively. PAC can provide higher performance over alum at the same conditions; thus, leading to the reduction in chemical consumption and cost. Consequently, this method can be applied to use in the wastewater treatment from oil production with polymer flooding before injecting this produced water back into the reservoir.

1. Introduction
During oil production process, water and chemicals are injected into the reservoir to sweep oil into the well [1], which is known as an enhanced oil recovery (EOR). EOR methods are not only injected the water but also injected polymer as well. Besides, polymer flooding is one of the main methods
injecting a water-soluble polymer such as partially hydrolyzed polyacrylamide (HPAM) with the flooding water into the reservoir in order to improve the oil movement. From the production, water is produced as a by-product along with oil and gas to the surface. Moreover, produced water with polymer is more difficult to treat than that from conventional water-flooding process because it is mixed with polymer as a contaminated wastewater [2]. In addition, the HPAM remain with anionic charge dissolved in PW enhances oil viscosity wastewater and deducts velocity raising inclination, which makes the suspended and oil constantly scatter in outflowing and arduous to remove [4]. Normally, produced water consists of dissolved oils, soluble organic solvents, metal salts and treatment chemicals [2] and produced water from polymer flooding (PWPF) is more difficult than other wastewater because polymer can stabilize the oil-water emulsion [3]. Furthermore, the small to fine particles in the produced are needed to be removed because these particles can cause plugging the reservoir. One of the effective method to treat this water is coagulation-flocculation [4] to combine the fine particles and remove them before injection the water into the reservoir [5-8]. Consequently, the aim of this study is to treat the produced water with HPAM from Fang oilfield production by using coagulants like polyaluminium chloride (PAC) and to investigate the effect of parameters such as the coagulant dosage and the polymer concentration on the treatment of produced water.

2. Materials and methods

2.1 Materials
Polyaluminium chloride (PAC) with the purity of 30wt% Al₂O₃, is obtained from Chemipan Co., Ltd. Potassium aluminium sulfate (Potash Alum) is purchased from Suksapanpanit Co., Ltd, with an average molecular weight (MW) of 474.39 g/mol. Hydrolyzed polyacrylamide (HPAM) is obtained from Sigma-Aldrich. Sodium chloride (NaCl) and sodium bicarbonate (NaHCO₃) are purchased from Ajax with 99.9% and 99.7% purity, respectively. Glass microfiber filter is purchased from Labvalley, with 47 mm diameter. The actual produced water is received from the Northern oilfield in Thailand.

2.2 Characteristics of PW
The simulated produced water characteristics is analyzed by using ASTM standard and shown in Table 1.

| Parameter               | Value |
|-------------------------|-------|
| Total dissolved solids (TDS) (mg/L) | 571   |
| Total suspended solids (TSS) (mg/L) | 253   |
| pH                      | 8.2   |
| Conductivity (mS/m)     | 114   |
| Temperature (°C)        | 26.8  |
| Turbidity (NTU)         | 273   |

2.3 Experimental procedures
In this study, Potassium alum and PAC as coagulants for wastewater treatment process are prepared at the desired concentration. The simulated produced water is also prepared at HPAM concentration from 500-2,000 mg/L. The coagulation-flocculation experiments are performed by adding 190 ml of PW in a 250 mL beaker with a magnetic stirrer. The wastewater is mixed rapidly at 890 rpm for 2 mins. After
flocculent is mixed, the wastewater is allowed to settle for 15 min and the 2 ml samples are taken for analysis. The operating conditions are presented in Table 2.

**Table 2. Experimental operating conditions for this study**

| Parameter                | Value                      |
|--------------------------|----------------------------|
| Type of polymer          | HPAM                       |
| Polymer concentration (mg/L) | 500, 1,000 and 2,000       |
| Type of coagulant        | Potassium alum, PAC        |
| Coagulant dosage (mg/L)  | 300, 400, 500, 700 and 900 |
| Mixing speed (rpm)       | 890                        |
| Temperature (°C)         | 30, 40 and 50              |
| Dose of injection (mL)   | 10                         |
| Precipitation time (min) | 15                         |

2.4 Analytical method
Total Suspended solid (SS) concentrations are measured based on the ASTM standard for wastewater treatment by the filtration of the water content known in pre-weighed and pre-weighed glass filters (at 105 °C for 1 hr). After filtration, the filters are dried at 105 °C for 1 hour and weighed again.

Standard Methods 2130 B - Nephelometric method is followed for the turbidity measurement. Turbidity in the wastewater is observed by using a turbidimeter (waterproof turbidimeter EUTECH TN-100, Thermo scientific). The turbidimeter is standardized periodically against Formazin Standards. It is checked before every experiments using calibration standards 0.02 NTU, 20.0 NTU, 100 NTU and 800 NTU, respectively. In the measurement, 10 mL wastewater is tested.

3. Result and discussion
3.1 The effect on total suspended solids (TSS)
The result of HPAM concentration at different potash alum concentration of 500, 1,000 and 2,000 mg/L wastewater using potassium is shown in Figure 1. The results indicate that HPAM concentration and the amount of potash alum have the effect on TSS in that TSS is reduced when the HPAM concentration decreases. It shows that the concentration of HPAM is increased and the efficiency of precipitation is decreased. The reason is that at higher HPAM concentration, the viscosity of the wastewater is increased and it reduces the tendency to performance of coagulation to combine the fine particles together. Also, when the HPAM concentration is increased, flood water treatment becomes more difficult to treat [3]. In addition, when there is no concentration of HPAM in the produced water, the TSS value is lower than the concentration of HPAM in the polymer flooding wastewater. All of the results explained the more the HPAM concentration, the more difficult in treating wastewater. To treat wastewater efficiently, more potash alum are used and it costs more for water treatment.

In addition, Figure 2 presents the effect of the amount of PAC and HPAM concentration on TSS. The results shows that PAC has effect on particle removal in produced water both with and without HPAM. With increasing PAC dosage, from the experimental result demonstrate that PAC is a better flocculent than potassium alum for treating produced water. Using 300 mg/L of PAC can remove 94% and 98% of TSS and turbidity respectively. According to Chen et al. [9], metal coagulants like PAC has an advantage of rapid reaction and low price.
3.2 The effect on turbidity

The results of the effect on turbidity with potassium alum are shown in Figure 3. It is clear that like the effect on TSS, the performance of potassium alum increases as HPAM concentration decreases. This indicates the high concentration of HPAM had negative effect on produced water treatment [7]. Hosny et al. [11] investigated the effect of precipitation concentration on turbidity, TSS and oil droplets which is widely used in making pre-treatment. Moreover, the result illustrates that the increasing potassium alum dosage can effect on turbidity.

Moreover, the original turbidity of produced water used in this study is 273 NTU. The results show that for produced water without HPAM, potassium alum dosage at 900 mg/L can reduce turbidity to 4 NTU or at 99% percent turbidity removal. This because the effective performance of potassium alum it must use the high dosage compared with turbidity removal 300, 400, 500 and 700 mg/L are 82%, 84%, 91% and 91%, respectively.
Figure 3. The effect of HPAM concentration on turbidity at 40 ºC

Figure 4 presents the results of PAC with various concentrations mixed with HPAM concentration at 500, 1,000, 2,000 mg/L and without HPAM. When the coagulant dosage increases, the turbidity decreased owing to the high positive charges from higher amount of coagulant added in the produced water [12]. Furthermore, the PAC performance can reduce the turbidity from 273 NTU up to 3 NTU accounting for 99% turbidity removal. Compared with potassium alum, PAC has a better performance in order to decrease the turbidity on produced water because PAC can use with less amount and the cost can be lowered. Moreover, it has higher percent of fine particle removal. Therefore, it can be applied to use in the oilfield to treat or reduce the fine particle in produced water with and without HPAM before injecting water to the reservoir.

Therefore, the results from the experiment can be applied in the real oilfield operation in Fang oilfield with the various types and sizes of suspended solids as well as the range of turbidity. Furthermore, both two types of coagulants are useful to enhance the coagulation-flocculation performance. The produced waste-water after the treatment can be used to inject into the reservoir instead of disposal to the environment.

Figure 4. The effect of HPAM concentration on turbidity at 40 ºC
4. Conclusion

The effects of HPAM mixed with produced water at different concentrations and two coagulants have been investigated. The results are compared to the performance of the conventional coagulant, potassium alum. The operating parameters of this study are coagulant dosage ranging from 300 to 900 mg/L and HPAM concentration from 500 to 2,000 mg/L. The turbidity and the total suspended solids (TSS) are also measured. The results indicated that the concentration of HPAM influences the coagulation performance with both types of coagulant for the treated water. Compared with potassium alum, PAC as a coagulant can improve the coagulation performance. It is the better coagulant in order to decrease effectively the turbidity of produced water because it can reduced the amount and costs of chemical used. With an increase in HPAM concentration, the TSS and turbidity increase gradually under the same conditions. The results clearly present that with 900 mg/L of coagulants, TSS and turbidity can be removed up to 89% and 94% with PAC and 39% and 27% with potassium alum, respectively. Based on the performance of PAC, this method can be used in the water treatment from oil production before injecting this treated produced water back into the reservoir.

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