Application of PAC and flocculants for improving settling of solid particles in oilfield wastewater with high salinity and Ca\(^{2+}\)

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**ABSTRACT**

The suspended solids in wastewater from Rekabak oilfield, Kazakhstan, were characterized and treated with flocculants to enhance settling. The wastewater contained a high concentration of total dissolved solids and calcium ion. Scanning electron microscopy and energy dispersive X-ray analyses showed that suspended solids were mainly composed of corrosion products (iron oxides) and silicon dioxide particles. Also, much salt deposition from wastewater caused a large increase in the suspended solids value. The settling of solid particles in wastewater was investigated by turbidity decrease within 60 min. The particle settling was enhanced by adding polyaluminum chloride (PAC) as coagulant and hydrolyzed polyacrylamide (HPAM) or cationic polyacrylamide (CPAM) as flocculant. At optimal dose, the particle settling ability with PAC and CPAM was better than that with PAC and HPAM. Particle size analysis showed that HPAM or CPAM with high molecular weight played an important role for enlarging the particle size. The experiments with simulated wastewater showed that particle settling by using HPAM deteriorated significantly compared to that by CPAM at high calcium ion. This study provides further understanding about the effect of high salinity and Ca\(^{2+}\) on solids formation, flocculant performance and particle settling. Meanwhile, the results are also helpful to develop novel flocculants used for high salinity wastewater.

**Key words** | calcium, high salinity, oilfield wastewater, salt deposition, settling test, solid particles

**INTRODUCTION**

Oilfield wastewater with dissolved salts and various pollutants is produced mainly during oil production and is called produced water. The common pollutants usually include crude oil, suspended solids (SS), scale, corrosion products, bacteria and residual chemicals. The wastewater is often reinjected in most cases due to shortage of fresh water, treatment cost or environmental consideration. It is necessary to remove these pollutants from the re-injected wastewater to avoid formation damage (Ahmadun et al. 2013). Nevertheless, formation damage caused by solid particles introduced with the injected water still occurred in some regions. The suspended solids (SS) are usually present in the form of fine colloidal particles with negative charge and are usually difficult to settle through gravity separation. It is necessary to identify the composition, size and quantity of suspended solids for selecting appreciate treatment technique and chemicals. The characteristic of suspended solids is influenced mainly by formation brine, mineral composition and injected chemicals. It was reported that FeS contaminant in unfiltered produced water caused downhole blockage and decline in injectivity during fracturing water injection (Ojukwu & van den Hoek 2004). Shubu et al. (2009) investigated the suspended solids samples from chemical flooding and confirmed the presence of organic substances (anionic polyacrylamide (PAM) and crude oil) as well as inorganic substance of SiO\(_2\), Fe\(_2\)O\(_3\), Fe\(_2\)O\(_4\) and BaSO\(_4\). Corrosion products, i.e., siderite (FeCO\(_3\)), iron oxide (Fe\(_2\)O\(_3\)) and pyrite (FeS\(_2\)), were also found in the deposition on a steam-injection boiler (Dong et al. 2015). Liet al. (2016) characterized the solids in produced water from fractured wells through X-ray photoelectron spectroscopy analysis and confirmed the presence of carbonate-based minerals and iron oxides.
To enhance the settling and removal of the solid particles, coagulants and flocculants are often used in the settling and filtration process for treating large volumes of oilfield wastewater. The widely used coagulants are polymeric inorganic salts, including polyaluminum chloride (PAC), polyferric sulfate (PFS) and their derivatives. Also, the inorganic salts of divalent and multivalent metal ions (such as Ca\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), Fe\(^{3+}\), Fe\(^{2+}\), Ti\(^{4+}\)) are important coagulants (Ozkan & Yekeler 2004; Bella et al. 2014; Chekli et al. 2015). The flocculants are mainly water-soluble polymers based on the PAM backbone with high molecular weight (MW) (Bolto & Gregory 2007). There are many reports about the application of coagulants and flocculants in oilfield, mineral, metallurgical and papermaking wastewater processing (Pan et al. 2005; Prasad & Kumar 2013; Lee et al. 2014).

It is generally known that multivalent metal ions are widely present in the oilfield wastewater and play an important role in the flocculation and settling of particles. Much work shows that the influence of metal ions on the flocculation process is very complicated, depending on ion concentrations, pH value, particle properties, flocculant types, dosage and mixed conditions (O’Shea & Tallón 2011; Ghimici & Nichifor 2012; Nasser 2014). It was reported that the flocculation of kaolin suspension with anionic PAM was inhibited by Ca\(^{2+}\) and Al\(^{3+}\) because of adsorption and hydro-complexation between multivalent metal ions and COO\(^{-}\) group on PAM (Peng & Di 1994). Ozkan & Yekeler (2004) showed that Mg\(^{2+}\) ion was more effective than Ca\(^{2+}\) and Al\(^{3+}\) ions for the coagulation of celestite mineral suspension at pH range of about 8.5–11.0 and adding Mg\(^{2+}\) or Ca\(^{2+}\) could improve the flocculation performance of anionic PAM at pH 11. Witham et al. (2012) indicated that the effect of Ca\(^{2+}\) on the performance of anionic acrylic amide/acylate copolymers for a calcite slurry was higher than that of Mg\(^{2+}\) and Na\(^{+}\) at 0.05 M concentration and the effect increased with increasing anionic character and ion concentration. Ji et al. (2013) showed that the settling of mineral tailings using acrylicamide/sodium acrylate copolymer with 27% charge density was enhanced by saline water containing 679 ppm Ca\(^{2+}\) and 701 ppm Mg\(^{2+}\). In summary, the metal ions significantly influence the electrostatic repulsion and the effective bridging between particle–particle or particle–polymer. Consequently, the size, density and settling rate of the produced aggregates (flocs) in the flocculated water are altered remarkably.

However, very limited research is available on the characteristics of suspended solids and the settling process in oilfield wastewater with high salinity and multivalent metal ions. This paper mainly investigated the enhanced settling of solid particles with PAC and PAM-based flocculants experimentally. Furthermore, the effect of multivalent metal ions on particle settling was studied using a simulated wastewater. This can provide technical support for oilfield wastewater treatment in large scale with low cost and high efficiency.

**EXPERIMENTAL**

**Materials**

PAC with 30.1% Al\(_{2}\)O\(_{3}\) content and 80.2% basicity (provided by Gongyi Yimin Co., China) was used as coagulant. Furthermore, two different PAM-based flocculants (provided by Beijing Hengju Chemical Group Co., China) were used in flocculation and settling tests. The cationic PAC (CPAM) type ‘HENGFLOC 87410’ had \(6\times10^6\) average MW and 42.1% cationicity. The anionic PAC flocculant (hydrolyzed polyacrylamide, HPAM) type ‘HENGFLOC 64018’ had \(6\times10^6\) MW and 40.5% anionicity. Inorganic salts (NaCl, CaCl\(_{2}\), MgCl\(_{2}\), etc.) and petroleum ether were purchased from Sinopharm Chemical Reagent Co., Ltd, Beijing. All solutions were prepared with deionized water.

**Water properties analysis**

The wastewater samples were collected from Rekabak oilfield in the Atyrau Province, Kazakhstan. The Rekabak oilfield with oil geological reserves of \(4.84\times10^4\) t is lying in the Pre-salt of the Caspian Basin (Figure 1). Rekabak oilfield contains a combined series of strata, i.e., Third series group, Cretaceous group and Jurassic group. Until June 2015, the cumulative oil production and liquid production were \(1.74\times10^4\) t and \(7.53\times10^4\) m\(^3\), respectively. The fresh water is very scarce in this area and therefore it is extremely necessary to treat the produced water to meet the injection standard for production.

The wastewater samples were preserved at 4°C in sealed glass bottles. The supernatant of the samples was taken through a syringe from the middle liquid. Prior to water quality analysis, the supernatant needed to be diluted with deionized water until the ion concentration was within the detection range. The metal ion concentrations (Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\) and Mg\(^{2+}\)) were measured by inductively coupled plasma mass spectrometry (NexION 500X ICP-MS, Perkin Elmer, USA). The chloride ion content was determined by...
titration with AgNO₃ aqueous solution. The sample turbidity was measured with an AQ4500 turbidity meter (Thermo Scientific Corp., USA).

SEM-EDX analysis

Firstly, the suspended solids were separated by filtering the wastewater supernatant through a microporous membrane with a 0.45 μm pore size under vacuum. Then petroleum ether and deionized water were used in turn to clean the membrane for removing oil and inorganic salts. The suspended solids in oilfield wastewater were collected on the membrane. After drying at 105°C and spraying with carbon, the membrane containing suspended solids was analyzed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) spectroscopy (JSM 6510A, JEOL Ltd, Japan).

Particle size measurement

The particle size analysis was conducted by a Mastersizer 2000 analyzer (Malvern Instruments, UK) with a detection range of 0.02–2,000 μm. The Hydro 2000A sampler was equipped with a stirrer, circulating pump, and 1,000 mL beaker. After starting the stirrer and pump, the wastewater sample, after being coagulated or flocculated, was added into the beaker until the appropriate shading degree was obtained. The results of the particle size distribution were recorded by the software in the computer automatically.
Settling test

An RT10 multi station digital magnetic hotplate stirrer (IKA Corp., German) was used to carry out the settling tests. The 200 mL of wastewater in six identical beakers with high form was homogenized for 20 min under magnetic stirring at room temperature (22 ± 1°C). The coagulant solution was added to the beaker at a rapid stirring speed of 200 rpm for 2 min and then the flocculant solution was added at a slow stirring speed of 50 rpm for 4 min. Then 10 mL of flocculated wastewater was collected using a syringe from a depth of 3 cm below the liquid surface and transferred to the sample bottle of the AQ4500. The bottle was inversed four times, placed into AQ4500 turbidity meter and allowed to settle. The turbidity (in NTU) of flocculated wastewater was measured at 1–5 min intervals for a duration of 60 min.

Each settling test was replicated three times and the average value of measured turbidity was adopted as a function of the settling time. The settling test of raw wastewater was performed with the same procedure except that no chemicals were used.

Simulated wastewater

The synthetic brine was made by dissolving inorganic salts (NaCl, CaCl₂, MgCl₂·6H₂O, etc.) in deionized water according to the ion content of the oilfield wastewater. To separate the solid particles, the wastewater was centrifuged (TDL-5-A, Shanghai Anting Co., China) and poured into a 200 mL cylinder for settling until the turbidity was below 5 NTU. The liquid in the cylinder was drawn off by a syringe and the solid particles were separated in the bottom. The simulated wastewater was prepared by mixing the separated particles with synthetic bine and sonicating the mixture using an ultrasonicator in Mastersizer 2000 to disperse the particles.

RESULTS AND DISCUSSION

Characteristics of the oilfield wastewater

The wastewater was characterized as having extremely high salinity (total dissolved solids, TDS) of 148,736 mg/L, as shown in Table 1. The data show that the most abundant anion ion is Cl⁻ and the most predominant metal ion is Na⁺, indicating that there is a great amount of dissolved sodium chloride in the wastewater. Also, the divalent metal ions are abundant with calcium ion concentration of 2,459 mg/L and magnesium ion of 526 mg/L. The high conductivity (172.3 mS/cm) could be related to the large amount of dissolved inorganic salts in the oilfield wastewater. The turbidity is 189.3 NTU, which is mainly due to the presence of the particles and oil drops. According to the salinity and chemistry, the wastewater from Rekabak oilfield was CaCl₂ water type, which is common in the Atyrau region and Caspian Sea basin. The formation of CaCl₂ brines is related to evaporation and accumulation of early period seawater rich in CaCl₂. The wastewater is weak acidic with pH value about 6.6, which is related to the hydrolysis of calcium and magnesium ions.

Figure 2 shows the particle size distribution of the suspended solids from wastewater as volume percentage and cumulative volume percentage. Most particles have a size in the range from 0.1 μm to 12 μm. The median particle size (D₅₀) of the suspended particles is about 3.8 μm, which means that 50% of particles are smaller than 3.8 μm. Also, the D₁₀ and D₉₀ are 0.7 μm and 8.1 μm, respectively. While the fine particles are difficult to settle and remove from the wastewater, they must be reduced to meet the re-injection requirement according to the reservoir permeability.

Morphology and main elements of the suspended solids

SEM-EDX analysis for suspended solids on the membrane was conducted to identify the solid morphology and elemental composition.

Figure 3 shows the SEM images of solids on the membrane without (Figure 3(a)) and with (Figure 3(b)) deionized water flushing. As is shown in Figure 3(a), there was a large quantity

Table 1 | Basic properties of oilfield wastewater for study

<table>
<thead>
<tr>
<th>Items</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺, K⁺ (mg/L)</td>
<td>55,012.3</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>2,459.4</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>526.0</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>89,573.8</td>
</tr>
<tr>
<td>HCO₃⁻ (mg/L)</td>
<td>196.1</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>13.2</td>
</tr>
<tr>
<td>Oil (mg/L)</td>
<td>78.2</td>
</tr>
<tr>
<td>pH</td>
<td>6.6</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>172.3</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>189.3</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>148,736</td>
</tr>
</tbody>
</table>
of incompact particles with blocky structure. Meanwhile, the suspended solids value measured was very high, reaching 450.2 mg/L. According to Figure 3(b), with sufficient deionized water flushing, the quantity of particles decreased significantly. The remaining particles had a rounded shape and smaller size. Meanwhile, there was an obvious reduction of the suspended solids value to 120.2 mg/L.

Figure 4 portrays the EDX spectra for the observed particles. Without deionized water flushing (Figure 4(a)), the signal intensities of chlorine and sodium are very high. With deionized water flushing (Figure 4(b)), Cl, Na and Ca signals disappear. It confirms that a large amount of salts (i.e., NaCl, CaCl₂, MgCl₂) were deposited from high salinity oilfield wastewater during filtration through the microporous membrane. Carbon and oxygen refers to the membrane matrix composition. In addition, the Si signal may arise from clay mineral SiO₂. The presence of Fe signals could be attributed to the corrosion products (i.e., iron oxides). Severe pitting corrosion of steel could be due to high concentration of chloride in the oilfield wastewater and the corrosion products could transform to suspended solids furthermore. It should be emphasized that the halite scale (NaCl) formation has been an increasing problem in regions of high salinity brine. Bagci et al. (2001) showed that the increase in NaCl concentration could cause salt crystals to precipitate in pore spaces, followed by pore plugging and formation damage. Although NaCl is highly soluble in water, halite scale occurs due to change in temperature, pressure and concentration during oil and gas production. Furthermore, the scale velocity and quantity of halite are very high once the halite precipitation has started (Lu et al. 2014). Due to the fresh water availability and its compatibility with the brine, removing
halite scale with much fresh water is usually not realistic. Therefore, halite inhibitors were applied to inhibit salt depositions and protect the formation in some fields (Graham et al. 1998; Guan et al. 2008).

Effect of PAC and different flocculants on particle settling and size distribution

During wastewater treatment, the combination of coagulants and flocculants is expected to enhance the particle removal and reduce the dosages. The chief function of coagulants is achieving particle destabilization through charge neutralization. The flocculants can prompt particles to form bigger and denser aggregates through adsorption and bridging between particles, increasing the efficiency of particle settling and subsequent processes. Usually, the flocculation efficiency increases with the MW.

Compared to traditional coagulants such as alum or iron salts, the PAC hydrolysis products are characterized by higher positive electric charges and MW. PAC can bring a rapid and better flocc formation. Also, PAC is pre-neutralized and effective in a wide pH range, minimizing pH adjustment. The polymers based on PAM are mostly used as flocculants in wastewater treatment. The MW of PAM flocculants can reach up to 10–25 millions. Also, PAMs with various charge properties can be prepared by copolymerizing acrylamide with other monomers. CPAM and anionic polyacrylamide (HPAM) are two representative PAM-based flocculants and are used in this study.

Turbidity is the key property to describe the settling activity of particles or flocs for coagulation and flocculation. The settling efficiency can be evaluated and compared through turbidity change with settling time.

Figure 5 shows the supernatant turbidity of wastewater treated by PAC and PAM-based flocculants after 30 min settling as a function of PAC dose (20, 40, 80, 120 and 160 mg/L). With a PAC dose range of 20–160 mg/L and no flocculant, the supernatant turbidity was high in the range of 50–60 NTU. With PAC and 4 mg/L HPAM addition, the supernatant turbidity decreased to 24.4 mg/L with the increasing amount of PAC dosage to 80 mg/L. However, the turbidity increased to 33.1 mg/L with further increasing PAC dosage up to 160 mg/L. Treatment with PAC and 4 mg/L CPAM appeared to perform better in decreasing supernatant turbidity with a similar varying trend and the minimum turbidity was 14.7 NTU. It can be found that the flocculants showed a significant effect on the supernatant turbidity of the PAC-coagulated wastewater, which could be contributing to the bridging of high MW polymer. Moreover, tests showed there was no obvious decrease in the turbidity or even increase when the flocculant dose was above 4 mg/L. Hence, 80 mg/L PAC and 4 mg/L CPAM was considered as the optimum with the minimum turbidity and minimum dose.

Figure 6 shows the variation of supernatant turbidity as a function of the settling time for raw, PAC-coagulated and flocculated wastewater. At the beginning of settling, there was a slight increase in turbidity for coagulated or flocculated wastewater compared to raw wastewater. Then, the turbidity decreased rapidly due to the settling of coarse particles or aggregations in the raw or flocculated wastewater. It can be observed that within the initial settling, the turbidity decrease for PAC-coagulated wastewater was slower than that of raw wastewater. This may be explained by the fact that small size particles were produced during the hydrolysis of PAC and brought the turbidity increase to some degree. After settling for 40 min, the turbidity of coagulated wastewater had an obvious decrease and became lower than that of raw wastewater. The main reason was that the flocs became larger gradually and their settling velocity increased, whereas the fine particles in raw wastewater had a slower
settling velocity. After 60 min settling the turbidity of raw and PAC-coagulated wastewater were 37.0 mg/L and 29.5 mg/L, respectively. It was noticeable that turbidity increase within a period of time occurred during settling in raw and PAC-coagulated wastewater. The reason could be that the large aggregates or flocs formed during the settling process broke up because of shearing stress (Jarvis et al. 2005; Yu et al. 2010).

It is apparent that the turbidity decrease of wastewater treated with PAC and additional flocculants was much faster than for the above two cases. At the beginning there was a rapid decrease in turbidity for wastewater with PAC and HPAM and the turbidity reached 25.7 NTU at 30 min. Thereafter the turbidity decreased slowly and reached 15.1 NTU at 60 min.

For wastewater with PAC and CPAM, the turbidity decreased rapidly at the initial settling and reached 12.5 NTU at 30 min. Thereafter the turbidity decreased more slowly and reached 7.5 NTU at 60 min. Visual observations showed that the particle size produced by additional flocculants was much larger than that by PAC. In summary, the particle settling for PAC-coagulated wastewater was enhanced significantly by
the addition of PAM-based flocculants due to the bridging of polymer. Moreover, there was almost no turbidity increase during settling in flocculated wastewater, which indicated the flocs had higher strength and were not easily broken into small flocs during the settling process.

Figure 7 shows the size distributions of particles in coagulated and flocculated wastewater as volume fraction versus particle diameter. The particle size for PAC showed two peaks of distribution (15 μm and 90 μm), indicating the presence of particles with small size and bigger size. The particle size was enlarged by the addition of PAC and HPAM with a single peak distribution (350 μm). For addition of PAC and CPAM, the particle size was further enlarged with a relatively narrow peak occurring at 500 μm.

PAC could cause some small particles to coalesce to form large ones through charge neutralization, but the bridging was insufficient. However, PAM flocculants played an important role in causing larger particle formation due to the strong adsorption bridging of high MW polymer. Consequently, the settling rate of particles with larger size was improved according to Stokes’ law, which can be confirmed by the turbidity curve shown in Figure 6.

### Effect of Ca$^{2+}$ concentration on particle settling for PAC and different flocculants

Simulated wastewater was used to investigate the effect of calcium ion concentration on the flocculation and settling of particles with PAC and HPAM or CPAM.

Figure 8 shows the turbidity variations as a function of time at different calcium ion concentration when PAC and HPAM were used with a dose of 80 mg/L and 4 mg/L, respectively. Compared to the turbidity curve at Ca$^{2+}$ concentration of 40 mg/L, there was a slight shift to the upper right for the curve for 2,000 mg/L Ca$^{2+}$. And the turbidity curve for Ca$^{2+}$ concentration of 6,000 mg/L shifted further to the upper right of the curve at 2,000 mg/L. Obviously, the results showed that the turbidity decrease at 6,000 mg/L Ca$^{2+}$ was significantly slower than that at 40 mg/L and 2,000 mg/L. Meanwhile, the turbidity after 60 min settling at Ca$^{2+}$ concentration of 6,000, 2,000 and 40 mg/L was respectively 26.5, 14.8 and 8.8 NTU.

Figure 9 shows the turbidity variations at the same conditions when PAC and CPAM were used with a dose of 80 mg/L and 4 mg/L, respectively. Compared with the turbidity curve at 40 mg/L Ca$^{2+}$, the shift of the curve for 2,000 mg/L Ca$^{2+}$ was almost negligible. The turbidity curve at 6,000 mg/L Ca$^{2+}$ shifted to the upper right of the curve for 2,000 mg/L Ca$^{2+}$ obviously. Therefore, the turbidity decrease at 6,000 mg/L Ca$^{2+}$ also became slower than that at 40 mg/L and 2,000 mg/L Ca$^{2+}$. The turbidities after 60 min settling at Ca$^{2+}$ concentration of 6,000, 2,000 and 40 mg/L were respectively 18.4, 8.2 and 6.5 NTU. In summary, the turbidity decrease at high Ca$^{2+}$ concentration with PAC and CPAM was faster than that with PAC and HPAM.

It can be found from turbidity curves that the influence of high concentration of Ca$^{2+}$ on HPAM performance was higher than that on CPAM. The HPAM molecule...
containing COO\(^{-}\) groups with negative charge could interact with positively charged Ca\(^{2+}\). The interaction between Ca\(^{2+}\) and HPAM included mainly three cases: (a) single or multiple Ca\(^{2+}\) was bonded to single HPAM molecule; (b) single Ca\(^{2+}\) was bonded to two HPAM molecules; (c) multiple Ca\(^{2+}\) was bonded to multiple HPAM molecules. At low concentration of Ca\(^{2+}\) and HPAM, the predominant cases were (a) and (b), which can improve the bridging between particles and polymers (Mpfou et al. 2005). However, the harmful effect occurred at high concentration of Ca\(^{2+}\) and HPAM because the case (c) was predominant and caused extensive formation of complexes, gel or precipitation with deterioration of flocculation and settling process (Mortimer 1991; Grima 2003). On the other hand, the high divalent ions or salinity could change the conformation and dimension for PAM-based flocculants, causing polymer coiling and decrease in adsorption and bridging between particles and polymer molecules (Bilanovic et al. 1998; Boisvert et al. 2002). As the salinity and multivalent ions are of frequently high concentration in the Kazakhstan area, their effect on the performance of polymeric flocculants and other flocculants needs to be carefully considered.

CONCLUSIONS

The characteristics and enhanced settling of suspended solids in oilfield wastewater with high salinity and Ca\(^{2+}\) were investigated. The TDS and Ca\(^{2+}\) concentration of wastewater reached up to 14.87% and 2,459 mg/L, respectively. SEM-EDX analysis showed that the suspended solids mainly contained corrosion products (iron oxides) and silicon dioxide particles. High salinity in wastewater led to a large increase in the suspended solids value by 330.2 mg/L due to salt deposition, which is a potential problem to be considered for high salinity wastewater. Settling tests and particle size distribution showed that HPAM or CPAM flocculants played an important role in enhancing the particle settling and enlarging the particle size compared to PAC. Moreover, staged turbidity increase occurred during settling in PAC-coagulated wastewater due to breakup of large aggregates but it did not appear in flocculated wastewater. The turbidity decrease with PAC and CPAM was faster than that with PAC and HPAM at the optimal dose (i.e. 80 mg/L PAC and 4 mg/L flocculant). The high concentration of Ca\(^{2+}\) (6,000 mg/L) could bring a harmful effect on performance of HPAM and CPAM, especially the former due to the bonding between Ca\(^{2+}\) and COO\(^{-}\) in HPAM. Moreover, high salinity and Ca\(^{2+}\) may cause polymer coiling and reduce the adsorption bridging between particles and polymer molecules. The above results would provide guidelines not only for effective application of flocculants in high salinity wastewater, but also for potential salt deposition and corrosion leading to solids increase.

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REFERENCES


Bagci, S., Kok, M. V. & Turksoy, U. 2001 Effect of Brine Composition and Alkaline Fluid on the Permeability Damage of Limestone Reservoirs. SPE 65394.


Chekli, L., Galloux, J., Zhao, Y. X., Gao, B. Y. & Shon, H. K. 2005 Coagulation performance and floc characteristics of polystyrene tetrachloride (PTC) compared with titanium tetrachloride (TiCl4) and iron salts in humic acid – kaolin synthetic water treatment. Separation and Purification Technology 42, 155–161.


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