

Optimization of the Coagulation Process to Remove Total Suspended Solids (TSS) from Produced Water

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Produced water is the largest waste stream generated in oil and gas industries. The disposal of this hypersaline wastewaters containing a mixture of different organic and inorganic compounds is a relevant issue. In this study the removal of total suspended solids (TSS) from a real Produced Water, sampled at a full scale oil refinery plant, was optimized. Coagulation experiments were conducted simulating the coagulation, flocculation and sedimentation phases. Ferric chloride and aluminium sulphate were used as alternative coagulants at doses from 5 to 100 ppm while the pH was varied from 6.68 (ambient pH) to 8 and 9. A cationic and an anionic polyelectrolyte, DF 492 and DF 973 were used as flocculants at doses from 2 to 30 ppm. Finally the produced sludge was quantified in order to select the optimal process conditions for fulfilling the required effluent standard while minimizing the sludge production. Obtained results showed a better performance of aluminium sulphate in the TSS removal, compared with ferric chloride, while the cationic polyelectrolyte (DF 492) performed better than the anionic polyelectrolyte (DF 973). Overall, the best performance was achieved dosing 5 ppm of $Al_2(SO_4)_3$, 30 ppm of DF 492, at ambient pH (6.68), while the optimal process condition was found dosing 5 ppm of $Al_2(SO_4)_3$, 5 ppm of DF 492, at ambient pH. The optimized condition can be used at full scale plant in the chemical-physical treatment units designed to remove the TSS.

1. Introduction

Produced Water is the wastewater produced during the extraction of crude oil and natural gas. Produced Water accounts for about 90 % of the total volume of exploration and production material brought to the surface by the oil and gas industry (Clark and Veil, 2009). Therefore, Produced Water is the largest waste product associated with the oil and gas industry (Stephenson et al., 1992), with a total volume estimates as thousands of m^3/d (OGP, 2002). Typically Produced water composition generated in the oily wastewater oil and gas industrial processes include 50 – 1,000 mg/L of total oil and grease and 50 – 350 mg/L of total suspended solids - TSS (Abbasi et al., 2012).

Produced Water is conventionally treated through different physical, chemical, and biological methods. However, no single technology to treat Produced Water can meet suitable effluent characteristics, thus a multi-barrier approach might be used as suggested for the removal of xenobiotic compounds from water (Roccaro et al., 2013). The choice of the best technology is based on Produced Water chemistry, cost effectiveness, space availability (off-shore vs. on-shore), reuse and discharge plans, durable operation, and by-products formation (Fakhru'l-Razi et al., 2009). For instance, in wastewater treatment plants, many traditional techniques are used for separation of oily wastewater.

Free oil can be easily separated by mechanical means such as gravity settling (API separator), skimming, dissolved air flotation, coalescence and centrifuging. For unstable or primary emulsions which contain oil droplets of diameter greater than 100 μm , chemical separation techniques such as coagulation and flocculation are applied. But the above techniques have limitations for separation of secondary emulsions which contain oil droplets of diameter less than 20 μm (Abbasi et al., 2012). Membrane processes are effective techniques for separating secondary emulsions and their application in the treatment of Produced Waters has grown in the last years (Alzahrani et al., 2013). However, membrane separation needs a pre-treatment step in order to remove Total Suspended Solids (TSS). Coagulation is an efficient process to

remove TSS and its application in the treatment of Produced Water result in a simultaneous removal of primary emulsion and TSS preserving membrane and adsorbent from fouling.

The objective of this study is the removal of TSS from a real Produced Water, sampled at a full scale oil refinery plant, by coagulation, flocculation and settling. Furthermore, the optimal process conditions for fulfilling the required effluent standard while minimizing the sludge production of the treatment process are investigated.

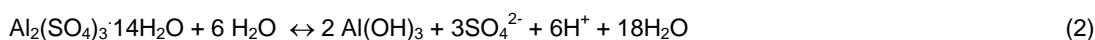
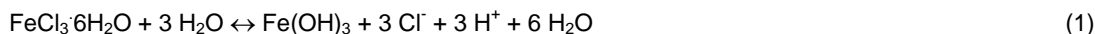
2. Materials and methods

Coagulation experiments were conducted using a Jar Test apparatus (JLT6, Velp) simulating the coagulation, flocculation and sedimentation phases (Roccaro et al., 2007). In particular, flash mixing (coagulation) was conducted for 1 min at 120 rpm, slow mixing (flocculation) was carried out for 20 min at 30 rpm and final setting retention time was 90 min. Ferric chloride and aluminium sulphate were used as alternative coagulants at doses from 5 to 100 ppm while the pH was varied from 6.7 (ambient pH) to 8.0 and 9.0. A cationic and an anionic polyelectrolyte, DF 492 and DF 973 (SNF Italia SPA), respectively, were used as flocculants at doses from 2 to 30 ppm. The Jar test conditions employed in this study are reported in Table 1.

Table 1: Jar test conditions employed

Coagulant type	Coagulant dose (mg/L)	Flocculant type	Flocculant dose (mg/L)	Initial pH	Final pH
FeCl ₃	25	-	-	6.68	6.82
FeCl ₃	50	-	-	6.68	6.77
FeCl ₃	100	-	-	6.68	6.55
Al ₂ (SO ₄) ₃	25	-	-	6.68	6.80
Al ₂ (SO ₄) ₃	50	-	-	6.68	6.77
Al ₂ (SO ₄) ₃	100	-	-	6.68	6.71
Al ₂ (SO ₄) ₃	5	DF492	5	6.68	7.26
Al ₂ (SO ₄) ₃	5	DF492	10	6.68	7.24
Al ₂ (SO ₄) ₃	5	DF492	20	6.68	7.28
Al ₂ (SO ₄) ₃	5	DF492	30	6.68	7.28
Al ₂ (SO ₄) ₃	5	DF492	35	6.68	7.27
Al ₂ (SO ₄) ₃	5	DF492	10	6.68	6.83
Al ₂ (SO ₄) ₃	10	DF492	10	6.68	6.81
Al ₂ (SO ₄) ₃	20	DF492	10	6.68	6.81
Al ₂ (SO ₄) ₃	50	DF492	10	6.68	6.80
Al ₂ (SO ₄) ₃	75	DF492	10	6.68	6.79
Al ₂ (SO ₄) ₃	100	DF492	10	6.68	6.77
FeCl ₃	25	-	-	8.00	7.94
FeCl ₃	50	-	-	8.00	8.04
FeCl ₃	100	-	-	8.00	7.96
FeCl ₃	5	DF492	2	8.00	7.81
FeCl ₃	10	DF492	2	8.00	8.01
FeCl ₃	20	DF492	2	8.00	7.93
FeCl ₃	5	DF973	2	8.00	8.02
FeCl ₃	10	DF973	2	8.00	7.99
FeCl ₃	20	DF973	2	8.00	7.95
Al ₂ (SO ₄) ₃	25	-	-	8.00	8.12
Al ₂ (SO ₄) ₃	50	-	-	8.00	8.22
Al ₂ (SO ₄) ₃	100	-	-	8.00	8.17
FeCl ₃	50	DF492	10	9.00	9.18
FeCl ₃	75	DF492	10	9.00	9.12
FeCl ₃	100	DF492	10	9.00	9.10
FeCl ₃	50	DF973	10	9.00	9.06
FeCl ₃	75	DF973	10	9.00	8.98
FeCl ₃	100	DF973	10	9.00	8.95

Ferric chloride and aluminium sulphate in water generate the reactions reported in Eq(1) and Eq(2), respectively.



Hydrochloric acid (HCl 37%, Merck) and sodium hydroxide (NaOH 4%, Sigma Aldrich) were used to adjust the pH, when necessary.

Initial and final pH was measured for all tests by using a digital pH-meter (mod. 340/SET-1, WTW), whose electrode was calibrated using buffer solutions (pH 4, 7 and 10), provided by the supplier. TSS were measured by following standard methods (APHA, 1998). Finally the produced sludge was quantified.

3. Results and discussion

Results from Jar test have shown that the removal of TSS from Produced Water is a difficult task. Indeed, as shown in Figure 1, the use of either ferric chloride or aluminium sulphate with doses from 25 to 100 mg/L did not result in a concentration of TSS lower than the discharge limit set by the Italian Regulation (80 mg/L).

Colloids are very small particles that have extremely large surface area negatively charged. As a result, settling is not effective for the removal of colloids because gravitational effects are negligible and surface phenomena predominate. Colloids are usually removed by charge neutralisation and sweep flocculation mechanisms which act on the anionic charge of the colloid by its neutralisation prior to its removal by sedimentation or filtration. Alum and iron (III) salts have been employed as coagulant chemicals since the beginning, with alum having the most widespread use (Ghernaout and Ghernaout, 2012). Therefore, the poor removal of TSS observed in this study for Produced Water could be due to the formation of small flocs not removed by sedimentation. pH 8 seems to enhance the TSS removal when ferric chlorine is used as coagulant (Figure 1).

The addition of polyelectrolytes (DF 492 or DF 973) as flocculant following the coagulation with ferric chloride at lower doses and at pH8 did not improve the TSS removal (Figure 2). This result is surprising because the use of flocculant is expected to enhance the floc size and strength and therefore the sweep flocculation effect.

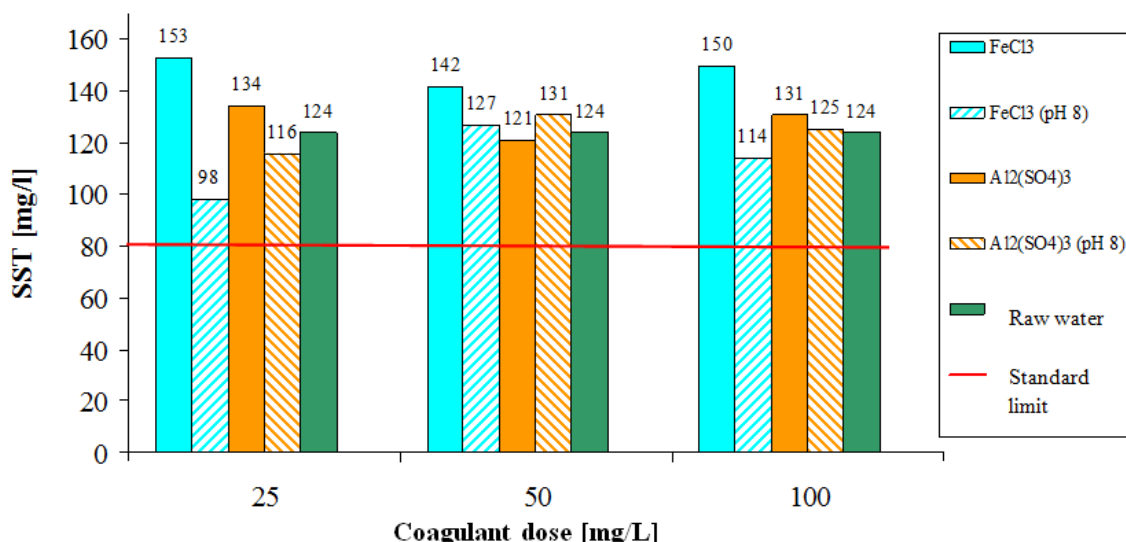


Figure 1: Concentration of SST in raw and treated Produced Water with ferric chloride and aluminium sulphate at pH 6.7 and at pH 8

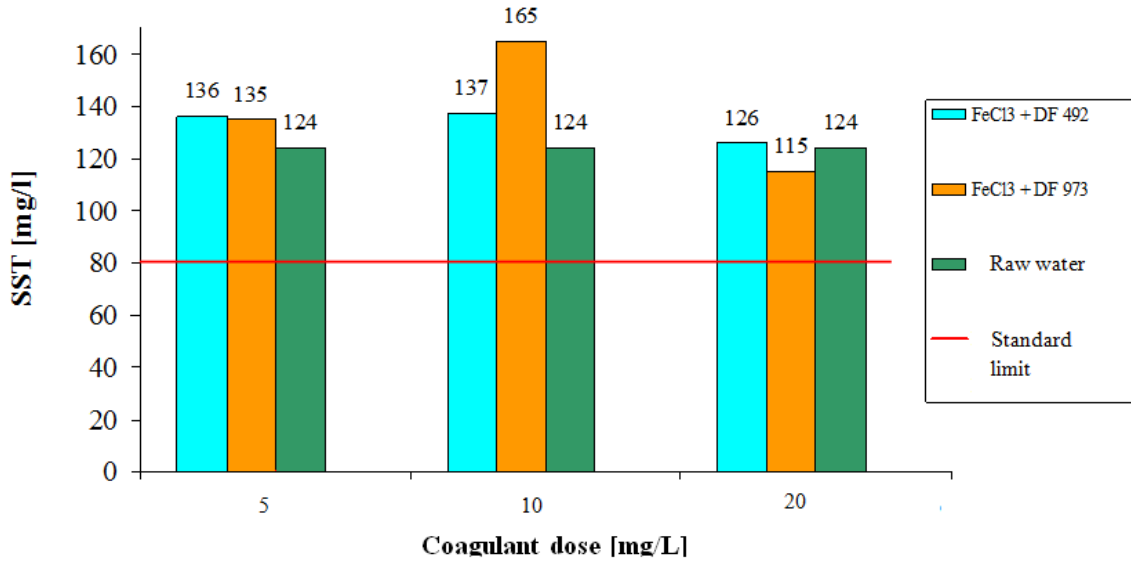


Figure 2: Concentration of SST in raw and treated Produced Water at varying ferric chloride dose, with polyelectrolyte (DF 492 or DF 973) dose of 2 mg/L and pH 8

The combined use of ferric chloride and polyelectrolytes at pH 9 enhanced the TSS removal but, although the employed doses of coagulant were high, yet the standard level was not fulfilled (Figure 3). The higher efficiency of TSS removal at pH 9 can be explained because bigger iron hydroxides are formed at higher pH. Furthermore, the cationic polyelectrolyte DF 492 performed better than the anionic polyelectrolyte DF 973, as shown in Figure 3. The latter result is in agreement with the well known efficient use of cationic polyelectrolyte as flocculant aid in water and wastewater treatment. The higher efficiency obtained by using the cationic polyelectrolyte is due to fact that the colloidal particles are electrostatically attached to the sweep flocs formed by the addition of iron (III) and cationic polyelectrolyte in the neutral pH water. Obtained results showed a much better performance of aluminium sulphate in combination with the cationic polyelectrolyte DF 492 for the removal of TSS at ambient pH (Figure 4). This result agree with the widespread use of alum as coagulant chemical in water and wastewater treatments (Ghernaout and Ghernaout, 2012). Furthermore, it is noteworthy that the ambient water pH is in the range of pH values

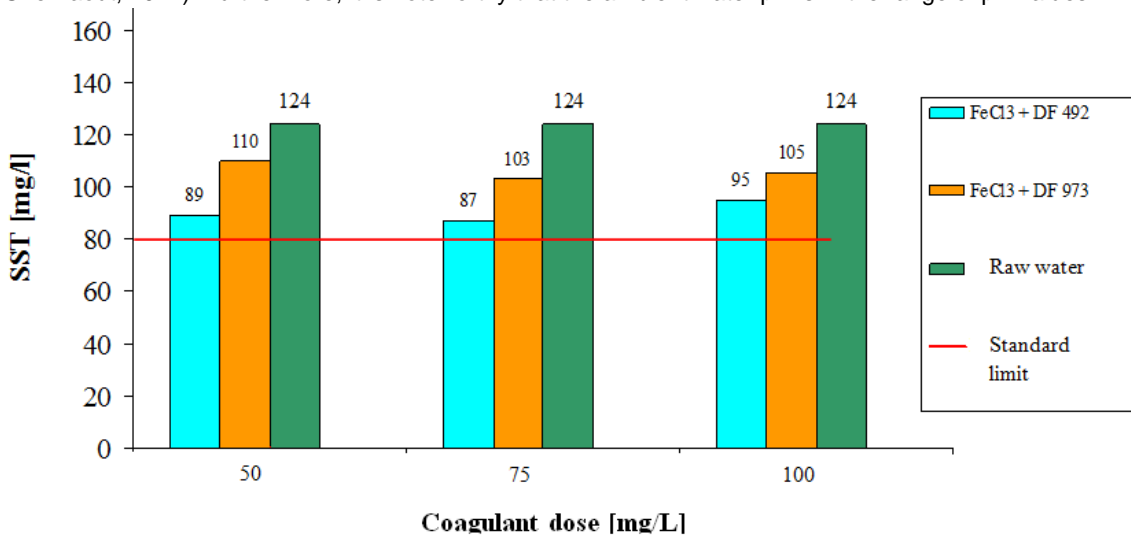


Figure 3: Concentration of SST in raw and treated Produced Water at varying ferric chloride dose, with polyelectrolyte (DF 492 or DF 973) dose of 10 mg/L and pH 9

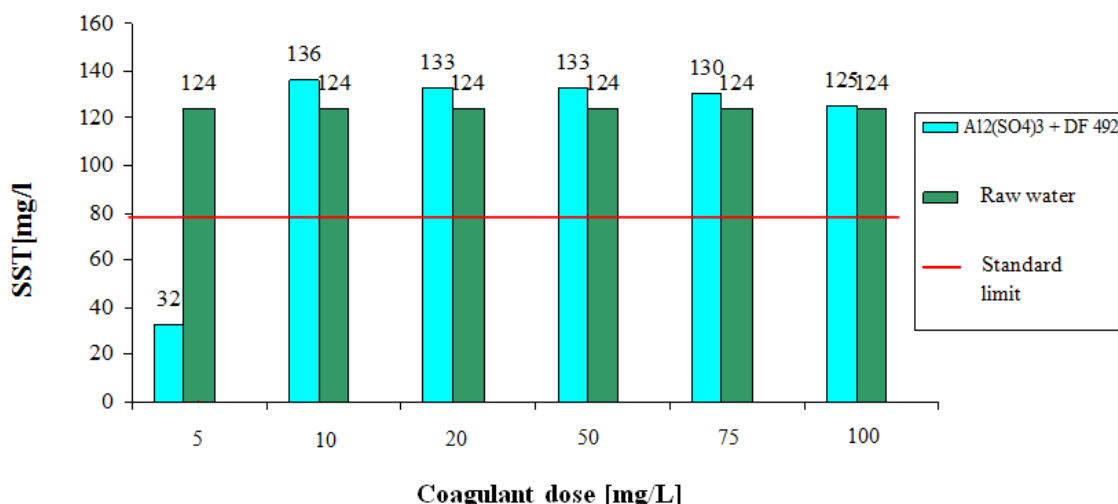


Figure 4: Concentration of SST in raw and treated Produced Water with aluminium sulphate at dose from 5 to 100 mg/L and polyelectrolyte DF 492 (10 mg/L) at pH 6.7

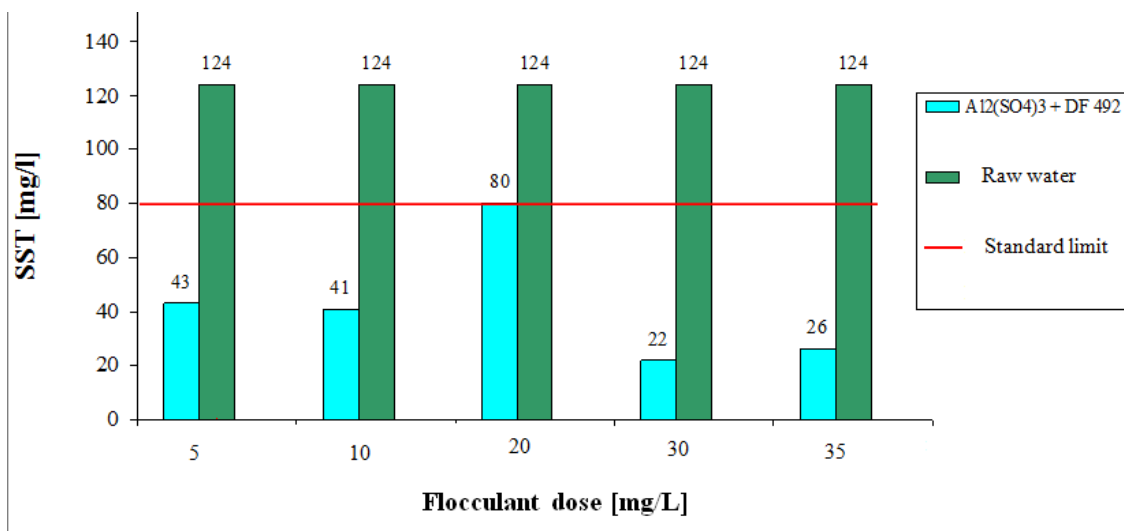


Figure 5: Concentration of SST in raw and treated Produced Water with aluminium sulphate (10 mg/L) and polyelectrolyte DF 492 at dose from 5 to 35 mg/L at pH 6.7

which enhance the formation of $\text{Al}(\text{OH})_3$. The best performance was achieved dosing 5 ppm of $\text{Al}_2(\text{SO}_4)_3$, 30 ppm of DF 492, at ambient pH (Figure 5).

As expected the higher flocculant dose resulted in a larger amount of sludge produced. Figure 6 clearly shows the increase of sludge production with the higher dose of polyelectrolyte. The amount of produced sludge increased by 50 % and 150 % when the dose of polyelectrolyte was increased from 5 to 10 mg/L and from 5 to 20 mg/L, respectively. Furthermore, the use of a polyelectrolyte dose equal or higher than 30 mg/L resulted in a sludge production 4 times higher compared with the dose of 5 mg/L of polyelectrolyte. Therefore, the optimal process condition was found dosing 5 ppm of $\text{Al}_2(\text{SO}_4)_3$, 5 ppm of DF 492, at ambient pH (Figure 5). The optimized conditions will allow to save operating cost.

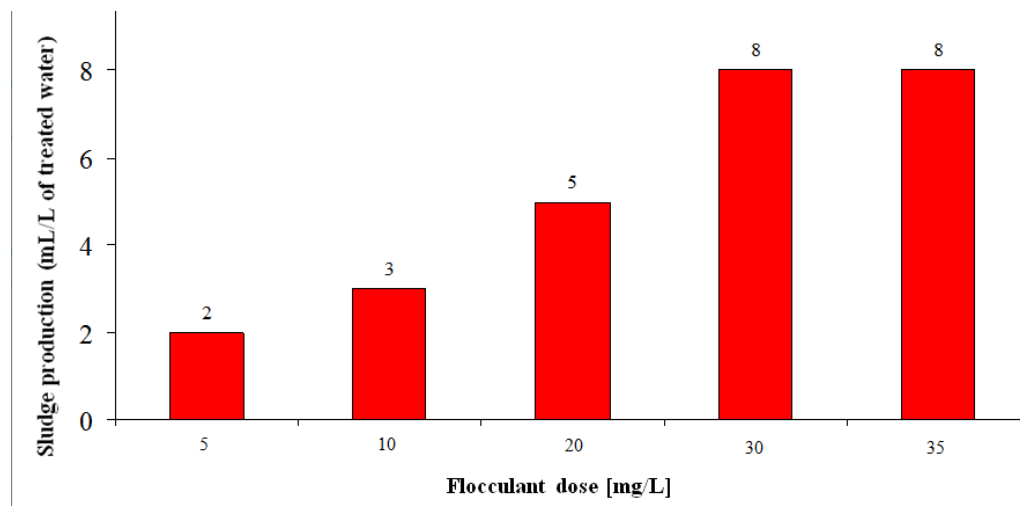


Figure 6: Sludge production at varying dose of polyelectrolyte DF 492, aluminium sulphate dose of 5 mg/L and pH 6.7

4. Conclusions

Neither aluminium sulphate nor ferric chloride used as coagulant for the removal of TSS from Produced Water fulfilled the standard set for TSS by the regulation on the discharge of wastewater in surface water (80 mg/L). The addition of the cationic polyelectrolyte DF 492 improved significantly the TSS removal and the combined use of aluminium sulphate and DF 492 allowed to fulfil the required standard for TSS. The best performance was achieved dosing 5 ppm of $Al_2(SO_4)_3$, 30 ppm of DF 492, at ambient pH, while the optimal process condition was found dosing 5 ppm of $Al_2(SO_4)_3$, 5 ppm of DF 492, at ambient pH. The optimized condition significantly reduced the sludge production and can be used at full scale plant in the chemical-physical treatment units designed to remove the TSS.

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