



## REMOVAL OF SULFIDES AND OIL FROM PRODUCED WATER

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### ABSTRACT

Produced waters are complex mixtures which contain a large number of contaminants including finely dispersed oil, metals, and gases such as H<sub>2</sub>S and CO<sub>2</sub>, that are originated from oil and natural gas. This work examines the use of solvent extraction to recover sulphides. It tested three commercial alkylamines as extractants, which were dissolved in aviation kerosene (JET FUEL). In this research, real samples of produced water from the oil industry with initial concentration of 0.660 mg/L H<sub>2</sub>S were used. The parameters studied were: Amine/JET FUEL ratio (0.25 v/v) and Organic/Aqueous Phase ratio (1/3 v/v). After the tests, it was concluded that the highest extraction efficiency occurred with the amine DUOMEEN<sup>®</sup> O, which removed 76% of sulfides, followed by the ARQUAD<sup>®</sup> 2C-75, yielding 59% in sulfide removal, and the DUOMMEN<sup>®</sup> T, which removed as much as 40% of sulfides.

### KEYWORDS

separation in aqueous medium; solvent extraction; extraction of oil and sulfides

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## 1. INTRODUCTION

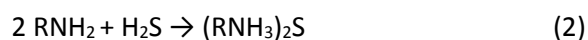
Oil exploration processes are associated with the generation of produced waters. The volume of produced waters from oil fields depends on factors such as geological structure of the generating rock and reservoir fluid production time (Bayati et al., 2011). These wastes are complex mixtures of suspended and dissolved organic and inorganic materials that may contain heavy metals (Moraes et al., 2011). They also contain characteristic elements of the reservoir rock from which the fluids were produced, in addition to chemicals added to prevent tube corrosion (Burns et al., 1999) and alkalization involved in the recovery of injection wells (Zang et al., 2010).

Acid gases such as CO<sub>2</sub> and H<sub>2</sub>S, also present as components in produced water, come from oil and natural gas. In conventional gas-removal processes with natural gas, they are removed in an Acid Gas Removal Unit (AGRU), by means of absorption operations with aqueous solutions of amines (Rufford et al. 2012). In particular, the H<sub>2</sub>S must be removed from oil industry fluids, due to its high toxicity and lethal potential. When mixed with water, it forms an acid that is corrosive to pipelines, flowlines, and other equipment (Rufford et al., 2012). In this context, acid gas concentrations may not be higher than the limits established by environmental law; sulfide concentrations should be lower than 0.3 mg/L in disposed water. Environmental agencies establish an oil concentration of 20 mg/L as the upper limit for disposal of waste from hydrocarbon processing (Burns et al., 1999).

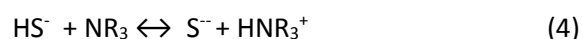
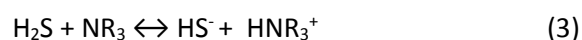
Absorption with alkylamines is one of the most widely used processes for removing acidic components. In this process, acid components react with a liquid alkylamine that works as a solvent when in contact with liquid and gas phases. In a later step, the acidic components are removed in a regenerator, usually at low pressures and high temperatures. Huttenhuis et al. (2006) studied gas solubility in aqueous solutions of alkylamines. The solubility data were assessed and correlated with an Equation of State (EOS), as originally proposed by Fürst and Renon (1993). Park (2008) used natural secondary metabolites as absorbents, obtaining a removal efficiency of 62%. The efficiency increased to 96 % using a complex absorbent mixed with 1.0 % of a chemical amine product.

According to the research of Kohl and Nielsen (1997), primary amines react directly with H<sub>2</sub>S, CO<sub>2</sub>, and COS. Secondary amines also react directly with H<sub>2</sub>S, CO<sub>2</sub>, and COS, the last to a lesser degree. Tertiary amines react directly with H<sub>2</sub>S, indirectly with CO<sub>2</sub>, and to a lesser extent with COS. The most common example is the tertiary amine methyl-diethanolamine (Kohl & Nielsen, 1997), but there are also sterically-hindered amines, characterized by the presence of a bulky substituent group next to the nitrogen atom. According to Kohl & Nielsen (1997), primary and secondary amines monoethanolamine (MEA) and diethanolamine (DEA), respectively, are very reactive and, therefore, exhibit high acid gas removal rates.

Sulfur components in hydrocarbons can be removed with the presence of appropriate catalysts, by forming hydrogen sulfide (Eq. 1). In the second step, H<sub>2</sub>S is removed from the gas stream by a washing solvent (amine), according to Eq. 2, followed by the same conversion to elemental sulfur.



Bara (2012) reported that aqueous amine solutions are the most common chemical solvents used to remove H<sub>2</sub>S. In these operations, acids can be neutralized with solutions of alkaline amines. H<sub>2</sub>S reacts quickly and directly with 1<sup>st</sup>, 2<sup>nd</sup>, or 3<sup>rd</sup> amines to form HS-disulfide and the cation of a protonated amine. It, then, reacts with other disulfide amines to form sulfides and other equivalent protonated amines, according to Eq. 3 and 4.



In this study, a process is proposed whereby contaminants are separated from the waste using a batch solvent extraction process. During this process, the constituents dispersed within the aqueous phase (oil and H<sub>2</sub>S) migrate preferentially to the organic phase, which is a solution of amines

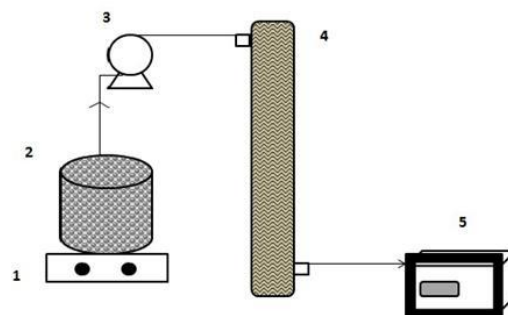
dissolved in aviation kerosene (jet fuel) after solvent action. The unit operation of solvent extraction initially involves the transfer of contaminants from the aqueous to the solvent phase, followed by a separation between organic and aqueous phases (Hadjiev et al., 1995). In addition to minimizing energy expenditure, this study presents an innovative aspect considering that amines, in general, are fairly soluble in water due to their polar character. Furthermore, H<sub>2</sub>S removal processes described in the literature do not generally report the use of amines to remove acid gases that could be soluble in an organic medium. In this respect, this paper presents the results of a preliminary investigation of the simultaneous removal of H<sub>2</sub>S and oil from real samples of produced water, using three commercial amines and varying the amount of this extractant in relation to the jet fuel solvent. This study presents the results of an investigation on the removal efficiency of sulfides and finely dispersed oil contained in real produced water samples. The variable studied was amine concentration (mg/L) in QAV on a volumetric basis (v/v). The results show the influence of this variable on the efficiency of simultaneous extraction of oil and sulfide.

## 2. MATERIALS AND METHODS

The amines investigated exhibited surfactant properties (high molecular weight alkylamines), and were tested as an organic solution of amines in jet fuel (QAV) in the solvent extraction process. The contents of H<sub>2</sub>S and petroleum (mg/L) were evaluated before and after contact between the phases.

### 2.1 Investigated system

The produced water used was obtained from the entrance of a Wastewater Treatment Plant (WTP) owned by Petrobras (Brazil). Thus, it consisted of an



**Figure 1.** General schematic diagram for sulfide and oil removal using a batch system.

actual sample for treatment in an H<sub>2</sub>S batch system, removing the finely dispersed oil. The organic phase was composed of aviation kerosene (JET FUEL) provided by Petrobras. Three different commercial amines (DUOMEEN<sup>®</sup> O, ARQUAD<sup>®</sup> 2C-75, and DUOMMEN<sup>®</sup> T) were obtained from AKZO NOBEL Co. (USA), and were added at different concentrations to the organic phase. The physicochemical properties of the system are presented in Table 1.

### 2.2 Experimental

The batch system is shown in Figure 1. It consists of a magnetic shaker (Tecnal-Brazil) (1) used to homogenize the extractant with the solvent (jet fuel), which was kept in a beaker (2). The organic material is sent through a micropump (Cole-Parmer, Brazil) (3) to a separation funnel (4), where the organic and aqueous phases, contaminated with sulfides and fine oil, are mixed. At the base of the separation funnel, the treated water was analyzed in a DR 2000 spectrophotometer (5), set at 665 nm, to measure sulfide concentration. The total oil and grease (TOG) content was obtained using the infrared absorbance technique with an equipment provided by Wilks Co. (not shown).

**Table 1.** Physicochemical properties of the system.

Products	Density (g/cm <sup>3</sup> )	Viscosity (Pa.s)	pH	Surface tension (x 10 <sup>-3</sup> N/m)
Produced water	1.15	0.001	8.01	72.45
Jet fuel (QAV)	0.76	0.001	6.60	24.95
DUOMEEN <sup>®</sup> O	0.84	0.021	7.00	30.81
ARQUAD <sup>®</sup> 2C-75	0.88	0.120	7.00	14.87
DUOMMEN <sup>®</sup> T	0.85	0.019	8.00	27.41

### 2.3 Sample preparation and experimental procedure

A volume of 2mL of 0.1 M sodium hydroxide (NaOH) solution was added to 5 L of produced water for sulfide stabilization for 48 h. An aliquot of 2mL of this prepared water was submitted to a spectrophotometric analysis to determine the sulfide content. Another aliquot underwent an infrared analysis. The amines were mixed with the jet fuel at predetermined proportions under continuous stirring and, then, sent to the separation funnel. During this step, the contaminated water was also injected in the funnel for interphase contact, which was performed manually.

The contaminants were transferred from the aqueous to the organic phase by agitation in the separation funnel. The sulfide removal occurred due

to a complexation reaction with the amines, forming a neutral complex, while the removal of fine drops of oil was attributed to their solubilization in jet fuel. The contaminant oil is soluble in jet fuel due to chemical affinity, since jet fuel is a byproduct of the original hydrocarbon.

At the exit of the funnel, the treated water should contain neither sulfides nor oil, which should be complexed and solubilized in the organic phase, respectively. Thus, the output samples were sequentially submitted to spectrophotometric analysis in a DR 2000 spectrophotometer. Other analyses such as TOG, pH, density, conductivity, turbidity, and nitrate concentration were performed on aliquots of input and output samples. Table 2 shows the operational conditions for bench essays.

**Table 2.** Operational conditions for bench essays.

AMINES	CONCENTRATION IN JET FUEL (V:V %)	O/A (ORGANIC/AQUEOUS RATIO) (V:V)
DUOMEEN® O	0.01 (level min) – 0.50 (level max)	1/3
ARQUAD® 2C-75	0.01 (level min) – 0.50 (level max)	1/3
DUOMMEN® T	0.01 (level min) – 0.50 (level max)	1/3

**Table 3.** Results of pH, conductivity, turbidity, nitrates, density, and TOG with three commercial amines.

RESULTS OF RAW WATER AND WATER TREATED WITH AMINES						
Parameter	RAW WATER	TREATED WATER				
		AMINE CONCENTRATION (Am/QAV) % v:v				
		0.01	0.05	0.10	0.25	0.50
<b>AMINE 1 - DUOMEEN® O</b>						
pH	8.01	7.71	7.93	8.01	8.16	8.51
Conductivity (mS/cm)	7.52	7.17	7.09	8.27	7.42	7.15
Turbidity (NTU)	73.50	23.01	18.00	15.00	11.00	9.80
Nitrate content (mg/L)	12.10	12.10	11.20	10.40	7.10	10.10
Density (g/mL)	1.15	1.00	1.00	1.00	1.00	0.99
TOG (mg/L)	147.00	14.00	10.00	8.00	5.00	4.00
<b>AMINE 2 - ARQUAD® 2C-75</b>						
pH	8.01	7.69	7.89	7.79	7.78	7.42
Conductivity (mS/cm)	7.52	6.50	6.45	6.50	6.35	6.30
Turbidity (NTU)	73.50	43.40	38.00	36.00	33.46	33.30
Nitrate content (mg/L)	12.10	10.40	11.50	8.00	12.00	11.01
Density (g/mL)	1.15	1.00	0.99	1.00	1.00	1.00
TOG (mg/L)	147.00	46.00	34.00	27.00	22.00	14.00
<b>AMINE 3 - DUOMMEN® T</b>						
pH	8.01	8.27	8.00	8.50	7.34	8.15
Conductivity (mS/cm)	7.52	6.06	7.80	6.17	6.23	5.81
Turbidity (NTU)	73.50	59.80	50.00	45.67	45.00	45.00
Nitrate content (mg/L)	12.10	10.37	11.00	11.46	10.76	9.78
Density (g/mL)	1.15	0.99	0.99	0.99	1.00	1.00
TOG (mg/L)	147.00	31.00	20.00	13.00	9.00	10.00

The removal efficiency for sulfides and oil, as determined in the bench tests, was calculated from DR 2000 spectrophotometer readings and the TOG was obtained by infrared analysis of samples, comparing concentrations at the entrance and exit of the separation funnel, according to Equation 5.

$$Efe = \left( \frac{C_e - C_s}{C_e} \right) * 100 \quad (1)$$

Where *Efe* is the separation efficiency (%); *C<sub>e</sub>* is the contaminant concentration at the entrance; and *C<sub>s</sub>* is the contaminant concentration at the exit of the funnel, respectively.

### 3. RESULTS AND DISCUSSION

The results of TOG, pH, density, conductivity, turbidity, and nitrate concentration of input and output samples are shown in Table 3.

Table 4 presents the results of sulfide removal using all three amines. The results show that the DUOMEEN® O promoted a better removal when dissolved in 0.25 v:v in jet fuel, providing approximately 76% sulfide removal. ARQUAD® 2C-75, at the same ratio (v:v) with jet fuel, showed approximately 59% removal. DUOMMEN® T, in its best assay, showed a lower efficiency (approximately 42%) if compared to the other amines, even when using a ratio of 0.50 v:v in jet fuel. Table 4 also shows the turbidity analysis and the TOG of treated water.

According the data shown in Table 4, samples of treated water using DUOMEEN® O in 0.25 v:v (amine:QAV), showed low TOG and turbidity values, resulting in the removal of considerable amounts of oil and sulfides.

Figure 2 shows the sulfide removal efficiency of three commercial amines in bench assays. DUOMEEN® O and ARQUAD® 2C-75 amines

**Table 4.** Results of sulfide removal, TOG and turbidity in treated water (output) with three commercial amines.

DUOMEEN® O			
Am/QAV(%)	Sulfide Removal (%)	TOG (mg/L)	Turbidity (NTU)
0.01	56.00	14.00	23.01
0.05	63.00	10.00	18.00
0.10	70.15	8.00	15.00
0.25	76.21	5.00	11.00
0.50	73.00	4.00	9.80
ARQUAD® 2C-75			
Am/QAV(%)	Sulfide Removal (%)	TOG (mg/L)	Turbidity (NTU)
<b>0.01</b>	<b>50.05</b>	<b>46.00</b>	<b>43.40</b>
<b>0.05</b>	<b>51.00</b>	<b>34.00</b>	<b>38.00</b>
<b>0.10</b>	<b>57.00</b>	<b>27.00</b>	<b>36.00</b>
<b>0.25</b>	<b>59.50</b>	<b>22.00</b>	<b>33.46</b>
<b>0.50</b>	<b>51.50</b>	<b>14.00</b>	<b>33.3</b>
DUOMMEN® T			
Am/QAV(%)	Sulfide Removal (%)	TOG (mg/L)	Turbidity (NTU)
<b>0.01</b>	<b>38.56</b>	<b>31.00</b>	<b>59.80</b>
<b>0.05</b>	<b>30.58</b>	<b>20.00</b>	<b>50.00</b>
<b>0.10</b>	<b>31.38</b>	<b>13.00</b>	<b>45.67</b>
<b>0.25</b>	<b>40.00</b>	<b>9.00</b>	<b>45.00</b>
<b>0.50</b>	<b>42.00</b>	<b>10.00</b>	<b>45.00</b>

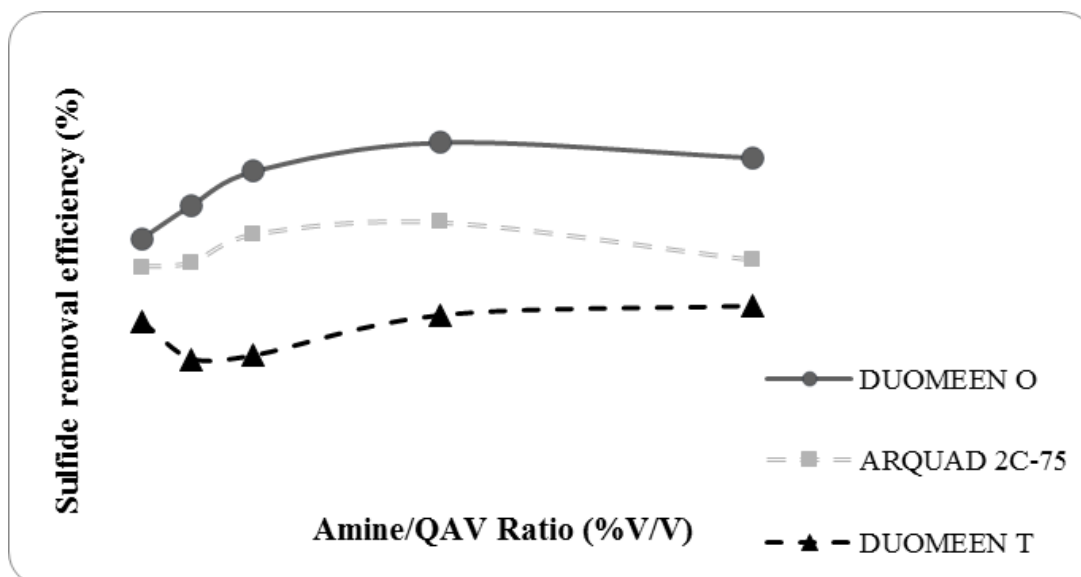


Figure 2. Sulfide removal efficiency.

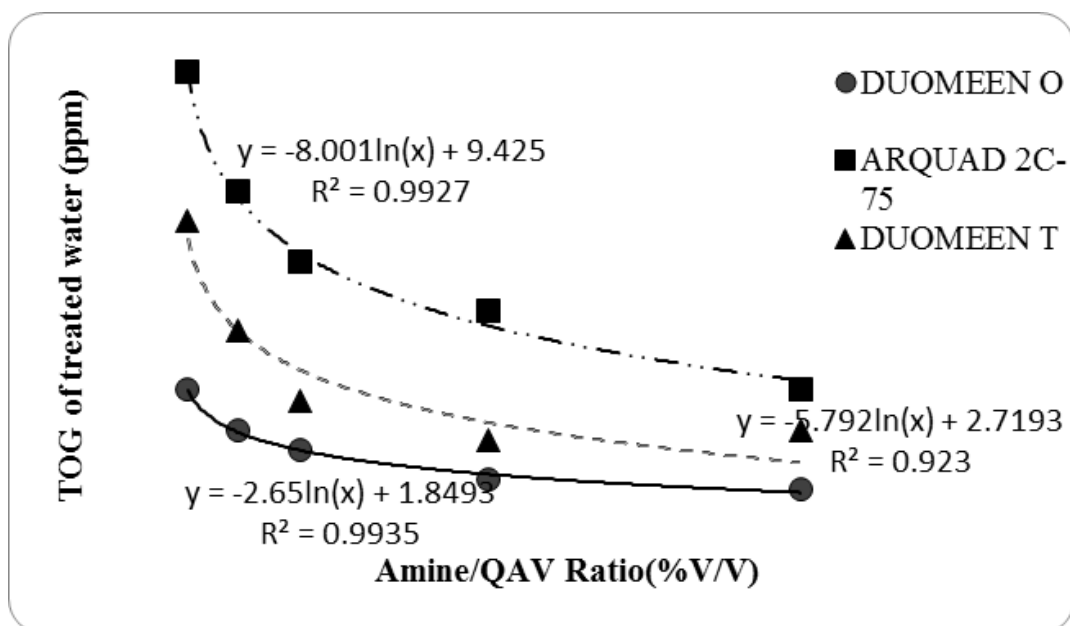


Figure 3. TOG results for treated water at different extractant concentrations.

exhibited the best results with 0.25 v:v (amine/QAV), at a ratio of 1/3 (organic phase/produced water).

Figure 3 presents the TOG results for treated water samples. In terms of final TOG, in 0.25 v:v the values are low (DUOMEEN<sup>®</sup> O and DUOMEEN<sup>®</sup> T), indicating good oil removal within this range. The TOG results were confirmed by the turbidity results (Figure 4).

Figure 4 shows that the higher turbidity values for DUOMEEN<sup>®</sup> T are due to its high solubility in water, which is attributed to the degree of insaturation (which is higher than the one of DUOMEEN<sup>®</sup> O). Although the results could improve the final TOG, the turbidity values increased over the same range, possibly due to the affinity of this amine with water.

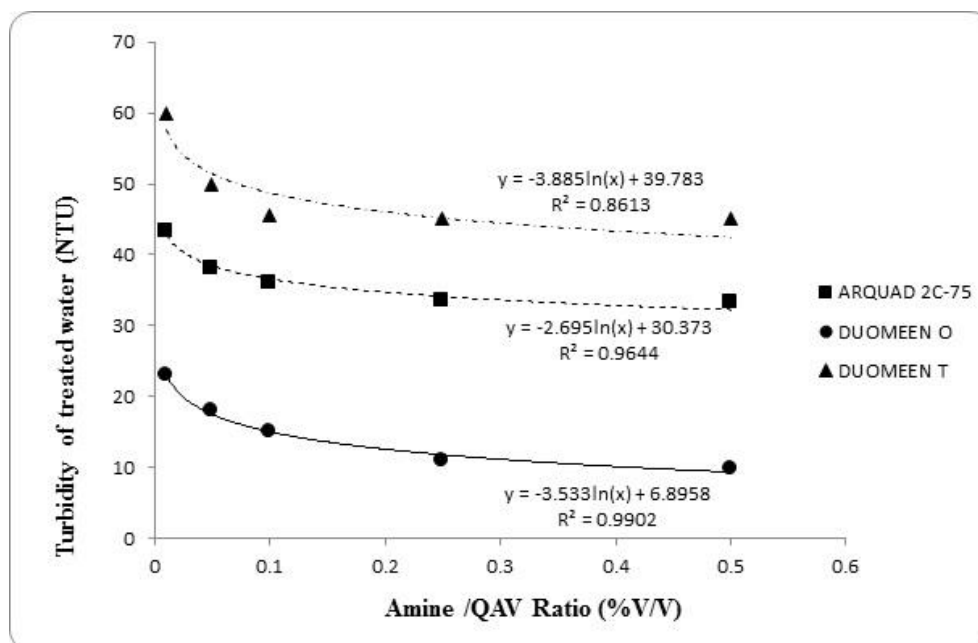


Figure 4. Turbidity results of treated water at different extractant concentrations.

#### 4. CONCLUSIONS

The results showed that the commercial amine DUOMEEN® O was the most efficient in removing sulfides (76 %) at a proportion of 0.25% v:v of amine in jet fuel. ARQUAD®2C-75 showed an efficiency of 59 % at the same ratio, and DUOMMEN® T yielded 42 % for a ratio of 0.50. The final TOG and turbidity results showed that it is possible to remove sulfides and oil simultaneously with DUOMEEN® O at 0.25% v:v. Although the DUOMMEN® T exhibited similar physical properties to DUOMEEN® O, the removal efficiencies were significantly different, given that TOG and turbidity values were higher than expected. It is known that DUOMMEN® T has the largest number of unsaturated bonds, which could lead to partial solubility in water.

The contribution of the paper lies in the fact that these commercial amines, mixed with aviation fuel (AF), simultaneously, can separate sulfides from petroleum samples to a considerable extent, leading to a minimization of corrosion by sulfides, one of the most serious problems in the oil industry. Thus, the study was satisfactory from the environmental and industrial viewpoints, highlighting the use of DUOMEEN® products, which provide better separation efficiency, in addition to reducing sulfide content in wastewaters.

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