INFLUENCE OF MAIN PROCESS VARIABLES ON THE TREATMENT OF WASTEWATERS USING A NEW TECHNOLOGY (MSPI)

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ABSTRACT

The prototype of a device on a semi-industrial scale to treat wastewaters from the oil industry has been widely studied as a viable alternative to conventional equipment. The device, called Mixer-Settler based on Phase Inversion (MSPI), uses the phase inversion method as operating principle. Using experimental planning (2^4 factorial with four repetitions in the central point), it was determined the influence of the main variables on the oil/water separation process for waters containing between 30 and 100 mg of oil per liter of water. The following variables were evaluated: specific throughput, organic/aqueous phase ratio, agitation in the mixing chamber, and coconut oil concentration. The response variable was the oil/water separation efficiency. The results show that the separation efficiency of the device is a function of the effective throughput and the organic/aqueous phase ratio.

KEYWORDS

wastewater; separation process in aqueous medium; MSPI technology; experimental planning

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1. INTRODUCTION

During the exploration and production of oil and gas, significant amounts of wastewaters are generated. This water often contains high levels of oil and grease (over 2000 ppm, TOG), in addition to other contaminants such as heavy metals. In order to dispose of or reuse this effluent it must be adequately treated.

The prototype of a semi-industrial scale device, developed by the team of researchers from the Postgraduate Program in Chemical Engineering at the Federal University of Rio Grande do Norte (UFRN), has been tested as an alternative technology to conventional methods. The device is called Mixer-Settler based on Phase Inversion (MSPI). It employs a solvent-assisted method and organic solvent as extracting agent. An organic solvent/vegetable oil mixture can be used to extract oil and heavy metals simultaneously (Oliveira, 2009; Santana, 2007). The device presented in this study is installed in a wastewater treatment plant (WTP) owned and operated by Petrobras.

Recent studies developed with MSPI at laboratory scale produced excellent oil/water (O/W) separation results, even under different levels of wastewater salinity in producing fields: approximately 73,000 mg NaCl/L for wastewaters from offshore fields, and 1,200 mg NaCl/L from onshore fields (Chiavenato and Paulo, 2000; Paulo and Hadjiev, 2005; Fernandes Jr. et al., 2006; Paulo and Hadjiev, 2006). In laboratory, the O/W separation efficiency obtained was up to 92 % in the treatment of oily water with concentrations between 500 and 1,930 mg/L. Efficiency levels as high as 76 % were obtained for an oil/water concentration between 50 and 150 mg/L. Results obtained by Oliveira (2009) show that oil/water separation and heavy metal extraction (Pb, Cd, Ni) can be performed simultaneously, reaching oil separation efficiencies of up to 84 % and heavy

metal extraction of up to 82.2, 96.6 and 83.4 % for Pb, Cd and Ni, respectively.

The semi-industrial MSPI was designed considering a scale factor of 100 times, with the laboratory model as reference, representing a mean flow rate of 10m³/h. All scale extrapolation calculations considered treatment of oily waters with oil concentrations between 50 and 150 mg/L, using turpentine as organic solvent (Fernandes Jr. et al., 2006).

Data obtained using the semi-industrial MSPI were analyzed by an experimental statistical planning software. Jet-fuel (JF) was used as organic solvent, added with a small amount of natural coconut oil in order to promote the extraction of possible heavy metals present in the water.

The results obtained in this study corroborate those reported in other investigations using MSPI, both at laboratory and semi-industrial scale. The present results show good agreement with those obtained by Fernandes Jr. et al. (2006), who worked with a semi-industrial prototype to treat wastewaters containing high oil concentrations (50 to 150 mg/L).

2. MATERIALS AND METHODS

2.1 System studied

The aqueous phase consisted of water contaminated with petroleum, a wastewater from one of PETROBRAS' WTPs. The organic phase used was composed of a complex mixture of hydrocarbons (jet-fuel, JF) obtained from PETROBRAS. Natural coconut oil, supplied by COCO & CIA (Brazil), was added to the organic phase.

The physicochemical properties of the products involved in this study are shown in Table 1.

Table 1. Physicochemical properties of the system studied.

Products	Density (ρ) 10 ³ kg/m ³	Viscosity (μ) 10 ⁻³ Pa.s	Surface tension (γ) 10 ⁻³ N/m	Interfacial tension (γ) 10 ⁻³ N/m
Wastewater	1.0022	0.851	70.48	–
Jet-Fuel	0.7841	0.910	27.14	32.67
Coconut oil	0.9127	61.38	30.81	–

2.2 Operating principle of the MSPI

Hadjiev and Kuychoukov (1989) described the operation of the mixer-settler based on phase inversion (Fig.1). Primary dispersion, consisting of produced water (aqueous phase) + pure solvent or extractant (organic phase) existing in the mixture chamber (1), is forced to pass by the action of gravity and with velocity U_d through a perforated plate disperser (2) that separates the decanter from the mixer. The originally continuous phase (aqueous phase) becomes the dispersed phase inside the decanter in the form of large drops (6), considered as carrier drops because they contain droplets from the preliminarily dispersed phase (organic phase), which are then considered carried drops. Along trajectory H, the carrier drops moves towards the interface (from time $t = 0$ to $t = 3$) and the carried droplets move and coalesce in the organic bed (3) of the same nature. Droplets not released into the organic bed during the trajectory can still be recovered near the interface (4). The organic phase exits from the top of the decanter (ORG) at velocity U_c , while the aqueous phase is removed from the base (5).

Hadjiev et al. (2004) reported that the mixer-settler based on phase inversion operating under specific high throughput conditions exhibited better performance, if compared to conventional devices. The vertical disposition of the equipment was also a space-saving advantage. **Paulo and Hadjiev (2005)** proposed another significant

advantage over conventional machines, namely, the fact that the MSPI could treat up to twice the amount of aqueous phase as an horizontal device three times its size, maintaining or even increasing separation and extraction efficiency. The MSPI also preserved the overall characteristics of conventional mixers-decanter: powerful operational loads, easy operation and maintenance, and simple operational startups. According to **Oliveira (2009)**, a mixture of organic solvent and natural coconut oil, as extractant, could be used as organic phase to extract oil and heavy metals, simultaneously, from the wastewater. **Oliveira (2009)** also reported that it is possible to prepare an organic phase as a mixture of organic solvent with coconut oil as extracting agent. The operation under this condition allows the separation of both oil and heavy metals from wastewaters.

Figure 2 illustrates a simplified flowsheet of the MSPI Treatment Unit (MSPI-TU), showing all flow lines and equipment used during field tests.

Wastewater is suctioned from the wastewater treatment plant outlet and pumped by P-01 to the mixing chamber of the MSPI at the top of the device. This aqueous phase is the first to be admitted into the equipment, becoming the continuous medium in the mixing chamber.

The MT-01 mechanical agitator is activated and the organic phase (JF + natural coconut oil) is, then, pumped through P-02 of V-01 accumulator vessel to the mixing chamber, so that the two phases – aqueous and organic – can be admitted in concurrent flow.

The mechanical agitation used in the organic/produced water system is performed to transfer crude oil (and other contaminants, if present) from the aqueous to the organic phase. Dispersal of the solvent transported in oil/water overflows and reaches the pure organic bed over the perforated plate. Dispersion passes through the perforated plate, reaching the settling zone, which is totally filled by the organic phase. The population of water drops, denominated carrier drops, is obtained. The system contains the organic solvent, consisting of the continuous phase and carrier water drops as dispersed phase, inside the MSPI-01 settling zone. Thus, phase inversion occurs with respect to the phases admitted into the mixing chamber.

Figure 1. Operating principle of MSPI.
(source: **Paulo & Hadjiev, 2006**).

Figure 2. Simplified flowsheet of the MSPI-TU.

The organic phase transported in oil exits through the top of the MSPI-01 decanting chamber of the MSPI and returns to the V-01 organic accumulator vessel. In this vessel the organic is separated from the accompanying aqueous and pumped back to the mixing chamber, operating in a closed circuit until total saturation.

The separation efficiency of the MSPI ($E\%$) is calculated using Eq. 1:

$$E\% = \left(\frac{C_{in} - C_{out}}{C_{in}} \right) \times 100\% \quad (1)$$

where C_{in} and C_{out} are oil (or metal) concentrations in water located at the inlet and outlet of the MSPI (mg/L), respectively.

The concentrations of oil in the produced water were obtained using the standard method for TOG determination (oil and grease contents) by radiation absorption in the infrared region. The HATR-T2 InfraCal® TOG/TPH (Wilks Enterprise, Inc.)

was used to analyze these levels. It should be pointed out that such a principle was adopted by the PETROBRAS' Research Center (Cenpes) for this type of monitoring. For concentrations of metals in water, the ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) technique, which can be applied to a large number of metals, was used. Samples were analyzed at the ANASOL Laboratory (Analytical Solutions Ltda.).

Samples for analysis were collected at two different points, one of which is at the inlet of the device, where a contaminated water sample is collected. The other collection point is located at the outlet at the base of the separation chamber, where a sample of treated water is obtained. Two samples were collected at each sampling point: one for TOG analysis and one for heavy metal analysis. Contaminated and treated water samples were collected after the operation time of the system (t_0), calculated with Eq. 2. This equation is recommended in the literature (Trambouze et al., 1984) as a practical rule to calculate the operation

time necessary for the device to reach the stationary regime, considering that the outflow is characterized as a plug-in-flow:

$$t_0 = 7 t_r \quad (2)$$

The retention time (t_r) is defined as:

$$t_r = V_c / Q_t \quad (3)$$

where V_c is the useful volume of the MSPI (3.8 m³), and Q_t is the total effective throughput (m³/h), corresponding to aqueous phase flow + organic phase flow.

2.3 MSPI Hydrodynamics

MSPI hydrodynamics is highly complex. There is a two-phase flow where one of the phases is in the form of drops. Authors like **Hadjiev and Kuychoukov (1989)**, **Hadjiev and Aurelle (1995)**, **Paulo and Hadjiev (2006)**, and **Fernandes Jr et al. (2006)** observed that, in addition to the stationary operating regime, the following factors related to each device component must be considered.

2.3.1 Mixing chamber reactor

Co-current flow is characterized by organic and aqueous phases flowing through the reactor in the same direction. It is considered that the flow regime for the system studied in laboratory and the field is turbulent. Eq. 4 shows the calculation for obtaining the regime in an agitation chamber:

$$Re_{agit} = \frac{N d_{imp}^2 \rho_c}{\mu_c} \quad (4)$$

where Re_{agit} is the Reynolds' number for the agitator, N is the rotational speed of the agitator (RPS), d_{imp} is the diameter of the impeller (m), ρ_c is the density of the continuous phase (kg/m³), and μ_c is the viscosity of the continuous phase (Pa.s).

In the regime condition under study there is no slip between the phases, that is, the displacement velocities of the organic and aqueous phases are considered equal and no segregation occurs between phases. Sufficient energy is applied to the system, through the agitator, to enable total dispersion of the organic phase in the aqueous phase to occur (perfect mixture). Thus, the global course that flows out of the reactor to the mixture chamber consists of a dispersion O/W. The

physicochemical properties of the global flow consider the properties of the aqueous and organic elements that it contains. Flow velocity at the outlet of the reactor is the ratio between the total flow of liquids that enter the reactor (aqueous phase + organic phase) and the total flow area in the reactor.

The relationship between the forces of inertia and rigidity in the mixing chamber, represented primarily by interfacial stress, is expressed by Eq. 5.

$$We_T = \frac{\rho_c N^2 d_{imp}^3}{\sigma} \quad (5)$$

where We_T is the Weber number for the turbine and σ interfacial tension (N/m).

2.3.2 Perforated plate

In this part of the device the continuous phase is the pure organic extractant used to fill the decantation column, the perforated plate, and part of the mixing chamber above the plate. The dispersion O/W that passes through the perforated plate that separates the mixing chamber of the decantation chamber is calibrated in the form of carrier drops containing inside of them the organic phase like carried droplets. The organic phase is re-circulated to the system until it reaches saturation in oil. This fact causes gradual changes in physicochemical properties of the fluids. It is noted that the aqueous phase (carrier drop) flows in descending sense, while the organic phase exits the decanter chamber in the top of the device. Flow velocity is proportional to the descending global flow and the total area of the holes of the perforated plate.

Global flow velocity through the holes of the distributor allows the establishment of two hydrodynamic regimes: the drop by drop or jet break-up formation regime. The two mechanisms depend on the physicochemical properties of the system, such as density difference between the phases, dispersion phase density, viscosity of the continuous phase, and interfacial tension.

Kumar and Hartland (1982) estimated the mean diameter of the drops produced in the perforated plate. The mean Sauter diameter, D_{32} , is given by Eq. 6:

$$\frac{D_{32}}{d_h} = 1.59(We)^{-0.07} E\ddot{o}^{-0.028} \quad (6)$$

where $E\ddot{o}$ is the number of Eötvös, We is the Weber number, and d_h is the diameter of the hole in the distributor (m).

The equation is valid for $0 < We < 2.0$. The Weber number (We) for the flow of the fluid into a hole is calculated by Eq. 7:

$$We = \frac{U_N^2 \Delta \rho d_h}{\sigma} \quad (7)$$

where $\Delta \rho$ is the density difference between phases (kg/m^3).

The velocity of the drop in a distributor hole (U_N) is determined by Eq. 8:

$$U_N = \left[\frac{4Q_t}{N_h \pi d_h^2} \right]^{1/2} \quad (8)$$

where Q_t is the total effective throughput into the holes (m^3/s) and N_h is the total number of distributor holes. The number of Eötvös is calculated by Eq. 9, according to **De Chazal, (1971)**.

$$E\ddot{o} = \frac{\Delta \rho g d_h^2}{\sigma} \quad (9)$$

where g is the gravitational constant (m/s^2).

2.3.3 Decantation chamber

Several authors have observed that this chamber acts like a spray column in terms of hydrodynamic behavior. The hydrodynamic behavior of a spray column is normally related to three characteristic velocities of the system:

- U_d , displacement velocity of the carrier drops (dispersed phase);
- U_r , resulting velocity of the drop displacement in relation to the continuous phase;
- U_c , displacement velocity of the continuous phase (organic bed).

The continuous phase into the decantation chamber is the pure organic extractant used to fill it and the dispersed phase consists of the aqueous

drops formed in the perforated plate (carrier drops), which contains organic phase droplets (carried droplets). Calculation of the resulting velocity of carrier drops displacement towards the base of the decantation chamber is given by Eq. 10.

$$U_r = U_d - U_c \quad (10)$$

Carrier drop displacement velocity (U_d) is determined by Eq. 11, which is a simplified Stokes' equation.

$$U_d = \frac{(\Delta \rho g d^2)}{18 \mu_c} \quad (11)$$

where d is the drop diameter of the dispersed phase (m) and μ_c is the dynamic viscosity of the dispersed phase (Pa.s).

Ascending velocity of the organic phase (U_c) is given by Eq. 12, which considers the displacement of this phase without the presence of aqueous drops moving within it.

$$U_c = \frac{Q_o}{A} \quad (12)$$

where Q_o is the organic phase flow to the device (m^3/s) and A is the cross-sectional area of the decantation chamber (m^2).

2.4 Experimental Statistical Planning

The Statistica Experimental Design® 7.0's (StartSoft, Inc.) software was used to study the statistical modeling of MSPI separation. The program plans experiments so that appropriate data are collected at cost-efficient time frame. Analysis of these data using statistical techniques can provide reliable results (**Werkema and Aguiar, 1996**).

Response surface was the statistical methodology chosen. This optimization technique is based on the use of factorial planning (**Myers and Montgomery, 1995**). The model allows the evaluation of the relationships between each variable and the result, as well as it predicts the findings and behavior under given experimental conditions.

This study used 2^4 factorial-planning with four repetitions at the central point. The following four independent variables that influence separation

Table 2. Real and coded values for the independent variables.

Coded Value	Real Values for Independent Variables			
	Dispersed Phase Retention (O/O+W)	Effective Throughput (m ³ /h)	Agitation Velocity (rpm)	Concentration of Coconut Oil (v/v)
	X_{ret}	X_{thr}	X_{agit}	X_{conc}
-1	0.11	6.5	90.0	0.00
0	0.21	8.8	100.0	0.10
1	0.31	11.1	110.0	0.20

efficiency of the MSPI were analyzed: effective throughput, dispersed phase retention, concentration of coconut oil dissolved in the organic solvent, and agitation velocity in the mixing chamber. The chamber height was maintained constant at 2m and the oil feed rate ranged from 40 to 100 mg/L.

All previous work with the MSPI defined hold-up or retention of the dispersed phase considering the volumes involved in the mixer of the device. Furthermore, it is considered that the operation performed in this mixer involves a perfect mixture.

The real and coded values are shown in Table 2.

Mathematical modeling based on physicochemical phenomena involved in the MSPI operation is very complex, since they involve a two-phase flow in which one of the phases is dispersed into the other in the form of drops. So, an empirical approach based on Statistica Experimental Design[®] 7.0 software was considered to explain experimental results in this study.

Ostra et al. (2007), Karatapanis et al. (2011), Lefèvre et al. (2011), and Meski et al. (2011) have used the software Statistica Experimental Design[®] 7.0 (StartSoft, Inc.) for statistical-experiment planning, which constitutes an important tool to compare experimental technological data with empirical models generated by the software.

3. RESULTS AND DISCUSSION

To obtain improved reliability, all the experiments with the MSPI were conducted in duplicate, for both TOG and heavy metal analysis. The separation efficiency test results are shown in

Table 3, which do not present heavy metal concentration values at the inlet and outlet of the MSPI, as well as their respective extraction efficiencies. This is due to the non-detection of heavy metals during the test period. The non-observance of metals may have been caused by alternating seasonal periods of heavy metals in the wastewater. In certain periods these waters may show concentrations within the detection limits of the equipment analyzed and even higher than those established by the legislation, as reported by Oliveira (2009) in his study.

It is known that pH has an influence on the extraction/complexation of heavy metals. Since no metals were detected in the water during the studied period, pH analysis was not necessary.

The results show that test 12 had the highest separation efficiency (68.89 %), whereas test 3 was the least efficient, with 24.87 %. A comparison of results shows that the total effective throughput and the dispersed phase retention are determinant variables for increased O/W separation efficiency. It was also observed that better efficiency results are associated with higher agitation speeds.

3.1 Model Equation

The data recorded with the experiments were fed to Statistica Experimental Design[®] program in order to obtain an empirical model capable of predicting the separation efficiency of the device, within the studied range (-1 to 1, in coded values), for the four variables evaluated (Eq. 13). The regression coefficient (R^2), obtained between the observed values and those predicted by the second order statistical model was 0.98463. Thus, Eq. 13, which was adjusted by the program, is statistically significant and useful for predictive purposes (Box et al., 1978).

$$\begin{aligned}
 E = & 51,39158 + 2,11163X_{\text{ret}} + 2,41959X_{\text{thr}} - 0,42823X_{\text{agit}} + 5,23962X_{\text{conc}} - 1,72269X_{\text{ret}}X_{\text{thr}} + \\
 & 0,80260X_{\text{ret}}X_{\text{agit}} + 2,79514X_{\text{ret}}X_{\text{conc}} + 0,09658X_{\text{thr}}X_{\text{agit}} - 5,78157X_{\text{thr}}X_{\text{conc}} + 0,06112X_{\text{agit}}X_{\text{conc}} - \\
 & 1,42655X_{\text{ret}}X_{\text{thr}}X_{\text{agit}} + 3,29844X_{\text{ret}}X_{\text{thr}}X_{\text{conc}} + 0,21114X_{\text{ret}}X_{\text{agit}}X_{\text{conc}} - 4,86380X_{\text{thr}}X_{\text{agit}}X_{\text{conc}}
 \end{aligned} \quad (13)$$

Table 3. Test results obtained for 2^4 factorial-planning with the MSPI-TU.

Test Number	Dispersed Phase Retention (O/O+W)	Effective Throughput (m ³ /h)	Agitation Velocity (rpm)	Concentration of Coconut Oil (v/v)	Average oil and Grease Contents (TOG)		Separation efficiency O/W (%)
					Inlet (ppm)	Outlet (ppm)	
1	0.11	6.5	90.0	0.0	45.0	26.0	42.22
2	0.11	6.5	90.0	0.2	73.0	34.0	53.42
3	0.11	6.5	110.0	0.0	63.0	47.0	24.87
4	0.11	6.5	110.0	0.2	56.0	23.0	59.76
5	0.11	11.1	90.0	0.0	62.0	29.0	53.48
6	0.11	11.1	90.0	0.2	88.0	42.0	52.65
7	0.11	11.1	110.0	0.0	70.0	23.0	66.51
8	0.11	11.1	110.0	0.2	76.0	45.0	40.79
9	0.31	6.5	90.0	0.0	84.0	47.0	44.44
10	0.31	6.5	90.0	0.2	59.0	25.0	57.63
11	0.31	6.5	110.0	0.0	43.0	26.0	40.00
12	0.31	6.5	110.0	0.2	60.0	19.0	68.89
13	0.31	11.1	90.0	0.0	52.0	28.0	46.15
14	0.31	11.1	90.0	0.2	63.0	23.0	64.02
15	0.31	11.1	110.0	0.0	50.0	24.0	51.01
16	0.31	11.1	110.0	0.2	53.0	24.0	55.35
17	0.21	8.8	100.0	0.1	93.0	45.0	51.44
18	0.21	8.8	100.0	0.1	87.0	40.0	53.64
19	0.21	8.8	100.0	0.1	66.0	33.0	50.25
20	0.21	8.8	100.0	0.1	64.0	31.0	51.31

Figure 3. Predictive versus observed values for separation efficiency of MSPI.

Figure 3 depicts the relationship between predicted and observed (experimental) values for separation efficiency of the MSPI. Good correlation

can be observed between the related values, a hypothesis confirmed by the value obtained for the regression coefficient.

3.2 Response surface analysis

Analyses of contour plots generated by the Statistica Experimental Design[®] program, with the O/W separation efficiency of the MSPI as response variable, are presented below.

Figure 4 shows a separation efficiency contour plot for a coconut oil concentration of 0.0 %, with fixed agitation speed of 110.0 rpm. Under this specific condition, heavy metal extraction is not performed. The O/W efficiency increased, with the rise in throughput for the entire dispersed phase retention range studied. The best efficiency (66.51 %) was obtained with the highest effective

Figure 4. Contour plot for MSPI-TU separation efficiency: dispersed phase retention versus effective throughput (Agitation = 110.0 rpm; Extractant concentration: 0.0 %).

throughput ($11.1 \text{ m}^3/\text{h}$) and the lowest dispersed phase retention (0.11). Elevated effective throughput associated with reduced dispersed phase retention enabled a larger amount of produced water to pass through the perforated plate. This was close to a jet regime outflow, generating smaller and more uniform carrier drops, facilitating the exit of the carried droplets inside of them. This condition is quite promising for the industry, since it involves high volumes of wastewater using a low throughput of circulating organic phase.

Figure 5 shows the contour plot for separation efficiency applied to a coconut oil concentration of 0.1 % v/v; with fixed agitation speed of 110.0 rpm (the addition of coconut oil allows simultaneous separation of crude oil and extraction of heavy metals, if present). As observed earlier, an increase in throughput influences separation efficiency, even with the addition of coconut oil. It was found that in relatively low flow rates, for example $6.5 \text{ m}^3/\text{h}$, the separation efficiency increases when the dispersed phase retention values rise, reaching the highest efficiency rate at 53.64 %. It is estimated that higher dispersed phase retention generates carrier drops with more carried droplets, allowing increased interdrop coalescence, thereby facilitating their separation from carrier drops to the organic bed. This increase in separation efficiency is minimized when higher flow rates are used ($11.1 \text{ m}^3/\text{h}$). In this case, the efficiency tends to remain more or less constant over the entire retention range studied (0.11 to 0.31). It should also be pointed out that the presence of coconut

Figure 5. Contour plot for MSPI-TU separation efficiency: dispersed phase retention versus effective throughput (Agitation = 110.0 rpm; Extractant concentration = 0.10 % v/v).

Figure 6. Contour plot for MSPI-TU separation efficiency: dispersed phase retention versus effective throughput (Agitation = 110.0 rpm; Extractant concentration = 0.2 % v/v).

oil extractant, diluted in jet fuel solvent, alters the hydrodynamics of the system, making it less stable and hindering control of the interface level. This effect is particularly observed when relatively high throughputs, such as $11.1 \text{ m}^3/\text{h}$, are used.

Figure 6 shows the contour plot for separation efficiency applied to a coconut oil concentration of 0.2 % v/v, with fixed agitation speed of 110.0 rpm. The highest separation efficiency found in this investigation was 68.69 %. The increase in coconut oil concentration (0.2 %) in the organic phase, conversely, causes the plot area in which the highest separation efficiency occurs to decrease, and restricts conditions of lower flow rates. These results lead the conclusion that, although it is possible to simultaneously remove metals and oil

from wastewaters, the operation is limited with respect to processing large throughputs. Depending on the situation, pretreatment to separate oil, followed by final polishing for heavy metal extraction may be more feasible. This observation becomes even more relevant when the presence of heavy metals in produced water is not always found at levels beyond those permitted by law. In Figure 6, it can be observed that the separation efficiency increases with increasing dispersed phase retention values.

4. CONCLUSIONS

Operating MSPI without the addition of coconut oil is a suitable technique indicated for the separation of oil and water only. The increase in effective throughput, at all retention values of the dispersed phase retention studied, results in an increase in separation efficiency, where the best result was obtained for the lowest retention level (0.11). It was concluded that it is possible to operate at low dispersed phase retentions with high effective throughputs. This operational condition is of interest to the industry because it represents an economy of solvent volume and the possibility of treating a greater volume of water for the same operation time, resulting in better device performance.

In the case of simultaneous treatment of wastewater, O/W separation and heavy metal extraction, the addition of coconut oil is an important variable for O/W separation efficiency. The addition of this extractant to jet-fuel may alter the physicochemical properties of the system. The high viscosity of coconut oil (Table 1) suggests that the presence of this extractant, until that in small concentrations, may modify organic phase viscosity, influencing MSPI hydrodynamics. Thus, with pure solvent a higher specific flow rate can be used, which is not possible in the presence of the extractant.

Considering this variable, the region of highest efficiency moves to the range of high retention in the dispersed phase and low flow rates. The best equipment performance, represented by a separation efficiency of 68.89 %, was obtained with the addition of a higher ratio of coconut oil to the organic solvent (0.2 % v/v). For the system studied, this separation efficiency meets water quality

standards established by environmental agencies (< 20 mg/L).

MSPI is a promising technology for treating wastewater in the oil industry under conditions of contaminated water with low oil concentrations (< 100 mg/L) and traces of heavy metals. The results obtained with experimental planning will be compared to those of dimensional analysis, in which dimensional groups are based on the physicochemical properties of the liquid phases involved.

5. REFERENCES

- Box, G. E. P.; Hunter, W. G.; Hunter, J. S.. **Statistic for experiments: an introduction to design, data analysis and model building**. USA, John Wiley & Sons, 1978.
- Chiavenato, M. C.; Paulo, J. B. A.. Nova tecnologia para tratamento de efluentes líquidos: MDIF. **Revista Brasileira de Engenharia Química**, São Paulo-SP, v. 19, n. Abril-Junho, p. 15-18, 2000. (in Portuguese).
- Fernandes Jr, W. E.; Paulo, J. B. A.; Moraes, N. A.; Lima, A. F.; Lacerda, G. M.. Tratamento de águas produzidas por meio de nova tecnologia (MDIF): aplicação para águas contendo baixas concentrações em óleo. **Boletim Técnico Petrobras**, v.49, n.1/3, p. 73-87, dezembro de 2006. (in Portuguese).
- Hadjiev, D.; Kuychoukov, G.. A separator for liquid-liquid dispersions. **The Chemical Engineering Journal**, n. 41, p. 113-116, 1989.
- Hadjiev D.; Aurelle, Y.. Phase inversion: a method for separation of fine liquid-liquid dispersions. **The Chemical Engineering Journal**, n. 58, p. 45-51, 1995.
- Hadjiev D.; Limousy L.; Sabiri N.E.. The design of separators based on phase inversion at low velocities in the nozzles. **Separation and Purification Technology**, n. 38, p. 181-189, 2004. [doi:10.1016/j.seppur.2003.11.006](https://doi.org/10.1016/j.seppur.2003.11.006)

Karatapanis, A. E.; Fiamegos, Y. C.; Sakkas, V. A.; Stalikas, C. D.. Effect of chromatographic parameters and detector settings on the response of HILIC–evaporative light-scattering detection system using experimental design approach and multicriteria optimization methodology. **Talanta**, n. 83, p. 1126–1133, 2011.

[doi:10.1016/j.talanta.2010.06.050](https://doi.org/10.1016/j.talanta.2010.06.050)

Lefèvre, S.; Ferrasse, J. H.; Boutin, O.; Sergent, M.; Faucherand, R.; Viand, A. Process optimisation using the combination of simulation and experimental design approach: Application to wet air oxidation. **Chemical Engineering Research and Design**, 2011.

Meski, S.; Ziani, S.; Khireddine, H.; Boudboub, S.; Zaidi, S.. Factorial design analysis for sorption of zinc on hydroxyapatite. **Journal of Hazardous Materials**, n. 186, p. 1007–1017, 2011. [doi:10.1016/j.jhazmat.2010.11.087](https://doi.org/10.1016/j.jhazmat.2010.11.087)

Myers, R. H.; Montgomery, D. C.. **Response surface methodology: process and product optimization using designed experiments**. USA, John Wiley & Sons, 1995.

Oliveira, A. K. C.. **Extração simultânea de petróleo e de metais pesados em águas produzidas usando o sistema MDIF com uma mistura de QAV e óleo de coco como extratante**. Natal-RN, 2009. 146 p. Dissertação de Mestrado - Programa de Pós-graduação em Engenharia Química, Universidade Federal do Rio Grande do Norte. (in Portuguese).

Paulo, J. B. A.; Hadjiev, D.. Extraction separation in mixer–settlers based on phase inversion. **Separation and Purification Technology**, n. 43, p. 257–262, 2005.

Paulo, J. B. A.; Hadjiev, D.. Mixer-Settler Based on Phase Inversion: Design of the Mixing Zone. **Industrial & Engineering Chemistry Research**, n. 45, p. 3821–3829, 2006. [doi:10.1021/ie050133z](https://doi.org/10.1021/ie050133z)

Ostra, M.; Ubide, C.; Zuriarrain, J.. Interference modelling, experimental design and pre-concentration steps in validation of the Fenton's reagent for pesticides determination. **Analytica Chimica Acta**, n. 584, p. 228–235, 2007. [doi:10.1016/j.aca.2006.11.028](https://doi.org/10.1016/j.aca.2006.11.028)

Santana, D. C.; Paulo, J. B. A.; Lima, R. F. S.; Brandão, P. R. G.; Fernandes Júnior, W. E.. Extração de metais pesados a partir de águas produzidas na indústria do petróleo utilizando derivados de óleo vegetal como extratante. **Boletim Técnico da Produção de Petróleo**, v. 2, p. 247–258, 2007. (in Portuguese).

Trambouze, P.; Van Landeghem, H.; Wanquier, J. P.. **Les réacteurs chimiques: conception, calcul, mise en oeuvre**. Paris: Technip, Publications de l'Institut Française Du Pétrole, p. 681, 1984 (in French).

Werkema, M. C. C.; Aguiar, S.. **Otimização estatística de processos: como determinar a condição de operação de um processo que leva ao alcance de uma meta de melhoria**, Minas Gerais/Brasil, Fundação Cristiano Ottoni, 1996, Série Ferramentas da Qualidade, v. 9. (in Portuguese).