# A clean technology to treat wastewaters produced in the oil industry: operation with static mixer

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This work presents a new device conceived on a laboratory scale, for treating wastewater in the petroleum industry. Up-stream water must be treated according to the specifications of the environmental legislation in force, which, in Brazil, establishes maximum total oil and grease (TOG) of 20 mg/L. The functioning principle of the equipment is based on the combination of liquid-liquid extraction and the innovative phase inversion method<sup>®</sup>. The paper presents a comparison between the utilisation of mechanical agitation and static mixer to improve the mass transfer of oil from aqueous to solvent phase. Two kinds of elements are used into the static mixer in view of evaluating the performance of them on the global separation efficiency. Results show the "honeycomb" static element is advantageous when compared with the plate one and mechanical agitation. By keeping all operational variables constants an increase of 30 per cent on efficiency of extraction was obtained by using the "honeycomb" element instead of the plate one.

### 1. Introduction

The new device, denominated MDIF® (Phase Inversion Mixer-Settler), uses liquidliquid extraction (without chemical reaction) to treat part of the water flowing into the Effluent Treatment Plant (ETP) belonging to the Petrobras oil company, where the process currently being used has proven to be costly. The operation transfers the oil dispersed in the produced water to an organic solvent by means of a static mixer. After the transfer we proceed with phase separation of the treated water/solvent impregnated with oil. This separation is done using a sufficiently compact vertical settler. The operational principle of the phase inversion mixer-settler is shown in Fig.1 by Paulo et al (1994), Hadjiev and Aurelle (1995). According to this figure, the first O/W dispersion generated by static mixer in the mixing chamber (1) causes the transfer of oil from the aqueous phase to the organic phase. This dispersion is forced through a perforated plate disperser (2) that separates the settler from the mixing chamber. The originally continuous phase becomes a dispersed phase inside the decanter in the form of carrier drops (6), which contain droplets from the preliminarily disperse phase. During the trajectory of the carrier drops towards the interface (4), the transported droplets, consisting of solvent + oil, move upwards and coalesce in the organic bed. The drops not released by the organic band during the trajectory can still be recovered near the interface (4). The organic phase impregnated with oil exits the top of the decanter (ORG), while the aqueous phase, represented by the treated water, is removed from the base of the decanter (5). Using this method, we intend to increase the coalescence rate by decreasing the distance between the dispersed drops and the interface, since each carrier drop acts as a microdecanter, Chiavenato (1999), Fernandes Jr. (2002).



Figure 1 - Principle of operation of the MDIF®. Source: Paulo et al. (1994).

The efficiency of oil/water separation can be calculated according to Eq. 1.

$$E = \frac{Ce - Cs}{Ce} \tag{1}$$

In this equation, Ce is the oil/water inlet concentration and Cs is the oil/treated water outlet concentration, both concentrations are expressed in mg/L. The present work deals of the mixing conditions into the mixing chamber (1). We perform a comparison

between mechanical agitation and two types of static mixers in view of improving the mass transfer of oil from aqueous to solvent phase.

A static mixer consists of a series of specially designed stationary elements placed transversely in a tube. These elements form crossed channels that promote division and longitudinal recombination of the liquid flowing through the static mixer. For a two-phase system, the two fluids are emulsified. The only power required for static mixers is the external pumping power that propels the fluids through the mixer, in contrast to the motor used in mechanical agitation. The advantages of static mixers include low maintenance costs, possibility of operating in continuous processing, compact installation, very low residence time (near 1 s) and low shear forces, relative to the turbine impeller, Strief (1977), Pahl and Muschelknautz (1982).

## 2. Materials and methods

The aqueous phase involves water contaminated with petroleum termed "formation water or produced water" originating at the ETP inlet. These wastewaters present a content of oil from 30 to 150 mg/L. The organic phase used is a complex mixture of hydrocarbons called aviation kerosene obtained from Petrobras. The physical-chemical properties of both phases are shown in Table 1.

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Product	Density (p)	Viscosity (µ)	Surface tension $(\gamma)$	Interfacial tension $(\gamma)$
	10 <sup>3</sup> kg/m3	10 <sup>-3</sup> Pa.s	10 <sup>-3</sup> N/m	10 <sup>-3</sup> N/m
Formation water	1.0022	0.851	70.48	
Aviation kerosene	0.7841	0.910	27.14	32.67
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Table 1 - Physical properties of the phases studied.

Source: Fernandes Junior (2006).

The concentrations used in Eq. 1 are obtained using the standard infrared absorbance method for determining oil and grease content (TOG). The device used for these measurements was the InfraCal® TOG/TPH Model HATR-T2 (Wilks Enterprise, Inc.). It should be emphasized that this method has been adopted by the national petroleum industry. In view of performing the mass transfer into the mixing chamber we used two designs of static mixers. Table 2 shows the characteristics of them.

Table 2 - Characteristics of static mixers.						
Type of	Number of	Lenght of	Lenght to	Void fraction		
mixing	mixing	static mixer	diameter ratio			
elements	elements	(mm)				
Honeycomb	4	318	16.6:1	0.26		
Plate	5	318	16.6:1	0.19		

Reynolds number for both of them were calculated according to Belyaeva et al. (2004) as  $\text{Re}_{\text{SM}}=\rho_c U_o d_h/\mu_c$  where  $\rho_c$  is the continuous phase density,  $U_o$  is the linear fluid velocity,  $d_h$  is the static mixer hidraulic diameter and  $\mu_c$  corresponds to the continuous phase viscosity. The maximum Reynolds number attained was 1863 for both kind of

mixing elements. This Reynolds characterizes a laminar flow. In the case of mechanical agitation we used a Rushton turbine with diameter of 0.03 m and six blades distributed orthogonally at the end of a disc. Reynolds number was evaluated by means of  $\text{Re}_{\text{AGIT}}$  =  $\text{Nd}^2\rho_c/\mu_c$  where N is the rotational velocity of the turbine and d is its external diameter. Reynolds number was always greater than  $10^{+4}$  for all operational conditions evaluated. So, we work in a turbulent flow when using mechanical agitation.

#### 3. Results and discussion

We show the results of experimental tests carried out with the MDIF® unit in terms of two important operational variables: total volume flow rate and fraction of dispersed phase. Both variables are relevant on treating waste water in the petroleum industry. Fig. 2 shows the total efficiency of separation of oil from wastewater as function of total volume flow rate entering the mixing chamber. Eq.1 was used to calculate E, efficiency of separation, by using the TOG method to evaluate the concentrations of oil into the inlet and outlet aqueous phases.



Figure 2 - Total efficiency of separation as function of total volume flow rate.

We realize a decrease on efficiency of separation when using mechanical agitation instead of static mixers (SM) principally at high flow rates. Above 65 L/h the efficiency of separation associated with mechanical agitation decreases in comparison with the static mixer which works with honeycomb elements. Over 78 L/h this efficiency is lesser than those observed for both design of static mixers. Probably the residence time into the mixing chamber is not sufficient to achieve a good mass transfer when operating with mechanical agitation at high volume flow rates. Oppositely the efficiency of separation increases for static mixers operating at high flow rates. In this case we can

achieve a good mass transfer over the same residence time. A comparison between static mixers filled with different elements of mixing shows the static mixer provided with honeycomb elements is more efficient than the other one which uses plate elements. An increase of about 30% in efficiency is noted in favour of the static mixer with honeycomb elements from 47 to 85 L/h.

Fig. 3 shows the total efficiency of separation of oil from wastewater as function of fraction of dispersed phase. We observe an equal behaviour for mechanical agitation and static mixer provided with honeycomb elements until 0.25 of fraction of dispersed phase. Up to this point an increase in fraction of dispersed phase causes a decrease on the efficiency of separation when using mechanical agitation. Probably at elevated fractions of dispersed phase the shear forces near the turbine are sufficiently high to generate small droplets which are more difficult to separate. Otherwise this effect is opposite when working with both static mixers. In this case, we can operate with relatively low shear forces. Also, it is relevant to remark that the operation with mechanical agitation on the studied range of volume flow rate was always in turbulent flow. A comparison between both static mixers shows the same increase of about 30% in efficiency of separation for all range of fraction of dispersed phase (0.17 to 0.29) when honeycomb elements are used.



Figure 3 – Total efficiency of separation as function of fraction of dispersed phase.

# 4. Conclusions

The mixing operation in a new device conceived for treating wastewater in the petroleum industry was studied. We perform this operation with mechanical agitation and static mixers alternatively. For volume flow rates upper than 65 L/h the static mixer with honeycomb elements showed a greater efficiency of separation when compared

with mechanical agitation or static mixer with plate elements. This is an important conclusion in view of an industrial application since the great volume of waste waters generate in the petroleum industry imposes hard operational conditions in terms of flow rates. We conclude the static mixer with honeycomb elements can be an advantageous alternative to perform the mass transfer into the mixing chamber of MDIF® (Phase Inversion Mixer-Settler) device.

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