STUDY OF MASS TRANSFER FOR THE RESIDUAL WATER-OIL SYSTEM IN A NEW MIXER-DECANTER DESIGN

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ABSTRACT
A new separator design for liquid-liquid systems has been proposed to decrease the coalescence time of dispersed phase drops. Aiming at making the separation process more efficient, the present work studies hydrodynamics and mass transfer in the mixer to estimate the overall mass transfer coefficient relative to the aqueous (water + oil) and organic (turpentine) phases involved. Samples were collected at the inlet and at the outlet of the system. The analyses were performed using the oil and grease content technique. A mass balance in the liquid phase calculated in the mixer allows us to determine the mass transfer coefficient, thereby optimizing the system. A correlation equation was found for the mass transfer coefficient as a function of the variables studied in the process. Transfer optimization in the mixing chamber will contribute significantly to an increase in the overall separation efficiency of the device.

KEYWORDS
clean technologies; wastewater treatment; mass transfer; equipment design

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1. INTRODUCTION

The awareness of society about preserving the environment has grown considerably in recent times. In particular, water supply is pointed out as the main problem to be faced in the coming decades. Industrial pollution is significant and must be controlled.

Petroleum, an essential raw material today, in addition to producing derivatives (gasoline, diesel, lubricants, kerosene, etc.), during its processing, also generates a number of solid, liquid and gas pollutants that must be treated before being eliminated in the environment. The treatment of liquid wastewater from the refineries located all over the world requires considerable space and energy expenditures, given the large flows of these wastewaters. It is therefore necessary to seek more efficient and feasible treatment methods.

A new type of liquid-liquid phase inversion separator was proposed for treating oil-contaminated waters. It is called the Mixer-Settler based on Phase Inversion, MSPI (Chiavenato and Paulo, 1999; Chiavenato, 1999). The development of the prototype was the subject of the Masters dissertation presented by the coordinator of this project, and obtained national recognition in Brazil after being awarded second prize (honourable mention) by OPP Petrochemicals, Inc. and ABEQ (Brazilian Association of Chemical Engineering) in 1999.

A design method for the settler zone in a mixer-settler was proposed by Hadjiev et al. (2004). Another method to design the mixer zone was designed by Paulo and Hadjiev, in 2006. It is based on the capacity of the settler to provide high separation efficiency with increasing throughput. This separation is improved when good-quality residual water has to be released. A number of correlations are identified that allow reasonable prediction of the diameter of carriers formed using perforated plates, as well as drop size distribution and the Sauter mean diameter of the primary dispersion.

A treating unit for produced waters, called “Unidade de Tratamento - Misturador Decantador à Inversão de Fases, UT-MDIF”, has been designed, installed and operated in industrial plants for treatment of effluents from the oil industry. This unit has a vertical configuration, which is an important characteristic when there is limitation on the lay-out of the plant, for example, on maritime platforms to explore oil. In semi-industrial scale, this equipment treats produced wastewaters contaminated with oil at low concentrations (ranging from 30 to 150 mg/L) and throughputs of 320 m³/d (47.4 m³ m⁻² h⁻¹) (Fernandes Jr. et al., 2004; Fernandes Jr., 2006).

The aim of the present study is to investigate the mass transfer process that occurs inside the MSPI to improve oil separation efficiency in decanting chambers.

2. EXPERIMENTAL

2.1 Materials

The oil/water aqueous phase from one field of the Ceará Sea, in Northeastern Brazil, and the turpentine were supplied by Petrobras.

2.2 Experimental device

To optimize oil transfer from the aqueous to the organic phase, the mass transfer coefficient (K,LS) that quantifies the speed of this process was obtained in a mixing chamber under controlled mechanical agitation (Fig. 1). This chamber is composed of a 500-mL stainless steel cylindrical container with an inner diameter of 7.5 mm and two outlets, one lateral for sample collection, located at mid height, and another at the center of the base for final disposal of the mixture. The experimental device is also composed of two reservoirs containing the aqueous (oil + water) and organic (turpentine) phases that feed the mixer. Phase flow is controlled by a digital frequency inverter coupled to flow pumps. An acrylic reservoir measuring 19 × 27 × 22 cm is placed under the mixer to receive the liquid mixture that comes from the mixing chamber.

2.3 Experimental procedure

After feeding the reactor with the aqueous phase and starting agitation at the desired frequency, organic phase feeding (dispersed phase) is then activated. Phase feeding is performed by the upper part and released for contact at the base of the mixer. The samples are collected directly in a
separation funnel (V = 250 mL), and after 30 min the oil-poor water samples are separated from the oil-rich turpentine phase and taken for analysis of oil concentration using the oil and grease content method, according to the Petrobras training manual (MT-37-0084, April 10, 1998). It is important to highlight that, as opposed to the process studied by Chiavenato and Paulo (1999), when the organic phase was recycled to the mixer, causing losses in extraction efficiency over time until saturation, in this study the organic phase feeding is conducted continuously in its pure form. In view of this, there is no recirculation of the organic phase in the present experiment, thereby avoiding that the organic phase saturation process hinder the assessment of the influence of the other variables under study.

3. RESULTS AND DISCUSSION

To estimate the overall mass transfer coefficient, the control parameters studied were agitation speed (N) and the ratio of organic and aqueous phase flows (Q_O/Q_A). Total phase flow during feeding (1100 mL/min) and the total phase volume in the reactor (500 mL) were maintained constant. The oil concentration present in the water at the mixer inlet (C_{AE}) varied between 450 and 600 mg/L. The operation range of the control parameters is shown in Table 1.

<table>
<thead>
<tr>
<th>N (rpm)</th>
<th>Q_O (mL/min)</th>
<th>Q_A (mL/min)</th>
<th>Q_O/Q_A</th>
</tr>
</thead>
<tbody>
<tr>
<td>285 – 700</td>
<td>157– 370</td>
<td>730 – 943</td>
<td>1/6 – 1/2</td>
</tr>
</tbody>
</table>

The symbols of the variables studied are listed below.

\[
Q_A = \text{Aqueous phase flow (oil + water), mL/min}
\]

\[
Q_O = \text{Organic phase flow (turpentine), mL/min}
\]

\[
C_{AE} = C_0 = \text{Oil concentration in the aqueous phase at the inlet, mg/L}
\]

\[
C_{OE} = \text{Oil concentration in the organic phase at the inlet, mg/L}
\]

\[
C_{AS} = \text{Oil concentration in the aqueous phase at the outlet, mg/L}
\]

\[
C_{OS} = \text{Oil concentration in the organic phase at the outlet, mg/L}
\]

\[
N = \text{Agitation speed, rpm}
\]

3.1 Influence of agitation speed on extraction efficiency

The extraction efficiency (E%) was determined with Equation 1 to assess the potential of oil extraction by the organic phase.

\[
E\% = \frac{C_{AE} - C_{AS}}{C_{AE}} \times 100\% \tag{1}
\]

In these assays, the volumetric ratio between the phases involved (organic and aqueous) was kept constant (Q_O/Q_A = 1/3), as was the oil concentration in the aqueous phase (in the range of 450-500 mg/L). Figure 2 shows that the oil extraction efficiency by the organic phase is nearly constant and around 90 %, which means that the extraction efficiency is independent of the agitation speed within the domain studied (285-700 rpm).
3.2 Influence of the volumetric feed flow ratio of the aqueous and organic phases on the extraction efficiency

In order to assess the influence of the volumetric feed flow ratio of the aqueous and organic phases on the extraction efficiency, the agitation speed was kept constant (N = 550 rpm) and the oil feed concentration present in the water varied between 550 and 600 mg/L. The range of volumetric ratio values between the phases was 0.16 - 0.5. The results in Figure 3 show that the extraction efficiency increases with increasing \( Q_O/Q_A \), reaching a maximum value of 93.5%. It can also be observed that the efficiency is limited to the \( Q_O/Q_A \) ratios starting from 0.25.

3.3 Determination of the overall mass transfer coefficient

To determine the mass transfer coefficient an overall mass balance was performed in the stationary mixer, according to Equation 2.

\[
Q_A (C_{AE} - C_{AS}) = Q_O (C_{OS} - C_{OE})
\]  

(2)

Considering that pure turpentine enters the reactor, one has \( C_{OE} = 0 \) as a process constant. Thus, Equation 2 can be described as follows:

\[
C_{OS} = Q_A (C_{AE} - C_{AS}) / Q_O
\]

(3)

Supposing the aqueous and organic phases are perfectly mixed, a mass balance is performed for the oil, considering only the terms that represent convection and mass transfer (Equation 4).

\[
Q_A (C_{AE} - C_{AS}) = K_L S (C_{OS} - C_{AS})
\]

(4)

As a result, the expression from which the \( K_L S \) product can be calculated is derived from Equations 3 and 4, as shown by Equation 5.

\[
K_L S = \frac{Q_A C_{AS} - C_{AE}}{C_{AS} - C_{AE}} \frac{V}{Q_A} \left( \frac{1}{Q_O \cdot (C_{AE} - C_{AS})} \right)
\]

(5)

3.4 Influence of agitation speed on the overall mass transfer coefficient

It is known, according to Lewis and Whitman (1924), that the increase in agitation speed contributes to the growth of the contact surface between the phases (\( S \)), due to the production of fine dispersed phase droplets (turpentine) and the reduced thickness of the liquid-liquid interface (Greaves and Loh, 1985). Figure 4 shows the behavior of the \( K_L S \) product as a function of the agitation speed applied in the process. In this study the oil concentration of the aqueous phase at the reactor inlet remained within 450 and 500 mg/L and the feed flow ratio of the phases (\( Q_O/Q_A \)) was kept constant at 1/3. It can be observed that \( K_L S \) is independent of agitation speed. The agitation speed of 285 rpm is sufficient to break the dispersed phase droplets compared to higher agitation speeds. The constant behavior of \( K_L S \) shows that it is possible to carry out experiments with agitation speeds less than 285 rpm. The increased agitation speed contributes to increase
the energy dissipated in the medium, rendering the process unfeasible.

3.5 Influence of the phases feed flow ratio on the overall mass transfer coefficient

Keeping the agitation speed constant at 550 rpm and the feed of aqueous phase in the mixer ranging between 550 and 600 mg/L, the influence of the phases feed flow ratio \( \frac{Q_O}{Q_A} \) on \( K_L S \) was studied at the following values: 1/6, 1/5, 1/4, 1/3 and 1/2. The total flow was kept constant at 1100 mL/min.

The effect of the feed flow ratio of the aqueous and organic phases on the overall mass transfer coefficient is significant (Fig. 5), since it rises linearly as the content of the organic phase is increased in the process. This effect may be explained by the considerable increase in the retention of this phase, resulting in effective growth on the liquid-liquid contact surface (Metcalf & Eddy, 1979). It is important to point out that the augmented \( \frac{Q_O}{Q_A} \) ratio to values above 1/2 will greatly hinder the process, since it already exhibits optimal efficiency (above 90%) within the studied range (see Fig. 3).

3.6 Correlation of the overall mass transfer coefficient

To establish a correlation between \( K_L S \) and the parameters studied, the Statistica 5.1 software was used. The estimation technique of the program that best fitted the experimental results was the combined Simplex and quasi-Newton method. For a correlation factor of 0.9978, the following correlation was obtained:

\[
K_L S = 1.34917 \times 10^{-5} N^\beta \left( \frac{Q_O}{Q_A} \right)^{0.9433}
\]

The factor \( \beta \), exponent of the agitation speed \( N \), is approximately zero, as predicted by the constant curve shown in Fig. 4. The correlation expressed by equation 6 shows that the effect of the agitation speed on the \( K_L S \) product was not significant within the operation range used in this study. In contrast, the effect of the \( \frac{Q_O}{Q_A} \) feed ratio is clearly significant and approximately linear.

4. CONCLUSIONS

The data obtained experimentally to determine the extraction efficiency and the overall mass transfer coefficient \( K_L S \) as a function of the studied variables, namely the agitation speed \( N \) and the flow ratio between the aqueous and organic \( \frac{Q_O}{Q_A} \), led us to conclude that the efficiency extraction and \( K_L S \) are independent of the agitation speed within the studied domain. The higher percentage of the organic phase is significant, since it increases considerably the percentage of oil extracted as well as the value of \( K_L S \), consequently increasing the speed of oil transfer effected by the organic phase. The maximum percentage of oil extraction obtained was around 93.5% and the maximum value found for \( K_L S \) was \( 7.0 \times 10^{-8} \text{ m}^3/\text{s} \), corresponding to a \( \frac{Q_O}{Q_A} \) ratio of 1/2.

The dependency of the overall mass transfer coefficient with the variables studied is represented by the correlation equation (Equation 6), which shows a linear effect of \( K_L S \) with the \( \frac{Q_O}{Q_A} \) ratio, with an exponent \( \beta \) of agitation speed \( N \) approximately equal to zero.
5. REFERENCES


