

## Regeneration of spent polymer resins in oily water treatment systems by application of nanoemulsion

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**ABSTRACT:** In step production of oil wells, along with oil, also produces a large volume of water oily, which must be properly treated for disposal. Several absorbent materials have been developed and are highly effective for this purpose. However, they need regeneration when they reach saturation, because their discharge after each saturation cycle makes the process unfeasible from the cost and environmental standpoints. In this study, we investigated the efficiency of regenerating a methyl methacrylate-divinylbenzene polymer resin spent in a system for continuous treatment of oily wastewater, *in loco*. The regeneration fluid used was an O/W nanoemulsion, which contain only 8% of environmentally friendly solvent and 80% of synthetic marine water. A kinetics desorption study of oil saturated resin was performed to identify the best times for desorption using the nanoemulsion. After one cycle of saturation, cleaning and resaturation, was observed that regeneration efficiency in continuous process of around 40%. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42050.

**KEYWORDS:** adsorption; colloids; kinetics; nanocrystals; nanoparticles; nanowires; porous materials

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### INTRODUCTION

The increasing exploration and production of oil in deep waters has raised environmental concerns among authorities and the public, especially regarding the quality of the wastewater discharged from this type of activity.<sup>1</sup>

Specific rules from the environmental agencies of several countries limit the oil content in water to a monthly average of 29 mg/L, causing rising demand for more efficient treatment systems and prompting scientists to search for new materials with ultrafiltration and adsorbent properties, such as membranes and polymer resins.<sup>2–5</sup>

While several such materials have been developed that are highly effective for this purpose, they need regeneration when they reach saturation, because their discharge after each saturation cycle makes the process unfeasible from the cost and environmental standpoints.<sup>6,7</sup>

Adsorbent polymer resins are generally amphiphilic and macro and/or mesoporous and require particular characteristics from the regenerating fluid depending on their purpose, such as affinity for the adsorbate with diffusion energy capable of overcoming the adsorption energy, so as to promote desorption and penetration of the pores with sufficient mobility to drag the adsorbate from the adsorbent's pores.<sup>8,9</sup>

Nanoemulsions are liquid dispersions in which the non-sized droplets of a liquid phase are dispersed in another liquid phase called continuous. They can be of the water-in-oil (W/O) or oil-in-water (O/W) type and present the classic behavior of colloids.<sup>10</sup> O/W nanoemulsions have promising characteristics for use as regenerating fluids of these new ultrafiltration materials, as the small size of their droplets, and hence the low viscosity, permits great mobility and easy penetration in macro and mesopores. Besides these features, they can be produced with sufficiently low oil phase content, such as an organic solvent that has a solubility parameter near that of the oil targeted for removal from the adsorbent material.<sup>10–13</sup>

In a previous study,<sup>14</sup> stable O/W nanoemulsions with average droplet diameters of 7–20 nm were obtained by the high-energy technique in a high-pressure homogenizer (HPH), using only 10–12% of the surfactant Utrol L70 (an ethoxylated laurel alcohol) and 5–10% of the oil phase in a base of 78–85% of water. The oil phase of this nanoemulsion is a commercial solvent of the Solbrax ECO line, which is obtained by hydrorefining naphtha and has low toxicity because it contains below 1% aromatics.<sup>15</sup> These nanoemulsions presented good efficiency when applied to clean samples of methyl methacrylate-divinylbenzene (MMA-DVB) polymer resins impregnated with crude oil in initial study of a batch process.

**Table I.** Characterization of the Crude Oil Sample

Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)	Density (°API)	Viscosity (cP)		
					30°C	40°C	50°C
40.7	34.1	22.9	2.4	21.2	134.74	75.21	46.61

Another study of the application of these nanoemulsions<sup>16</sup> showed that their high power to dissolve petroleum allows their use to replace conventional solvents in methods to determine the total oil and grease (TOG) content of oily wastewater samples. In this case, the big advantage is the reduction or elimination of the toxic organic solvents used routinely in laboratories in conventional TOG measurement methods, thus allowing compliance with more rigorous environmental protection standards.

In this work, a systematic study of crude oil desorption kinetics of MMA-DVB resin was performed by applying the nanoemulsion, to determine the parameters necessary for cleaning saturated resin in treatment of oily wastewater system, directly in the column bed. From of saturation, cleaning, and resaturation cycles was estimated resin regeneration efficiency in the oily water treatment system. The polymer resin (MMA-DVB) was obtained from the Laboratory for Macromolecules Applied in the Petroleum Industry (LMCP) of the Institute of Macromolecules of Rio de Janeiro Federal University and presented average pore diameter of about 50 nm.<sup>9</sup> The regeneration fluid used was an O/W nanoemulsion based on Solbrax, obtained by the high-energy method in a HPH. The aqueous phase used to obtain the nanoemulsion was a solution of NaCl and CaCl<sub>2</sub>, as the results of a previous study<sup>16</sup> showed that the presence of salts allows better incorporation of the oil phase in stable nanoemulsions and increases their solvent power. The nanoemulsion had droplets with diameters in the range of 7–30 nm and was also used as a solvent to measure the TOG of the oily water used to saturate the column packed with the polymer resin in the treatment system.

## EXPERIMENTAL

### Materials

- The crude oil sample came from the Campos Basin and was donated by the Petrobras Research Center (CENPES). Table I shows the characteristics of this sample.
- The polymer resin, produced at the LMCP, was composed of poly(methacrylate-divinylbenzene) (MMA-DVB) and was synthesized and characterized according to the method presented in a previous study.<sup>9</sup> This resin has specific area (*A*) of 70 m<sup>2</sup>/g, pore volume (*V*) of 0.56 cm<sup>3</sup>/g, apparent density (*D*<sub>ap</sub>) of 0.34 g/cm<sup>3</sup> and average pore diameter (*φ*) of 463 Å.
- The nanoemulsion, containing 12% m Ultral L70 and 8% m Solbrax ECO 235 in a 55,000 ppm saline solution (CaCl<sub>2</sub>: 10 NaCl), was obtained by a method developed at the LMCP and described in a previous study.<sup>16</sup>

### Methods

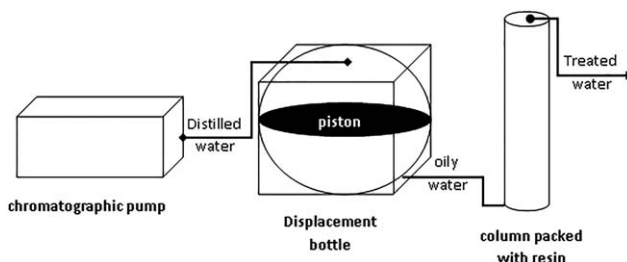
**Saturation of the Polymer Resin with the Oil Using the Oily Wastewater Treatment System.** The oily wastewater treatment system was also developed at the LMCP, as reported by Queirós

*et al.*<sup>9</sup> It is composed of a stainless steel column packed with MMA-DVB resin coupled to a displacement bottle, which in turn is connected to a chromatographic pump. The resin is kept swollen in a water/ethanol solution and on being packed in the column the swelling is maintained by passing distilled water through the column until its use to treat the oily water. The displacement bottle has a spherical interior, with capacity of 1000 mL, and contains a rubber piston that divides it into two compartments: one filled with distilled water and the other with oily water. Distilled water is pumped continually to the distilled water compartment by the chromatographic pump. Hence, the piston impels the oily water to move through the column packed with resin, as indicated in Figure 1. The resin packed in the column adsorbs the oil from the oily water until it reaches saturation and cannot retain any more oil in its pores.

Various oily water samples were prepared so as to present a theoretical concentration of 200 ppm, by the addition of 200 μL of oil in 1 L of a 55,000 ppm saline solution (CaCl<sub>2</sub>: 10 NaCl), under constant shaking, as described in a previous study.<sup>16</sup>

The displacement bottle was then filled with the oily water and connected to the chromatographic pump, as indicated in Figure 1. The pump was set to operate at a flow of 20 mL/min, as in a previous study,<sup>9</sup> this flow allowed good efficiency of retaining oil in the column. The TOG values (μL/L) of the oily water samples eluted through the column were measured before and after passage by the method developed in a previous study.<sup>16</sup> This method involves adding 1 mL of nanoemulsion in 100 mL samples of oily water. The oil droplets from the oily water migrate inside the droplets of the nanoemulsion forming a homogeneous colloidal suspension. This solution is then examined under a Cary 50 ultraviolet-visible spectrophotometer and the absorbance value is converted into TOG (μL/L) with the help of a calibration curve of the oil in nanoemulsion diluted in saline solution, obtained for the device.

The resin reaches saturation when the output TOG is equal to the input TOG. The number of bottles full of oily water used in this experiment was recorded.



**Figure 1.** Diagram of the oily water treatment system by adsorption in MMA-DVB resin.

**Table II.** Contact Times in Function of the Flows from the Chromatographic Pump to Study Desorption in a Shaker Bath, where  $t = 1.325/Q$ 

Q (mL/min)	0.2	0.1	0.05	0.025	0.02	0.015	0.01	0.005	0.001
t (min-s)	6'37"	13'15"	26'30"	53'	66'25"	88'33"	132'32"	256'	1325'

**Determination of the Desorption Parameters of the Continuous Process from Studying the Desorption Kinetics of the Oil from the Resin by Application of the Nanoemulsion in a Shaker Bath.** The resin regeneration process developed in this study involves the use of the same oily water treatment system. However, this time the displacement bottle contains the nanoemulsion, which is impelled to the saturated column, thus promoting the desorption of the oil from the resin to the nanoemulsion, in a continuous process. The chromatographic pump can operate at pressures of 0.001 to 30 mL/min, and the best flow for the process depends on the contact time necessary for maximum desorption of the oil in a determined column bed volume.

Therefore, we first carried out a study of desorption of the oil from the resin in a shaker bath (Haake model SWB 25m), relating the desorption times to the possible flows at which the pump can operate, according to eq. 1.

$$Q = h.A/t \quad (1)$$

Where:  $Q$  is the volumetric flow;  $h$  is the column height (3 cm);  $A$  is the cross-sectional area ( $0.44 \text{ cm}^2$ ) of the column; and  $t$  is the time of contact between the nanoemulsion and the resin packed in the column.

The maximum flow for the experiments was selected so as to allow a minimum contact time to promote some desorption. The minimum flow was chosen in function of the pump's lower operating limit. Table II presents the contact times used to study the desorption in the shaker bath, relating the possible flows at which the chromatographic pump can operate.

**Impregnation of the MMA-DVB resin with oil.** As the saturation of the resin in the column's bed takes a long time (approximately 1 month for each sample), and various samples are necessary for desorption kinetics test, for this study we developed a special method for impregnation of the polymer resin, as described next:

Aliquots (1 g) of the moist resin were weighed in tubes suitable for centrifuging. An aliquot (0.2 g) of oil was added to the tubes, which were then spun with a Boeco C-28A centrifuge, which was programmed with a velocity of 3000 rpm for 20 min. The procedure was carried out multiple times until the coloration was homogeneous, indicating maximum adsorption of the oil in the resin.

The impregnation of the resin with the oil samples was evaluated under an Olympus S2H10 optical stereomicroscope.

**Desorption of the oil from the resin by applying the nanoemulsion in a shaker bath.** An aliquot (2.7 mL) of the nanoemulsion was added to each of 9 samples in centrifuge tubes containing the resin impregnated with oil. The tubes were then placed in the shaker bath, at a temperature of  $24^\circ\text{C}$  and agitated

at a rate of 150 cycles/min. Each tube was sequentially removed from the shaker bath at times equivalent to the flows selected for the chromatographic pump, as shown in Table II. Aliquots of the nanoemulsion containing the desorbed oil were removed from the tubes and filtered through steel screen (100 mesh) to keep the resin particles in suspension from interfering in the analyses conducted in the UV-Vis spectrophotometer. The aliquots were diluted in the nanoemulsion until absorbance values were within the calibration curve of the oil in the nanoemulsion obtained for the device, for all the desorption times.

The data obtained were applied in a linearized model of pseudo-first-order and second-order equations (eqs. 2 and 3, respectively) to determine the kinetics model that best describes the system and sorption rate. From the intraparticle diffusion equation (eq. 4) it was possible to predict the mechanisms and limiting step in the sorption process.<sup>17–21</sup>

$$\text{Log}(q_e - qt) = \text{Log} q_e - k_1 \cdot t / 2303 \quad (2)$$

$$t/qt = 1/k_2 q_e^2 + t/q_e \quad (3)$$

$$qt = k_{in} \cdot t^{1/2} \quad (4)$$

Where:  $k_1$  and  $k_2$  are the pseudo-first-order and pseudo-second-order sorption rate constants, respectively;  $t$  is the sorption time;  $q_e$  and  $qt$  are the quantities adsorbed in equilibrium and at time  $t$ , respectively; and  $k_{in}$  is the intraparticle diffusion rate constant.

**Obtaining Desorption Profile of the Oil from the Resin by Applying the Nanoemulsion in the Treatment System.** After saturation of the resin in the column, the displacement bottle was disconnected, washed and filled with nanoemulsion, after which it was again connected to the chromatographic pump and the column containing the saturated resin. The pump was adjusted to a flow equivalent to the best contact time, according to the desorption kinetics experiment. Aliquots of 2.7 mL were collected successively during the entire cleaning procedure, that is, until the concentration of oil in the nanoemulsion became constant. A continuous process desorption profile was plotted from the data.

**Estimating the Efficiency of Resin Regeneration by Applying the Nanoemulsion in the Continuous Process.** After the cleaning process, the displacement bottle was disconnected from the system and the remaining nanoemulsion was discarded. Then the bottle was washed with distilled water and reconnected to the column containing the cleaned resin. The pump was turned on at a flow of 20 mL/min to elute about 3 liters of water, to remove any vestiges of nanoemulsion still retained in the resin.

Once again the displacement bottle was disconnected from the system and filled with oily water at 200 ppm (theoretical). The bottle was again reconnected to the pump and column

containing the cleaned resin and the same saturation procedure was carried out again. The number of bottle volumes used in this experiment was recorded.

The efficiency of regeneration by applying the nanoemulsion was estimated from the data on saturation of the column packed with virgin resin and with cleaned resin.

## RESULTS AND DISCUSSION

### Saturation of the Resin with Oil Using the Oily Water Treatment System

The average mass of resin that the treatment column could hold was approximately 2.09 g.

The TOG values of the oily water samples before and after elution in the column are presented in Table III. These values were obtained by the method reported in a previous work,<sup>16</sup> by adding the nanoemulsion in the oily water and analysis under UV.

It took 35 displacement bottle volumes for the resin to be fully saturated. However, for the calculations here we considered the resin saturation after 25 bottles. The bottle holds an average volume of 800 mL of liquid, so 20 L of oily water were eluted for the resin to reach saturation.

The average absorbance value for the pure nanoemulsion was 0.21998, with a percentage deviation of 2%. In Table III, the TOG is considered to be zero for absorbance values of the water after elution lower than that of the pure nanoemulsion.

Considering the average experimental TOG value of the input oily water of 180  $\mu\text{L/L}$ , and as up to the 25th liter only 10% on average of this value was not retained in the column, we estimated that the resin retained 3.24 mL of oil until becoming saturated. However, in these calculations we did not consider the losses on the walls of the displacement bottle and its connections to the column.

**Determination of the Desorption Parameters in the Continuous Process Based on the Desorption Kinetics Study of the Oil from the Resin by Application of the Nanoemulsion in the Shaker Bath Impregnation of the MMA-DVB Resin with Oil.** As the aim of this study was to learn the potential of the nanoemulsion to regenerate resin, mainly by desorbing the oil adsorbed in the pores, we used a mass of oil (0.2 g) in each sample (1 g) of moist resin sufficient to assure the resin would not be saturated with oil.

Observation of the micrographs of the resin in Figure 2 shows that the impregnation procedure succeeded, as the oil was well distributed throughout the resin, including being adsorbed in its pores.

**Desorption of the Oil from the Resin by Application of the Nanoemulsion in the Shaker Bath.** A previous experiment of the solubilization of oil in the nanoemulsion showed that the latter can be considered a good solvent of oil, as the entire mass of oil added to the nanoemulsion migrates into its droplets and is uniformly distributed, producing a homogeneous dispersion.

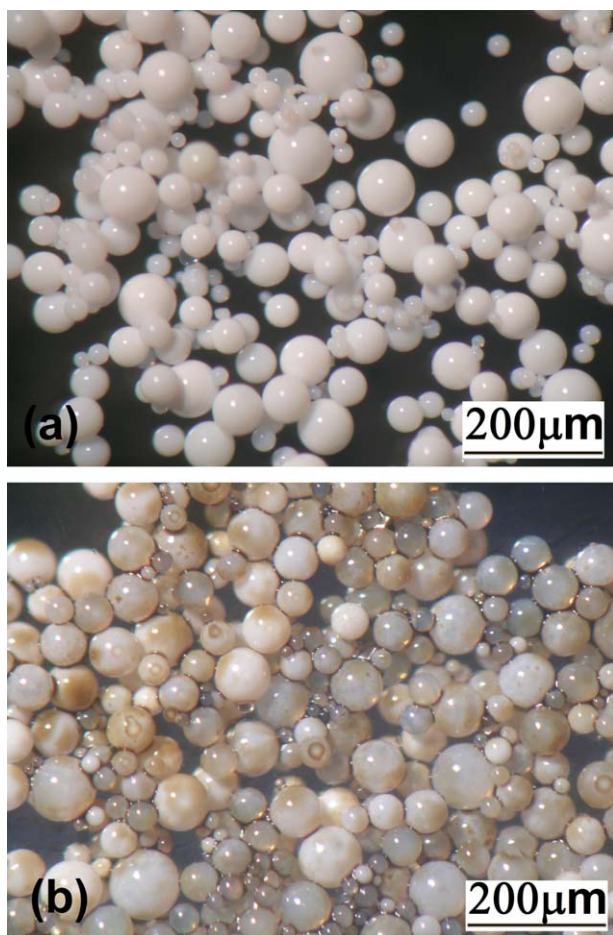
Figure 3 presents the photos and micrographs of the pure nanoemulsion and the solution of oil in the nanoemulsion. This solution became saturated at a concentration of 10%, at which

**Table III.** TOG Values of the Synthetic Oily Water Samples Obtained Before and After Elution in the Treatment Column Containing Virgin Resin

Samples	Oily water (before elution)		Oily water (after elution)	
	Absorbance	TOG ( $\mu\text{L/L}$ )	Absorbance	TOG ( $\mu\text{L/L}$ )
1	0.322194	146	0.19986	0
2	0.294925	107	0.22459	6
3	0.302338	117	0.20958	0
4	0.358240	197	0.19539	0
5	0.386127	237	0.23454	20
6	0.386947	238	0.22215	3
7	0.302773	118	0.21477	0
8	0.302386	117	0.21095	0
9	0.322194	146	0.23077	15
10	0.328523	155	0.20491	0
11	0.335426	165	0.20376	0
12	0.341485	173	0.19788	0
13	0.352472	189	0.22465	7
14	0.346135	180	0.19933	0
15	0.358785	198	0.23177	17
16	0.342693	160	0.22498	5
17	0.341203	157	0.22671	8
18	0.340659	156	0.22380	3
19	0.330036	141	0.22581	6
20	0.351959	188	0.22899	14
21	0.349613	185	0.22788	11
22	0.344441	162	0.22691	8
23	0.355975	178	0.22716	8
24	0.329191	140	0.22816	12
25	0.339911	155	0.243603	34
26	0.345042	178	0.27598	80
27	0.351902	188	0.25789	54
28	0.301064	115	0.29357	105
29	0.318114	140	0.32789	154
30	0.294925	107	0.34989	186
31	0.273956	77	0.325819	180
32	0.344631	178	0.34989	185
33	0.349233	184	0.24008	29
34	0.385179	236	0.33888	169
35	0.317862	134	0.33078	158

point the droplets lost their spherical form by creaming, Ostwald ripening and destabilization.

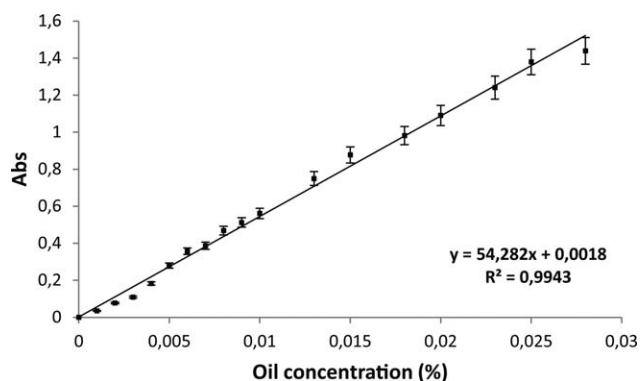
As the nanoemulsion studied here has low absorption in the visible region of the UV absorption spectrum, we plotted a calibration curve of the oil in the nanoemulsion for the UV-Vis spectrophotometer, using an optical path of 5 mm and wavelength of 400 nm, the conditions that produced the best linear correlation coefficient (Figure 4).



**Figure 2.** Micrographs of the MMA-DVB resin: (a) virgin and (b) impregnated with crude oil. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The volume of nanoemulsion utilized for this study represented twice the volume of the column bed and guaranteed that the nanoemulsion would not become saturated with the oil impregnated in the resin.

The desorption kinetics study of the oil in the shaker bath showed that the system reached equilibrium after 132.5 min, after which the oil concentration in the nanoemulsion became constant and the experimental value of  $q_e$  was equal to 27.2 mL



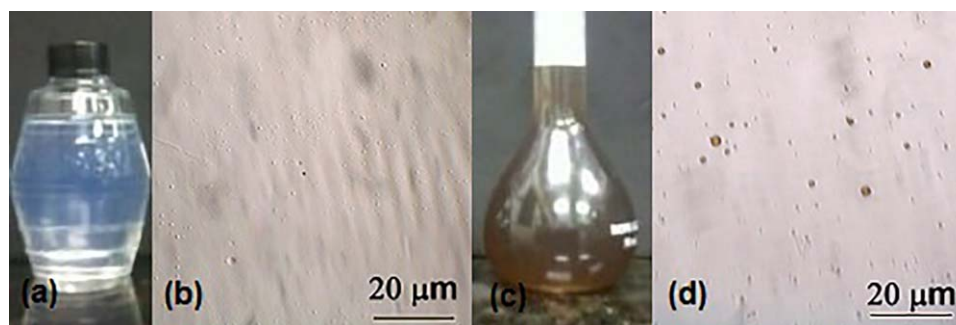
**Figure 4.** Calibration curve of the oil in the nanoemulsion for the UV-Vis spectrophotometer, at a wavelength of 400 nm and optical path of 5 mm.

$L^{-1}$ . The concentration values obtained from the desorption kinetics study, with the aid of the calibration curve, until the system reached equilibrium were used to obtain the fitted kinetics curves presented in Figure 5.

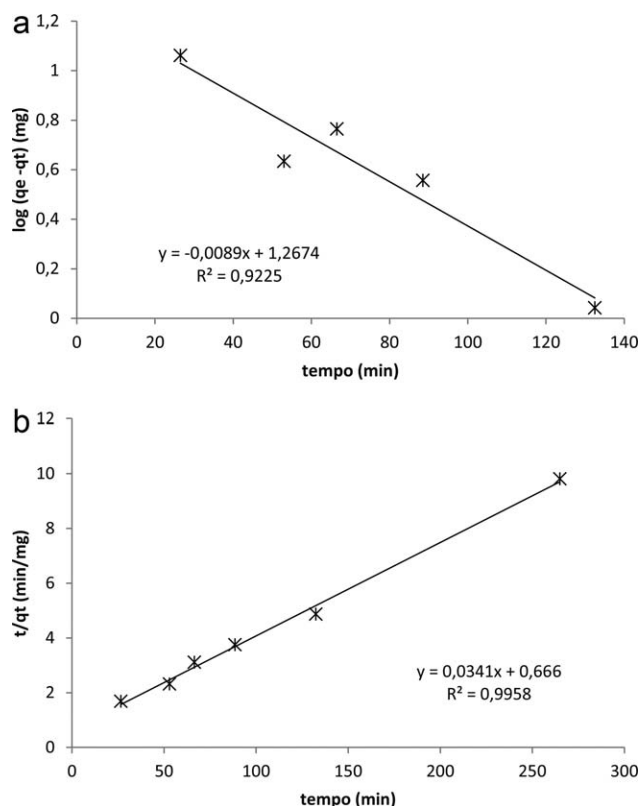
The pseudo-second-order kinetics model best described the system, as it presented the highest correlation coefficient. In this case, the sorption rate for the system was  $k_2 = 2.23 \times 10^{-3} L mL^{-1} min^{-1}$  and the value of  $q_e$  obtained from the linearized model of the pseudo-second-order equation was equal to 29.3 mL  $L^{-1}$ , which is the value obtained experimentally. In this case, desorption kinetics study presented a kinetics model similar to that attained by other desorption methods such as, desorption by ultrasound and using supercritical carbon dioxide.<sup>22,23</sup>

Figure 6 presents the fitted curves of the intraparticle diffusion kinetics, showing that desorption profile of the oil from the resin by application of the nanoemulsion presents a multilinear pattern. This model assumes that the sorption is controlled by three linear stages: a first stage, which starts with rapid diffusion from the external surface of the particles; a second stage, of gradual sorption, where the intraparticle diffusion is the limiting rate; and a final stage, which starts at the final equilibrium, where the intraparticle diffusion starts to decline due to the high concentration of solute in the solution.<sup>19</sup>

The fact that the highest linear regression coefficient was obtained for the second stage of the process indicates that the process is strongly controlled by the gradual sorption stage of



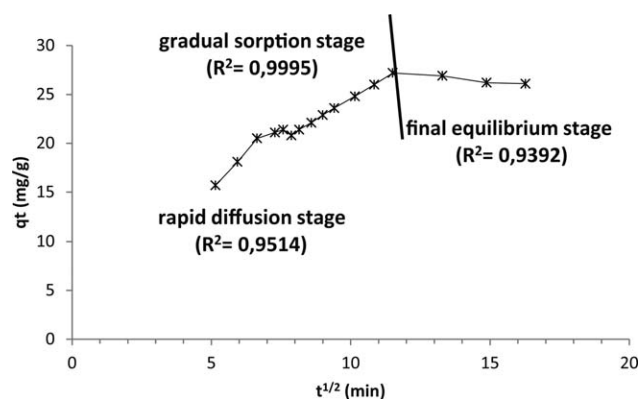
**Figure 3.** (a) photo and (b) micrographs of the pure nanoemulsion; (c) photo and (d) micrograph of the 1% oil solution in the nanoemulsion. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



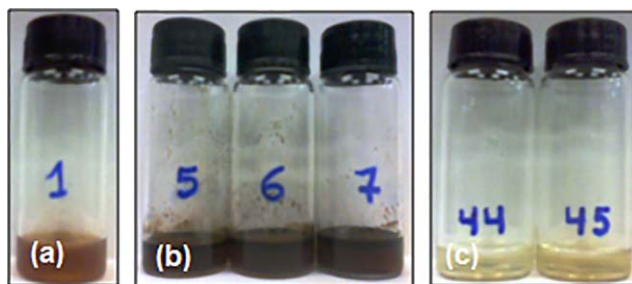
**Figure 5.** Fitted desorption kinetics curves of the oil from the resin by application of the nanoemulsion: (a) pseudo-first-order and (b) pseudo-second-order.

the intraparticle diffusion. However, it can be seen from the graph that the curve does not pass through the origin, indicating that the intraparticle diffusion mechanism is not the only limitation of the sorption process, so that other interaction mechanisms must be acting simultaneously.<sup>17</sup>

**Obtaining the Desorption Profile of the Oil from the Resin by Applying the Nanoemulsion in the Oily Water Treatment System.** To obtain the desorption profile in the process continuous, we used a flow of  $0.01 \text{ mL min}^{-1}$ , as in the kinetics study the system reached equilibrium after 132.5 min. Elution of 121.5 mL of nanoemulsion was necessary for the resin to be



**Figure 6.** Fitted intraparticle diffusion kinetics curve in desorption of oil from the resin by application of the nanoemulsion.



**Figure 7.** Aliquots collected during the continuous cleaning process: (a) start of desorption, (b) maximum concentration reached and (c) end of desorption. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

considered clean. This volume was distributed in 45 aliquots of 2.7 mL each, which were collected during the cleaning procedure until the absorbance value read by the UV-Vis spectrophotometer remained virtually constant and very near the value of the pure nanoemulsion.

Figure 7 presents photos of the nanoemulsion samples collected at the start of desorption [Figure 7(a)], at the maximum concentration reached [Figure 7(b)], and at the end of the desorption [Figure 7(c)].

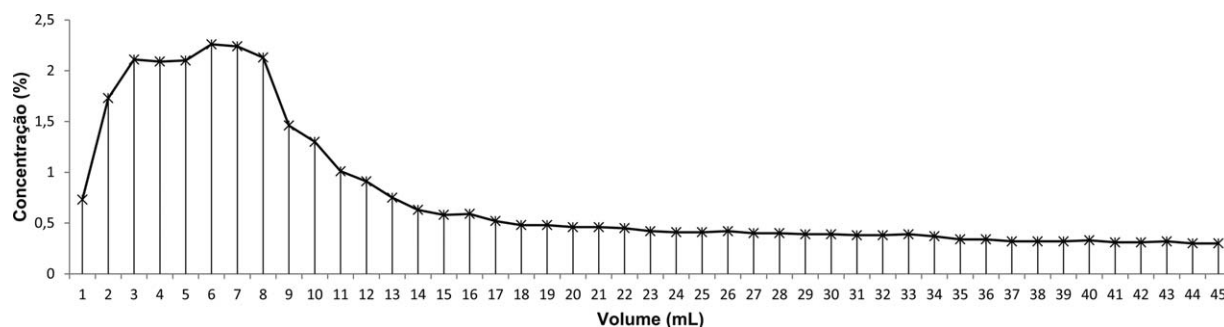
The graph in Figure 8 shows the desorption profile of the oil in the nanoemulsion. It can be seen that the highest oil concentrations in the nanoemulsion were obtained from the start of the process to the 15th aliquot, with a maximum concentration of 2.3%, not yet at the saturation point of the oil in the nanoemulsion. As each aliquot had a constant volume of 2.7 mL, it can be estimated that 0.54 mL of the oil retained in the column was extracted in this first desorption stage.

This first desorption stage can be attributed to the cleaning of the outside surface of the resin, with rapid diffusion of the oil to the nanoemulsion. This conclusion is corroborated by the clean appearance of the resin beads shown in the micrograph of Figure 9. Although the resin beads are dark when compared to the micrograph of virgin resin beads [Figure 2(a)], they are not stuck together and have clean surfaces when compared to the micrograph of the resin impregnated with oil [Figure 2(b)].

In the second desorption stage presented in Figure 8, which covers the 15th to the 45th aliquot, there is a linear profile with nearly constant concentration values. This second stage thus appears to involve slow and gradual intraparticle diffusion. To estimate the volume of oil desorbed in this stage, we considered a constant concentration of 0.5%, so that the volume desorbed in the second stage was 0.405 mL. In this case, the total volume desorbed in the first two stages of the continuous desorption process was 0.945 mL, representing 29.5% of the total volume retained in the column.

#### Estimate of the Regeneration Efficiency of the Resin by Application of the Nanoemulsion in the Continuous Process

The resaturation of the cleaned resin in the column was carried out by the same procedure as for saturation of the virgin resin. Table IV presents the TOG values of the synthetic oily water before and after elution in the column packed with cleaned resin.



**Figure 8.** Desorption profile of the oil from the saturated resin by application of the nanoemulsion in the continuous process in the oily water treatment system.

The TOG values of the oily water before elution in the column containing the cleaned resin are very near those obtained with the virgin resin. However, the TOG values obtained for the oily water after elution through the cleaned resin are higher than those for elution through the virgin resin, and no TOG value of zero was obtained, even at the start of the elution. In this case, the loss of efficiency in removing the oil is observed from the first aliquots. This phenomenon can be explained by the low efficiency in removing the oil adsorbed on the internal surface of the resin pores using the nanoemulsion, as the intraparticle diffusion limits the desorption process.

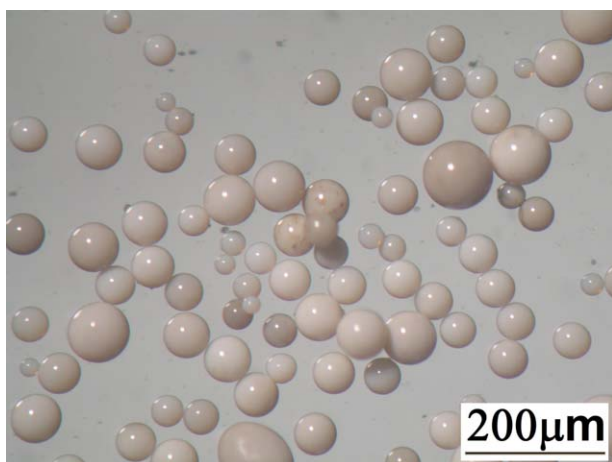
To estimate the regeneration efficiency of the resin in the continuous process *in situ* at the flow rate used in this study, we used 12.8 liters of oily water in 16 displacement bottles for the cleaned resin to reach complete saturation. We then calculated the TOG retained in the column by the difference between the input and output TOG values in each displacement bottle, obtaining a volume of 1.28 mL of oil. As the volume of oil retained in the column packed with virgin resin was 3.24 mL, the ratio between the oil volumes retained in the cleaned and virgin resin was 0.395. In other words, the regeneration efficiency was about 39.5%.

Furthermore, as the volume of oil desorbed by the nanoemulsion was calculated at 0.945 mL and the volume of oil retained in the column packed with cleaned resin was 1.28 mL, the dif-

ference between these figures can be considered the loss on the displacement bottle's walls and connections with the column. In percentage terms, this difference was 26.18%. As 3.24 mL was the oil volume estimated to saturate the column containing virgin resin, then application of this loss percentage means the real volume of oil retained in the virgin resin was 2.39 mL. Therefore, the ratio between the oil desorbed by the nanoemulsion (0.945 mL) and the volume (2.39 mL) retained in the virgin resin can also indicate the regeneration efficiency, which was also around 39.5%.

**Table IV.** TOG Values of the Synthetic Oily Water Samples Obtained Before and After Elution in the Treatment Column Containing Cleaned Resin

Oily water samples	Before elution		After elution	
	Absorbance	TOG ( $\mu\text{L/L}$ )	Absorbance	TOG ( $\mu\text{L/L}$ )
1	0.322194	146	0.227602	11
2	0.328523	155	0.226390	9
3	0.335426	165	0.221526	2
4	0.322194	146	0.246402	38
5	0.340659	156	0.251339	45
6	0.330036	141	0.234943	21
7	0.351959	188	0.249551	42
8	0.349613	185	0.254091	49
9	0.301064	115	0.257367	53
10	0.318114	140	0.269916	71
11	0.294925	107	0.260702	58
12	0.273956	77	0.258732	55
13	0.344631	178	0.276084	80
14	0.342698	160	0.253699	48
15	0.341201	157	0.284595	92
16	0.340659	156	0.286276	95
17	0.330034	141	0.314678	135
18	0.351949	188	0.298765	113
19	0.322194	146	0.348221	183
20	0.294925	107	0.332652	161
21	0.386947	238	0.407156	267
22	0.358230	197	0.320164	143
23	0.386127	237	0.376475	224



**Figure 9.** Micrograph of the resin after cleaning with the nanoemulsion in the continuous process in the column. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## CONCLUSION

The study of the desorption in a continuous process showed that the nanoemulsion was most efficient at removing the crude oil adsorbed at the external surface of the resin, and was less efficient in removing the oil adsorbed inside the resin's pores. However, desorption kinetics study presented a kinetics model similar to that attained by other desorption methods such as, desorption by ultrasound and using supercritical carbon dioxide. Therefore, the nanoemulsion investigated here is a promising fluid for regeneration of materials that adsorb organic matter, with the advantage of using under 10% organic solvent in its composition in a base of 80% water.

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