

Produced water treatment by microemulsions: one-step process for simultaneous removal of metals

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ABSTRACT

This work examines the simultaneous removal of barium, chromium, manganese, and iron from produced water using microemulsion systems (Winsor II) in a one-step process. The Scheffé net experimental design was used to assess the effect of microemulsion composition in the removal efficiency. The optimum extraction point for the simultaneous removal of metals was composed by (w/w): 72 % aqueous phase (synthetic produced water), 9 % oil phase (n-hexane), and 19% cosurfactant/surfactant (butan-1-ol/saponified coconut oil = 4); reaching values above 94% for all studied metals, demonstrating the viability of the developed methodology for the correct management of metals from produced water.

Keywords: Produced water; Metals; Simultaneous removal; Surfactants; Microemulsions

1. Introduction

Produced water is a complex mixture of different organic and inorganic compounds. It is a byproduct of hydrocarbon production in the oil industry, accounting for the largest portion of the generated waste. It needs an appropriate treatment to be discharged in the environment or reused in reservoir drilling and fracturing operations [1], in crop irrigation [2], or in households as drinking water [3].

Produced water contains high concentrations of contaminants, including metals, whose compounds are deemed dangerous for being soluble in water [4]. Considering that the health and welfare of living beings, as well as the ecological balance, can be affected by the decline of environ-

mental quality, the presence of metals in wastewater must be regulated by law [5]. In Brazil, the National Council of Environment (CONAMA) regulates the disposal of this effluent in salt, brackish, and fresh waters [6–8].

Physical, chemical, and biological methods are used to remove harmful compounds from produced water [9–11]. In offshore platforms, where physical space is limited, compact physical and chemical systems are used to remove dispersed/dissolved materials [12]. When analyzing the alternatives to treat produced water, it is important to keep in mind that some chemical treatments have high initial and/or operating costs [1,13–15].

The flocculation-flotation process is one of the processes used in the treatment of produced water [11,15]. Membrane technology is also applied, with membranes being made from either polymeric or ceramic materials

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[3,16–18]. Other treatment technologies include hydrocyclones, gravitational and plate separators, bed coalescers, dissolved gas flotation, ion exchange, chemical precipitation, bioreactors, adsorption on active carbon or synthetic zeolites [9,10,12,14, 19–23]. All the treatments listed above present advantages and disadvantages; there is no single complete treatment available. Usually, the oil industry uses an arrangement of techniques for better efficiency, raising the cost of treatment.

Surfactants are molecules formed by two groups with different polarities, a hydrophobic tail group (apolar) and a hydrophilic headgroup (polar). The surfactants have the ability to form oriented monolayers at interfaces, lowering the surface or interface tension of the systems where they are dissolved [24]. Microemulsions are systems formed by the dispersion of two immiscible liquids in two so-called phases: the dispersed phase (microdroplets) and the continuous phase. These phases are stabilized by an interfacial membrane, which is comprised by a surfactant and, sometimes, other components such as a cosurfactant and a cosolvent. Microemulsions are thermodynamically stable, optically isotropic, and homogeneous systems [25–27]. Surfactant and microemulsion systems have been used in several studies involving metal removal [28–33].

Microemulsion systems were classified by Winsor [34] considering a variety of types of equilibrium between this system and its forming phases. A microemulsion can be in equilibrium with an oil phase in excess (Winsor I) or with an aqueous phase in excess (Winsor II). It can also constitute a middle phase of a three-phase system (Winsor III), in which the oil and water phases can be found in excess. A Winsor IV classification refers to a single-phase system, in macroscopic scale, consisting of a unique microemulsion phase.

According to Paul and Moulik [35], Winsor I (O/W) and Winsor II (W/O) microemulsion systems can be used as liquid membranes that enable the transfer of solutes. In this way, Winsor I systems are used for removal of oil-soluble compounds, and Winsor II are ideal for the removal of water-soluble species. The transport of materials through the middle phase (membrane) depends on the way the solute is transferred from the source phase to the receiving phase, where it can be trapped in microdroplets by complexation or entrapment phenomena with suitable agents.

In this research the authors developed a new one-step methodology to simultaneously remove metals from a synthetic produced water. Winsor II systems were applied with different compositions, seeking to understand how their formulation affects the metal removal process, considering that produced water is a complex mixture. In view of environmental concerns, a biodegradable surfactant that was obtained by the saponification of coconut oil was employed.

2. Materials and methods

2.1. Surfactant

The surfactant was derived from coconut oil, which is a ubiquitous regional product in the State of Rio Grande do Norte, in Brazil. Its main chemical composition was described by Castro Dantas et al. [30]. In a 1000-mL round-bottomed flask 100 g of coconut oil, 300 mL of ethyl

alcohol (Neon, 99.5%), and 21.22 g of NaOH (Synth, 100%) were mixed with 80 mL of distilled water. The flask was connected to a reflux condenser, keeping the system in a heating mantle (Fisaton, Mod. 52E) during 2 h (80°C). After this time, the material was placed in a 300-mL beaker and heated at 120°C (700 rpm) in a magnetic hot plate stirrer (Fisaton, Mod. 754-A) to evaporate the alcohol in excess and promote soap crystallization. The surfactant thereby produced is known as “saponified coconut oil” (SCO), and is a mixture of sodium fatty carboxylates (soaps). The solid material was then pulverized and maintained in a glass desiccator.

2.2. Synthetic produced water (PW)

To obtain the PW, initially a saline solution of metals (SSM) was prepared, composed by 0.13 g·L⁻¹ BaCl₂ (Vetec, 99%); 3.27 g·L⁻¹ CrCl₃·6H₂O (Dinâmica, 98%); 0.04 g·L⁻¹ FeCl₃·6H₂O (Vetec, 98%); and 0.006 g·L⁻¹ MnSO₄·H₂O (Vetec, 98%). All salts were weighed individually and transferred to a 1-L volumetric flask, being the salts dissolved and the volume calibrated using distilled water. In the second step, 500 mL of the saline solution were placed in a 1-L beaker and blended with 1 g of crude oil (Ubarana Oilfield, Off-shore Potiguar Basin, Petrobras, Macau/RN/Brazil; density: 0.8582 g/cm³; viscosity at 30°C: 33.23°API, 14.94 cP). The system was kept under constant stirring (2,000 rpm) in a mechanical shaker (Fisatom, Mod. 752) until total dispersion of crude oil. After dispersion, the remaining 500 mL of saline solution were added. To homogenize the solution, due to the low solubility of crude oil, the system was mixed during 1 h in an ultrasonic bath (Elma, Transsonic 460). Table 1 presents the salts, the final concentrations of cations determined by high-resolution continuous-source atomic absorption spectroscopy (HR-CS FAAS; Analytik Jena AG, Mod. ContrAA 700), and the maximum allowed level according to CONAMA legislation [6–8].

2.3. Microemulsion systems

The microemulsion systems were composed by: PW as aqueous phase (AP); n-hexane (Vetec, 99%) as oil phase (OP); saponified coconut oil as surfactant (S); and butan-1-ol (Vetec, 99.5%) as cosurfactant. The mass ratio between cosurfactant and surfactant was equal to 4 (C/S = 4) [31]. n-Hexane was chosen as oil phase due to its solvency, as well as its rapid evaporation. The pseudoternary phase diagram with the Winsor regions was obtained using the titra-

Table 1
Concentrations of metals in PW and the maximum allowed levels for effluent disposal according to Brazilian legislation

Salt	Cation concentration, ppm	Maximum allowed level, ppm
BaCl ₂	38.14	5.00
CrCl ₃ ·6H ₂ O	1.15	1.00
MnSO ₄ ·H ₂ O	2.33	1.00
FeCl ₃ ·6H ₂ O	3.40	1.50

tion methodology. First, the oil phase and the C/S phase were mixed in a fixed ratio in glass vials, at 27°C. Then, the mixtures were continuously titrated dropwise with the water phase, until the system changed its appearance, from turbid to clear, or vice-versa. The percentage of each phase in the system was calculated by mass balance. The pseudoternary phase diagram was constructed by plotting triangular coordinates to represent the observed compositions, considering the proportions between the oil, water, and C/S phases [29–32].

2.4. Determination of metal concentrations

Metal concentrations were determined in the PW and in all aqueous phases obtained after Winsor II extraction by HR-CS FAAS (Analytik Jena AG, Mod. ContraA 700). The flame technique was used for barium analysis, with

553–5480 nm wavelength range, and air/acetylene and acetylene/nitrous oxide flames. The graphite furnace technique was used for chromium, iron and manganese, with integrated computer-control and transverse heat. A Pd/Mg was used as a modifier to ensure thermal stability of analytes. The atomization pyrolysis temperatures (°C) and wavelengths (nm) adopted were: chromium: 1500–2600°C and 357 nm–8687 nm; iron: 1000–2450°C and 248 nm–3270 nm; manganese: 1200–2500°C and 279 nm–4817 nm.

2.5. Metal removal by Winsor II microemulsions

All experiments were carried out using Winsor II systems, with the presence of two well-defined phases: the top one, a water-in-oil (W/O) microemulsion, and the bottom one, an aqueous phase in excess. Each extraction point was prepared in a Falcon 50-mL conical graduated centrifuge tube at 27°C. The compositions of the studied systems are shown in Table 2. The Falcon tubes were transferred to a centrifuge (Quimis, mod. Q-222T28) and kept under stirring during 5 min (2000 rpm) to allow phase separation. Finally, the WII aqueous phases were collected to determine metal concentrations, as shown in Fig. 1. All tests were performed in duplicate and made in random order to avoid systematic errors.

Table 2

Composition of the selected points in the WII region and the codified design matrix

Point	Composition (wt. %)			Design matrix			Response %E
	X_{AP}	X_{OP}	$X_{C/S}$	X_{AP}	X_{OP}	$X_{C/S}$	
A	85	3	12	1	0	0	Y_1
B	65	23	12	0	1	0	Y_2
C	65	3	32	0	0	1	Y_3
D	75	3	22	1/2	0	1/2	Y_4
E	65	13	22	0	1/2	1/2	Y_5
F	75	13	12	1/2	1/2	0	Y_6
G	78	7	15	2/3	1/6	1/6	Y_7
H	68	17	15	1/6	2/3	1/6	Y_8
I	68	7	25	1/6	1/6	2/3	Y_9
J	72	9	19	1/3	1/3	1/3	Y_{10}

2.6. Scheffé net experimental design

The Scheffé net, an experimental design applied to mixtures, was used to investigate the efficiency in the process of removal of metals from PW [36]. The variation of the composition of a Winsor II pseudoternary mixture composed by OP (n-hexane), AP (synthetic produced water), and C/S (butan-1-ol/SCO) was considered. First, the region of interest with experiment points was defined in the pseudoternary phase diagram, as shown in Fig. 2. Then, the mixtures were prepared according to Table 2 and the responses were acquired.

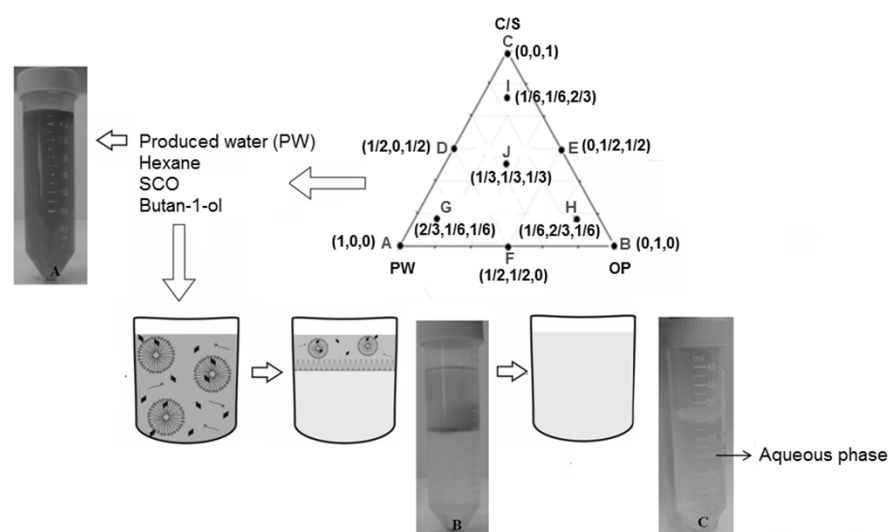


Fig. 1. Flowchart showing the Winsor II extraction process. Extraction steps: (A) Synthetic produced water; (B) WII system; (C) Aqueous phase after extraction.

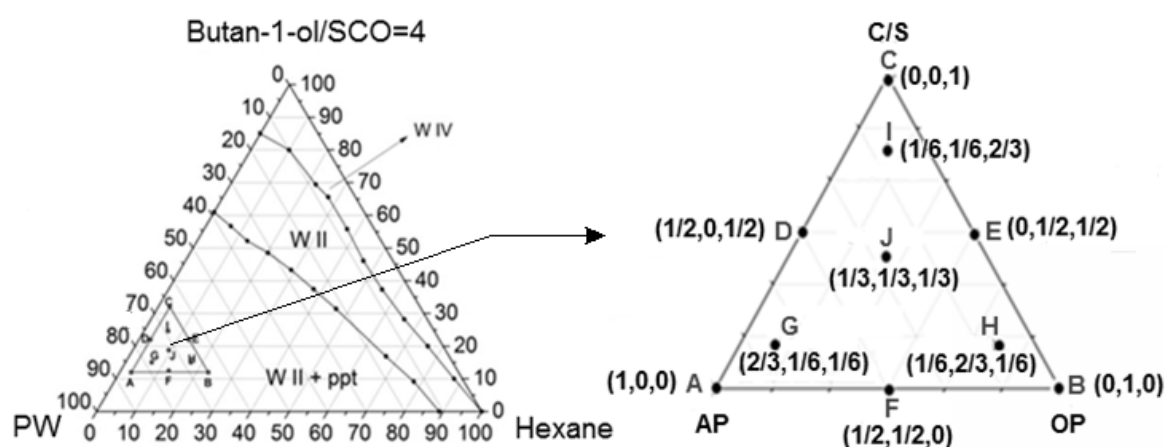


Fig. 2. Pseudo-ternary phase diagram for the studied system showing the interest region with the experimental points. WII+ppt indicates a Winsor II region with presence of precipitates (pH = 3.5; T = 27 °C).

3. Results and discussion

3.1. Influence of water phase composition on Winsor regions

The characteristics of the produced water depend on the nature of the rock formation from which oil is produced, as well as the operational conditions, and the chemicals used during its production [10]. A study was conducted to assess the influence of the aqueous phase in microemulsion systems, considering the effects of salinity (Systems 1 and 2) and the presence of metals (SSM- System 3). The study also used synthetic produced water (PW- System 4), which is a more complex system. Table 3 lists the compositions of the evaluated systems, and Fig. 3 shows the obtained pseudoternary diagrams with the observed Winsor's regions.

The systems with brine as aqueous phase show all Winsor regions. By increasing the salt concentration, the solubility of surfactant in water is impaired and the Winsor IV region progressively decreases. On the other hand, the Winsor II region increases due to a decrease in the ability of the water-in-oil microemulsion to solubilize brine as dispersed droplets. In System 3, one can observe the presence of Winsor II and Winsor II + precipitate (ppt) regions. This occurs due to the formation of a complex among the surfactant headgroups and metal ions, forming precipitates. In System 4, there is a decrease in Winsor II region and the increase in the (Winsor II + ppt) one. The presence of petroleum and other hydrocarbon molecules (saturated, unsaturated, and aromatics) in the synthetic produced water leads to the growth of the oil phase, thereby impairing the solubilization of the aqueous phase by the microemulsion [33,37,38].

3.2. Extraction of metals by Winsor II systems

According to the data presented in Table 4 and Fig. 4, one can observe that removal efficiencies (%) were higher than 87%. In acidic pHs, as in the evaluated synthetic produced water (pH = 3.5), the studied metals (Ba, Cr, Mn and Fe) exhibited high mobility and interaction with the active matter (cosurfactant + surfactant), being transferred from the PW to the W/O microemulsion. The extraction efficiency of each ion is directly related to its initial concen-

Table 3

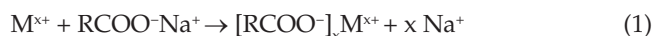
Compositions of the systems used to obtain the pseudoternary phase diagrams to evaluate the influence of the aqueous phase

System	C/S=4	AP	OP
1	Butan-1-ol /SCO	2% NaCl solution	n-hexane
2	Butan-1-ol /SCO	5% NaCl solution	n-hexane
3	Butan-1-ol /SCO	SSM	n-hexane
4	Butan-1-ol /SCO	PW	n-hexane

tration and ionic strength. The results for chromium were slightly lower due to its lower initial concentration in PW (1.15 ppm) and its lower ionic strength when compared to the other studied metals.

According to Watarai [39], the extraction of metal ions in aqueous phase with water-in-oil microemulsions using Winsor II systems is often very effective due to the increase in the micro-interfacial surface area and also the participation of the microemulsion droplets to transport metal ions from the aqueous phase to the organic phase.

Metal ions are attracted by the anionic surfactant (SCO), which behaves like an extracting agent. The Na⁺ ions of the surfactant are replaced by the metal ions that are in the aqueous solution, as shown in Eq. (1).



Initially, the metal ions dissolved in the aqueous solution (M^{x+}) are transferred to the core of the microemulsion droplet containing the anionic surfactant (RCOO⁻Na⁺). The bivalent and trivalent metals ions (Ba²⁺, Cr³⁺, Mn²⁺ and Fe³⁺) interact with the anionic head group of the surfactant molecule releasing Na⁺ ions. Surfactant/metal lipophilic complexes ([RCOO⁻]_xM^{x+}) are formed and migrate to the continuous oil phase of the Winsor II system, as shown in Fig. 5. This mechanism of interfacial formation of reverse micelles at the liquid-liquid interface (membrane) was also suggested by Plucinski and Nitsch [40] and Paul and Moulik [35].

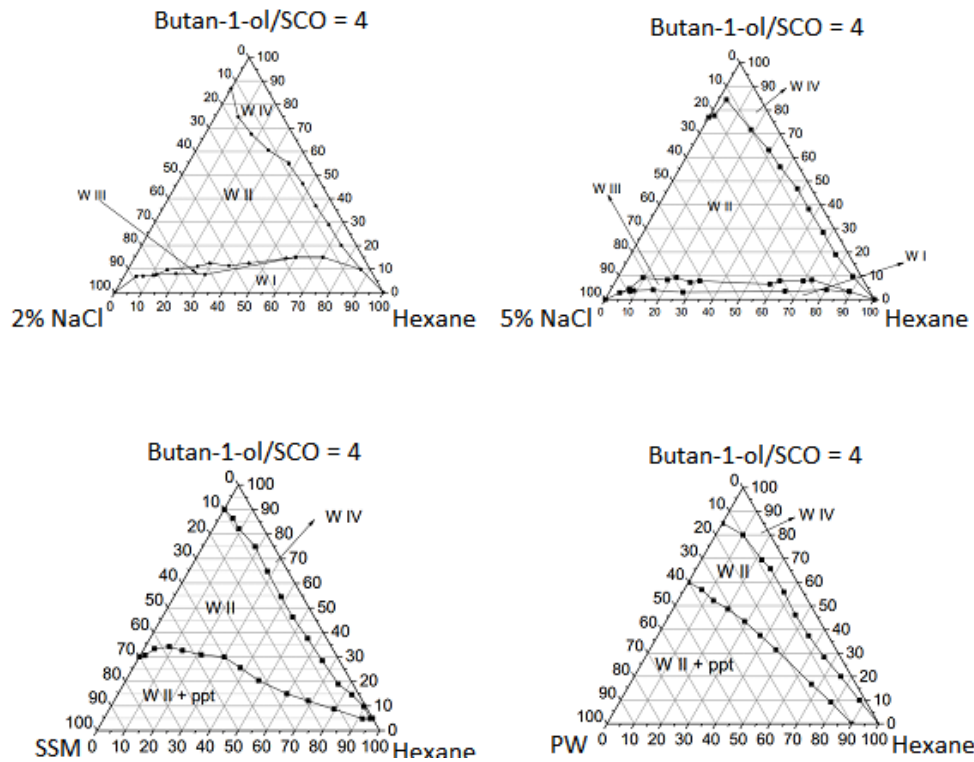


Fig. 3. Pseudo-ternary phase diagram for the studied systems showing the Winsor areas. WII+ppt indicates a Winsor II region with presence of precipitates (pH = 3.5; T = 27 °C).

Table 4

Experimental mixtures evaluated in metal removal by Winsor II systems, according to the design matrix (T = 27°C). The indexes 1 and 2 represent the duplicate assay

Point	Composition (wt. %)			Metal removal (E %)				MR*
	X _{AP}	X _{OP}	X _{C/S}	Ba	Cr	Mn	Fe	
A1	85	3	12	92.1	96.0	97.0	99.0	3.91
A2	85	3	12	91.8	94.1	99.1	99.4	3.92
B1	65	23	12	93.8	93.7	99.5	98.8	3.94
B2	65	23	12	94.0	90.2	97.3	99.1	3.88
C1	65	3	32	92.6	87.6	98.2	95.0	3.81
C2	65	3	32	96.0	93.3	98.6	98.4	3.94
D1	75	3	22	94.4	87.5	99.3	99.6	3.89
D2	75	3	22	92.7	92.9	98.6	97.8	3.90
E1	65	13	22	95.5	96.7	99.7	99.1	3.99
E2	65	13	22	95.9	94.3	98.5	99.0	3.96
F1	75	13	12	90.8	90.3	98.8	98.8	3.86
F2	75	13	12	92.8	88.6	97.3	98.1	3.85
G1	78	5	15	92.5	94.8	99.6	98.8	3.93
G2	78	5	15	93.1	93.4	98.0	98.6	3.91
H1	68	18	15	93.8	89.5	99.3	98.1	3.90
H2	68	18	15	93.5	90.6	96.7	97.2	3.86
I1	68	7	25	95.2	96.4	99.6	99.0	3.98
I2	68	7	25	95.7	96.0	98.5	99.2	3.98
J1	72	9	19	94.6	96.5	99.6	98.3	3.98
J2	72	9	19	95.5	95.2	99.1	98.9	3.95

* MR is the multiple response function.

3.3. Mathematical models and response surfaces

Linear, quadratic, and cubic models were tested to find the best response for the extraction process, with the special cubic model providing the best answer. This is a more complete model for considering the interactions between two ($X_{AP} \cdot X_{OP}$, $X_{AP} \cdot X_{C/S}$, $X_{OP} \cdot X_{C/S}$) and three factors ($X_{AP} \cdot X_{OP} \cdot X_{C/S}$). The obtained mathematic models are presented in Table 5.

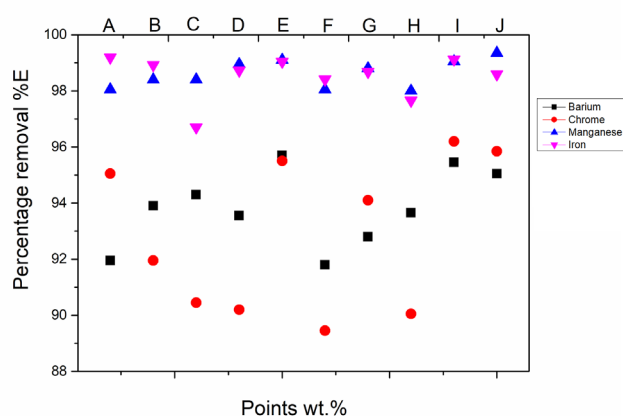


Fig. 4. Average metal removal (%E) considering each studied system.

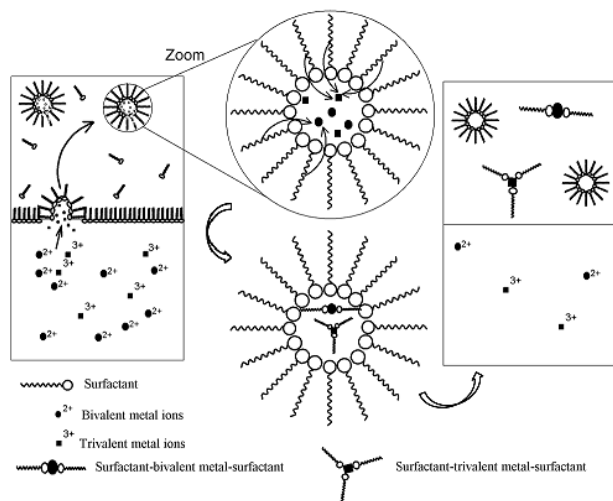


Fig. 5. Schematic mechanism showing the interfacial formation of Winsor II droplets and capture of metal ions.

Plots of response surfaces for metal removal (% E) were obtained using the mathematic models. For barium (Fig. 6A), points A (92%) and G (93%) represent the best choice for presenting higher percentages of produced water and lower amounts of active matter in their compositions, although the best quantitative results were obtained for points C, E, I, and J, with recovery rates as high as 95%.

For chromium, the surface obtained (Fig. 6B) shows values above 96% for points A and J. Points J and E are in a water-rich region, but with higher percentages of oil and C/S phases. Point A is considered the best choice because it has the highest percentage of aqueous phase and the lower amounts of oil and C/S phases.

The response surfaces for manganese (Fig. 6C) and iron (Fig. 6D) show, in the studied domain, removal efficiencies above 97%. Point A, as previously explained, was considered the best system for these metals.

In conclusion, the increase in metal removal is related directly with the increase of C/S phase and OP. Barium removal was influenced by the increase of C/S phase, while for calcium the OP had the greatest influence. The PW phase was considered as having the greater influence for chromium and iron removal. Manganese removal was influenced by the interaction of the three factors, reaching 99% of removal.

3.4. Optimization of metal removal

The multiple response (MR) function was used to optimize the extraction process and to determine the optimal condition for simultaneous removal of all studied metals [41]. The values of MR are determined by the normalization of the results for each point. First, the maximum removal value (%) is determined for each metal. Then, the removal value (%E) for each point, considering a given metal, is divided by its maximum removal value (%E max), as in Eq. (2).

$$MR_{m,i} = \frac{\%E_{m,i}}{\%E_{max_m}} \quad (2)$$

where m is the metal (Ba, Cr, Mn, Fe) and i is the experimental point. Eq. (3) is used to calculate the sum of multiple responses for each point.

$$MR_i = MR_{Ba,i} + MR_{Cr,i} + MR_{Mn,i} + MR_{Fe,i} \quad (3)$$

In Fig. 7 one can observe the iso response surface for simultaneous recovery of metals by using the multiple response function (MR). Point J [72 wt.% AP, 9 wt.% OP, 19 wt.% C/S] has the best composition for simultaneous removal of metals from produced water.

Table 5
Mathematic models obtained using the special cubic model for all metals assessed

Metal	Equation
Ba	$\%E = +91.99 \cdot X_{AP} + 93.66 \cdot X_{OP} + 94.47 \cdot X_{C/S} - 4.67 \cdot X_{AP} \cdot X_{OP} + 1.847 \cdot X_{AP} \cdot X_{C/S} + 6.31 \cdot X_{OP} \cdot X_{C/S} + 33.72 \cdot X_{AP} \cdot X_{OP} \cdot X_{C/S}$
Cr	$\%E = +95.29 \cdot X_{AP} + 90.87 \cdot X_{OP} + 91.16 \cdot X_{C/S} - 17.66 \cdot X_{AP} \cdot X_{OP} - 0.33 \cdot X_{AP} \cdot X_{C/S} + 16.59 \cdot X_{OP} \cdot X_{C/S} + 110.3 \cdot X_{AP} \cdot X_{OP} \cdot X_{C/S}$
Mn	$\%E = +98.15 \cdot X_{AP} + 98.13 \cdot X_{OP} + 98.42 \cdot X_{C/S} - 0.714 \cdot X_{AP} \cdot X_{OP} + 3.09 \cdot X_{AP} \cdot X_{C/S} + 2.77 \cdot X_{OP} \cdot X_{C/S} + 11.93 \cdot X_{AP} \cdot X_{OP} \cdot X_{C/S}$
Fe	$\%E = +99.14 \cdot X_{AP} + 98.50 \cdot X_{OP} + 97.14 \cdot X_{C/S} - 2.89 \cdot X_{AP} \cdot X_{OP} + 3.38 \cdot X_{AP} \cdot X_{C/S} + 4.94 \cdot X_{OP} \cdot X_{C/S} - 8.41 \cdot X_{AP} \cdot X_{OP} \cdot X_{C/S}$

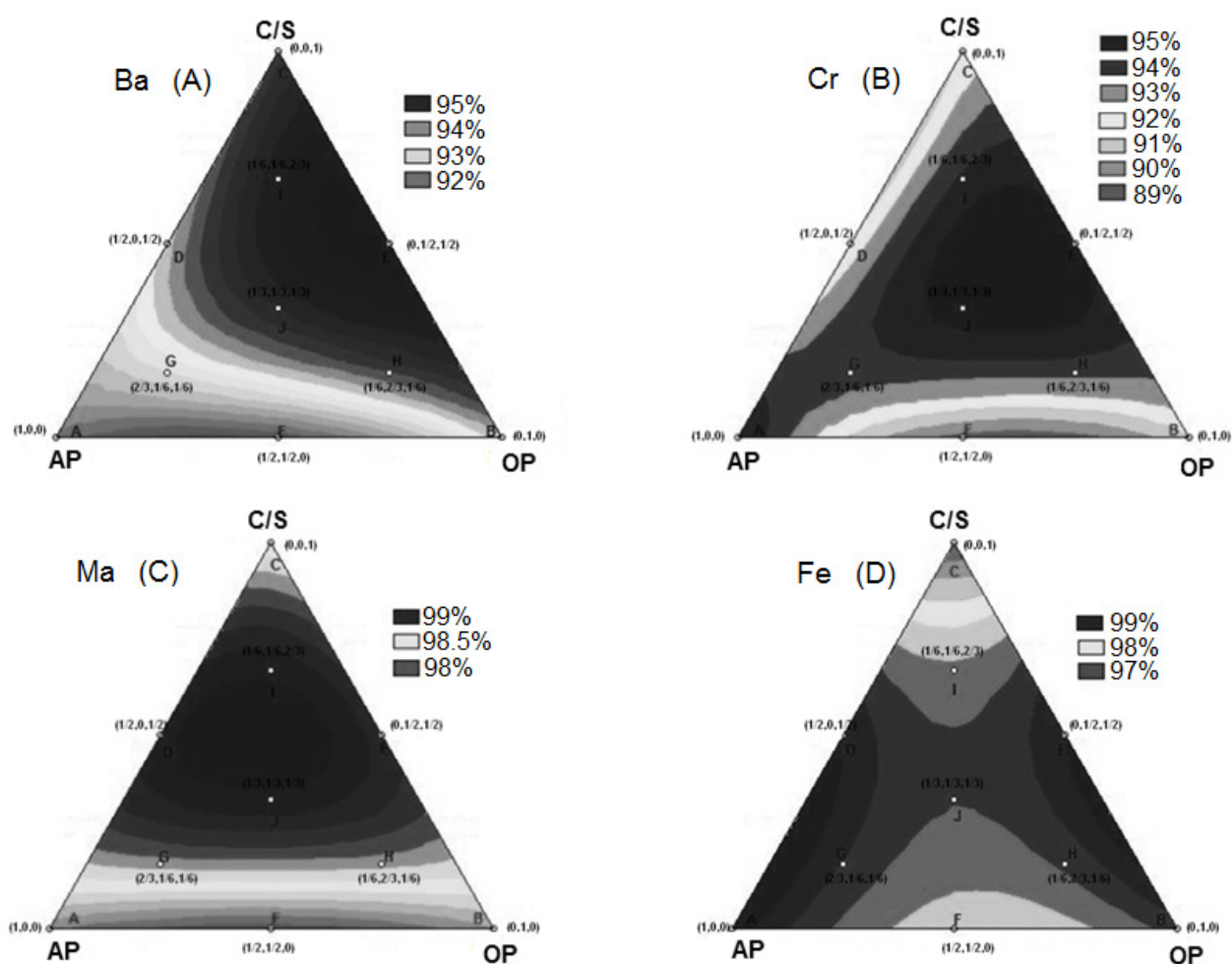


Fig. 6. Response surfaces for the removal percentiles (%E) using the special cubic model. (6A) Barium, (6B) Chromium, (6C) Manganese, and (6D) Iron.

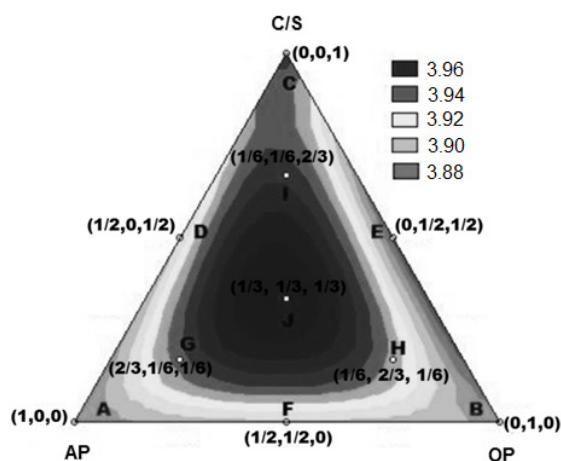


Fig. 7. Response surface for the simultaneous removal of metals under the special cubic model, using the multiple response (MR) function.

Fig. 8 shows Point J results for all studied metals, considering: metal initial concentration $[Me_i]$, metal concentration after microemulsion removal $[Me_f]$, and Brazilian standards for effluent release in natural waters [6,8]. One can observe that all metals are in agreement with the maximum contaminant level allowed by Brazilian standards. Barium, which was found at a concentration higher than those admitted by Brazilian standards (CONAMA), presented a sharp removal ($[Me_i] = 38.14$ ppm and $[Me_f] = 1.99$ ppm), reaching a value well below the maximum allowed limit. The results obtained in this research showed that the metals evaluated can be individually and simultaneously extracted by the developed systems, representing a viable option for the treatment of produced water.

4. Conclusions

The results obtained in this study show that the Winsor II (WII) extraction methodology, using saponified coconut oil as surfactant, is a viable alternative for simultaneous

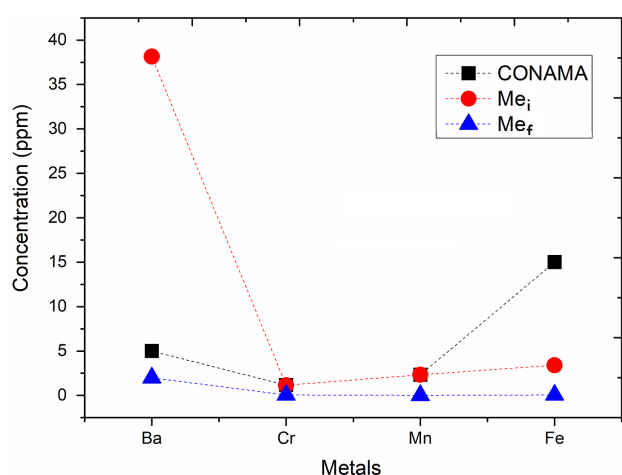


Fig. 8. Results in Point J for Ba, Cr, Mn, and Fe: $[Me_i]$ is the initial concentration; $[Me_f]$ is the final concentration, and CONAMA standards for effluent release in natural waters [6,7].

removal of metals from produced water. The Scheffé net experimental design allowed understanding the influence of the composition of systems in the metal removal and the optimization of the process, with removal rates as high as 99% for barium, chromium, manganese and iron, in only one step. When considering the simultaneous removal of metals in one step, a point composed by (w/w): 72% aqueous phase, 9% oil phase, and 19% active matter (cosurfactant and surfactant) presents the best results, with up to 94% removal. From an economic standpoint, the main advantage of this process is the removal of metal ions using a single-step extraction process. The metal ions are removed by forming complexes with surfactant molecules. However, it is necessary to carry out a study to evaluate the recovery of metals ions individually, aiming its further use in industrial processes.

Symbols

% E	—	Removal value $[mg \cdot L^{-1}]$
% E _{max}	—	Maximum removal value $[mg \cdot L^{-1}]$
AP	—	Aqueous phase
C/S	—	Mass ratio between co-surfactant and surfactant
CONAMA	—	National Environment Council (Brazil)
M ^{+x}	—	Metal ion in aqueous solution $[mg \cdot L^{-1}]$
Me _f	—	Concentration after microemulsion removal
Me _i	—	Metal initial concentration
MR	—	Multiple response
MR _{m,i}	—	Multiple response for each metal (m) and experimental point (i)
OP	—	Oil phase
PW	—	Produced water
RCOO ⁻ Na ⁺	—	Anionic surfactant (SCO) $[mg \cdot L^{-1}]$
RCOO _x ⁻ M ^{+x}	—	Surfactant with the extracted metal ion $[mg \cdot L^{-1}]$
S	—	Surfactant

SCO	—	Saponified coconut oil
SSM	—	Saline solution of metals
WI	—	Winsor I
WII	—	Winsor II
WIII	—	Winsor III
WIV	—	Winsor IV
X _{AP}	—	Mass percentage of produced water (aqueous phase) $[mg \cdot L^{-1}]$
X _{C/S}	—	Mass percentage of SCO/butan-1-ol $[mg \cdot L^{-1}]$
xNa ⁺	—	Ions released by surfactant $[mg \cdot L^{-1}]$
X _{OP}	—	Mass percentage of n-hexane (Oil Phase) $[mg \cdot L^{-1}]$

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