

CHROMIUM EXTRACTION BY MICROEMULSIONS IN TWO- AND THREE-PHASE SYSTEMS

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Abstract - Microemulsion systems were used to remove chromium from an aqueous solution obtained from acid digestion of tannery sludge. The systems were composed by: coconut oil soap as surfactant, 1-butanol as co-surfactant, kerosene as the oil phase, and chromium solution as the aqueous phase. Two- and three-phase microemulsion extraction methods were investigated in the experiments. Viscosity, effective diameter of the droplets, and extraction and re-extraction efficiencies were evaluated for each system. Two- and three-phase systems showed small variations in droplet diameter, which can be attributed to the formation of micellar structures. Chromium recovery efficiencies for the studied systems were over 96%. The re-extraction step showed that the stripping solution used can release more than 96% of the chromium from the microemulsion phase. Experimental results confirm that chromium can be recovered efficiently using microemulsion systems.

Keywords: Tannery sludge; Chromium; Microemulsion; Coconut oil soap; Winsor system.

INTRODUCTION

Chromium salts (Cr^{3+}) are used in tanning processes to transform hides or skins into leather (wet-blue). During the processing of these hides, large amounts of chemicals are used, producing solid and liquid wastes (Mant *et al.*, 2005; Haroun *et al.*, 2007; Lofrano *et al.*, 2013). According to Kiliç *et al.* (2011), tannery sludge contains high levels of chromium, and the disposal of this residue in landfills represents a loss of chromium, a commercially valuable raw material. The recovery of chromium is important to minimize the potential health risks associated with the landfill disposal of sludge. From an economic point of view, it reduces the volume of landfill waste.

Chromium is usually found in the environment in the +3 and +6 oxidation states. Its hexavalent form is very soluble, toxic, and potentially carcinogenic, whereas its trivalent form is more stable and presents lower toxicity (Gayathri & Senthil Kumar, 2010). It is well known that legal standards for environment control are becoming stricter and, consequently, the discharge of heavy metals into environment is being controlled more rigorously. Chromium is released into the environment by several industrial activities, such as: steel mills, electroplating, tanning, chemical manufacturing, pulp and paper manufacturing, wood preservation, dyes, ceramics, textiles, and coal beneficiation among others. (Lofrano *et al.*, 2013; Sharma & Adholeya, 2011; Gayathri & Senthil Kumar, 2010; Stasinakis *et al.*, 2003; Kotás & Stasicka, 2000; Selvi

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et al., 2001; Adriá-Cerezo *et al.*, 2000; Parks *et al.*, 2004).

Microemulsions are single-phased systems formed by the spontaneous solubilization of two otherwise immiscible liquids in the presence of surfactants, with or without the aid of a co-surfactant. They are dispersed, macroscopically homogeneous, thermodynamically stable, and optically transparent (Dantas Neto *et al.*, 2011; Qiu & Texter, 2008; Dantas Neto *et al.*, 2007; Moulik & Paul, 1998). According to Dantas Neto *et al.* (2009), the simplest structural model for microemulsions involves the dispersion of spherical droplets with diameters ranging between 10 and 100 nm. These structures may feature a monolayer of surfactants at their interface, depending on the composition and structure of the surfactant molecule used.

The microemulsion is considered to be water-continuous (Winsor I - WI) when it is in contact with excess oil, and oil-continuous (Winsor II - WII) when in contact with excess water. In a Winsor III system (WIII) three phases are present. The middle phase microemulsion is in equilibrium with the excess aqueous and organic phases. In a Winsor IV (WIV) system, only a microemulsion phase is formed (Moulik & Paul, 1998; Dantas Neto *et al.*, 2009; Castro Dantas *et al.*, 2003).

In a previous work, Castro Dantas *et al.* (2009) evaluated the use of Winsor II and Winsor IV microemulsions to remove chromium from leather tannery sediments. The sludge was treated by a solid-liquid extraction process (acid digestion), considering the effects of particle size, digestion temperature, and digestion time in chromium release. Chromium extraction values were up to 73.3% for Winsor II systems ([Cr] = 163.16 ppm, pH = 3.7), and up to 93.4% for Winsor IV ([Cr] = 479.86 ppm, pH = 0.6).

This paper investigates and compares two- and three-phase microemulsion systems, using saponified coconut oil as surfactant, for the recovery of chromium from a chromium-rich solution obtained from acid digestion of tannery sludge.

MATERIALS AND METHODS

Tannery Sludge Digestion Process and Chromium Quantification

The tannery sludge was collected from a local industry. It was dried under normal ambient condition (30 °C). The composition of the raw material and the methodology for sludge digestion are available in Castro Dantas *et al.* (2009). The quantification of chromium in the sediment was performed using an

X-ray fluorescence spectrometer (Shimadzu - model XRF 1800). The equipment detected all metals present in the sediment sample. Among these metals, chromium represented 13.32% of the dry weight. The determination of chromium concentration in aqueous solutions was carried out before and after the microemulsion extraction using a Varian SpectrAA-10-Plus atomic absorption spectrophotometer. All experiments, including the characterizations of the microemulsions, were performed in duplicate.

Microemulsion Systems

The composition of the coconut oil used in the experiments and the saponification reaction employed to obtain the saponified coconut oil (SCO) are described in Castro Dantas *et al.* (2009). The microemulsion system was composed of SCO as anionic surfactant (S), 1-butanol as co-surfactant (C), kerosene as the oil phase (OP), and chromium sludge solution as the aqueous phase (AP). A pseudo-ternary phase diagram with all Winsor regions was obtained in accordance with Castro Dantas *et al.* (2009).

Extraction Methods

Two extraction methods were tested. The first one, Method A, consisted of mixing predefined quantities of chromium sludge solution (acid digestion solution diluted in water and pH adjusted to 3.7 with 0.01N NaOH, [Cr] = 616ppm), 1-butanol/SCO, and kerosene until a phase separation was reached in the WII region (water-in-oil microemulsion phase in equilibrium with an aqueous phase in excess). The second one, Method B, consisted of mixing predefined quantities of the same constituents until a phase separation was obtained in the WIII region (microemulsion phase in equilibrium with aqueous and oil phases in excess). After the determination of the Winsor systems inside the pseudoternary phase diagram, four points in WII and four points in WIII regions were selected to evaluate chromium extraction, effective size of the droplets, optical microscopy, and viscosity. The extraction percentages were calculated by using the following equations:

$$M_{\text{added}} = V_E \times C_E \quad (1)$$

$$M_{\text{aqueous phase}} = V_{\text{AP}} \times C_{\text{AP}} \quad (2)$$

$$E_{\text{Cr}} (\%) = \frac{(M_{\text{added}} - M_{\text{aqueous phase}})}{M_{\text{added}}} \times 100 \quad (3)$$

where M_{added} is the total amount of metal in the sys-

tem (mg); $M_{\text{aqueous phase}}$ is the total amount of metal in the aqueous phase after extraction (mg); V_E is the volume of acid digestion solution used in the system; V_{AP} is the volume of aqueous phase after extraction; C_E is the concentration of metal in the acid digestion solution; C_{AP} is the concentration of metal in the aqueous phase after extraction; and E_{Cr} is the percentage of chromium recovered.

Chromium Re-Extraction from the Microemulsion Phase

After the extraction process, a re-extraction process was performed to recover the chromium from the chromium-bearing microemulsion phase. The re-extraction process was made by adding 6 mL of a 10 M HCl solution to the chromium-bearing microemulsion phase. The presence of hydrochloric acid reduced the hydrophilicity of the surfactant, allowing the formation of a new aqueous phase rich in metal. The excess aqueous phase was separated using a syringe, and it was analyzed by Flame Atomic Absorption Spectroscopy (FAAS). The re-extraction percentile (RE_{Cr}) was calculated by using the following equations:

$$M_{\mu E} = V_{\mu E} \times C_{\mu E} \quad (4)$$

$$M_{re} = V_{re} \times C_{re} \quad (5)$$

$$RE_{Cr} = \frac{[M_{\mu E} - (M_{\mu E} - M_{re})]}{M_{\mu E}} \times 100$$

$$= \frac{M_{re}}{M_{\mu E}} \times 100 \quad (6)$$

where $M_{\mu E}$ is the total amount of metal in the microemulsion phase (mg); M_{re} is the total amount of metal in the aqueous phase after re-extraction (mg); $V_{\mu E}$ is the volume of microemulsion used in the re-extraction process; V_{re} is the volume of aqueous phase after re-extraction; $C_{\mu E}$ is the initial concentration of metal in the microemulsion; and C_{re} is the concentration of metal in the aqueous phase after re-extraction.

Physicochemical Characterization of Microemulsion Systems

Viscosity

According to Moulik and Paul (1998), measurements of viscosity are crucial when studying fundamental physicochemical reactions in colloidal dispersions. These data can provide first hand information

on the internal consistency of colloidal dispersions, as well as furnish knowledge on the overall geometry of the particles of the dispersed phase. In this study, a Haake Mars rheometer was used to measure all viscosities. The measurements were taken at room temperature (27 ± 0.2 °C), with a shear rate ranging from 0.00 to 500 s^{-1} .

Effective Droplet Size

This study determined the droplet size for systems with two- and three-phase regions. The characterization of particle size correlated size with the distribution of micelle droplets. The diameters of the droplets and their distribution in the microemulsions investigated were determined by using a dynamic light scattering particle analyzer (Microtrac Granulometer - Nanotrac 252) and the microtrac FLEX application software program.

Microscopic Study of Chromium Extraction by WII and WIII Microemulsion Systems

Winsor II (two-phase) and Winsor III (three-phase) microemulsions were evaluated by optical microscopy (Olympus BX51M), and the behavior of the phase separation was identified by using a 50x magnification. The active matter and the oil phase were placed in a Petri dish, according to the experimental composition of the studied system. The required amount of digested acid solution (wt.%) was then slowly added to the Petri dish to obtain either a WII or a WIII system. The dynamic behavior of the phases was observed through the microscope when the chromium solution was added.

RESULTS AND DISCUSSION

Pseudo-Ternary Phase Diagram

The first step in this research was to obtain the Winsor regions inside the pseudo-ternary phase diagram (Figure 1). Based on work conducted by Castro Dantas *et al.* (2003), the co-surfactant/surfactant ratio (C/S) was set at 4 and the metal aqueous solution pH at around 3.7. One can observe that the WII and WIII regions are present in the water-rich side, in the oil-rich side, and in the central portion of the pseudo-ternary phase diagram.

Chromium Extraction by Microemulsion

As explained in the Experimental section, the chromium extraction used Method A to evaluate the

results. It consisted of placing the digested acid solution in contact with the oil phase and the active material (surfactant + co-surfactant) in concentrations predefined to form two-phase systems (W II). Method B used the same procedure to form the three-phase systems (W III). Table 1 shows the composition of the evaluated points and the results for chromium recovery.

Table 1 shows that all points had chromium extractions over 96%. Systems inside the WII region (5, 6, 7, and 8) have w/o micelles (reverse micelles). Systems within the WIII region (1, 2, 3, and 4) have o/w and w/o micelles (bi-continuous systems). All systems showed very similar extraction behavior, which indicates that the shape of the micelle and the proportion between the oil and water phases are not determining factors in chromium extraction. Systems within the WIII region were considered appropriate because a chromium-rich microemulsion was obtained with a lower volume and with excess oil after the extraction process. Another important factor is the small amount of C/S used in WIII systems. Considering chromium extraction and economic factors, Point 4 represents the best choice.

After the extraction process, a re-extraction step was performed. The results for re-extraction are

shown in Table 1. The chromium recoveries for microemulsions using WII and WIII showed similar behaviors, with results ranging from 96 to 98%.

Viscosity Studies

Several systems with different compositions inside the WII and WIII regions were chosen to determine their viscosities (Table 2). These systems were selected from the water-rich, the oil-rich, and the central portion of the pseudoternary phase diagram. The goal was to observe the behavior of micellar aggregates with varying proportions of oil and water. To obtain the composition of the microemulsion phase after the separation, the volume of the oil phase in excess (WIII systems) and the aqueous phase in excess (WII and WIII systems) were measured and it was assumed that all active material (C/S ratio) remained in the microemulsion phase. According Sripriya *et al.* (2007), in microemulsion systems, viscosity is a macroscopic property which largely depends upon to the type of aggregates present, on their interactions, and on its concentration. Thus it is mainly used to monitor the microstructure of the system.

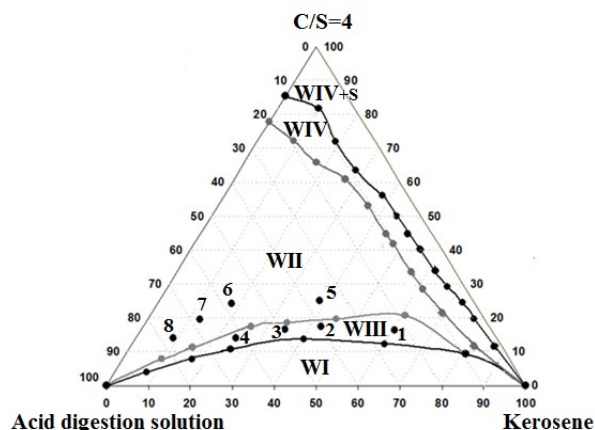


Figure 1: Pseudo-ternary phase diagram showing the Winsor regions and the extraction points for the studied system ($[Cr] = 616$ ppm, pH 3.7, $T = 27$ °C).

Table 1: Composition of the extraction points and results for chromium extraction (%) ($[Cr] = 616$ ppm, pH = 3.7, $T = 27$ °C) and re-extraction ($T = 27$ °C).

	1 WIII	2 WIII	3 WIII	4 WIII	5 WII	6 WII	7 WII	8 WII
C/S (wt.%)	16	18	17	14	25	24	20	14
OP (wt.%)	61	42	35	24	39	18	12	9
AP (wt.%)	23	40	48	62	36	58	68	77
C_{AP} (ppm)*	12.7	13.4	12.6	14.8	17.5	17.2	20.1	20.0
E_{Cr} (%)*	96.49	99.18	98.71	98.29	98.43	97.82	97.14	97.05
RE_{Cr} (%)	96.34	98.71	98.66	98.18	97.37	96.68	96.55	96.20

Table 2: Viscosity, volume, and composition of the microemulsion phase inside the WII and WIII regions after chromium extraction, at 27 °C.

Exp. Points		1(WIII)	2(WIII)	3(WIII)	4(WIII)	5(WII)	6(WII)	7(WII)	8(WII)
Viscosity (Pa.s)		4.90	4.80	4.70	3.82	3.52	4.70	4.70	3.70
μE (wt.)	AP	7.72	4.45	9.77	8.59	5.97	8.71	13.05	8.03
	OP	49.77	55.47	35.45	33.25	57.31	39.22	32.61	35.93
	C/S	42.51	40.08	54.78	58.16	36.72	52.07	54.34	56.04

One can observe that low viscosity values were obtained for all studied systems. For WIII microemulsions, the oil phase had a major influence on the results. The three-phase system contained a microemulsion which could not be identified as w/o or o/w (bi-continuous structure). For WII systems, it was not possible to observe a general trend. Considering the microemulsion volume after chromium extrac-

tion, Point 4 represents the best choice.

Effective Droplet Size

Figure 2 shows the results for effective droplet size (diameter) for all systems studied. It is important to highlight that only the microemulsion phase of each system was evaluated in the present study.

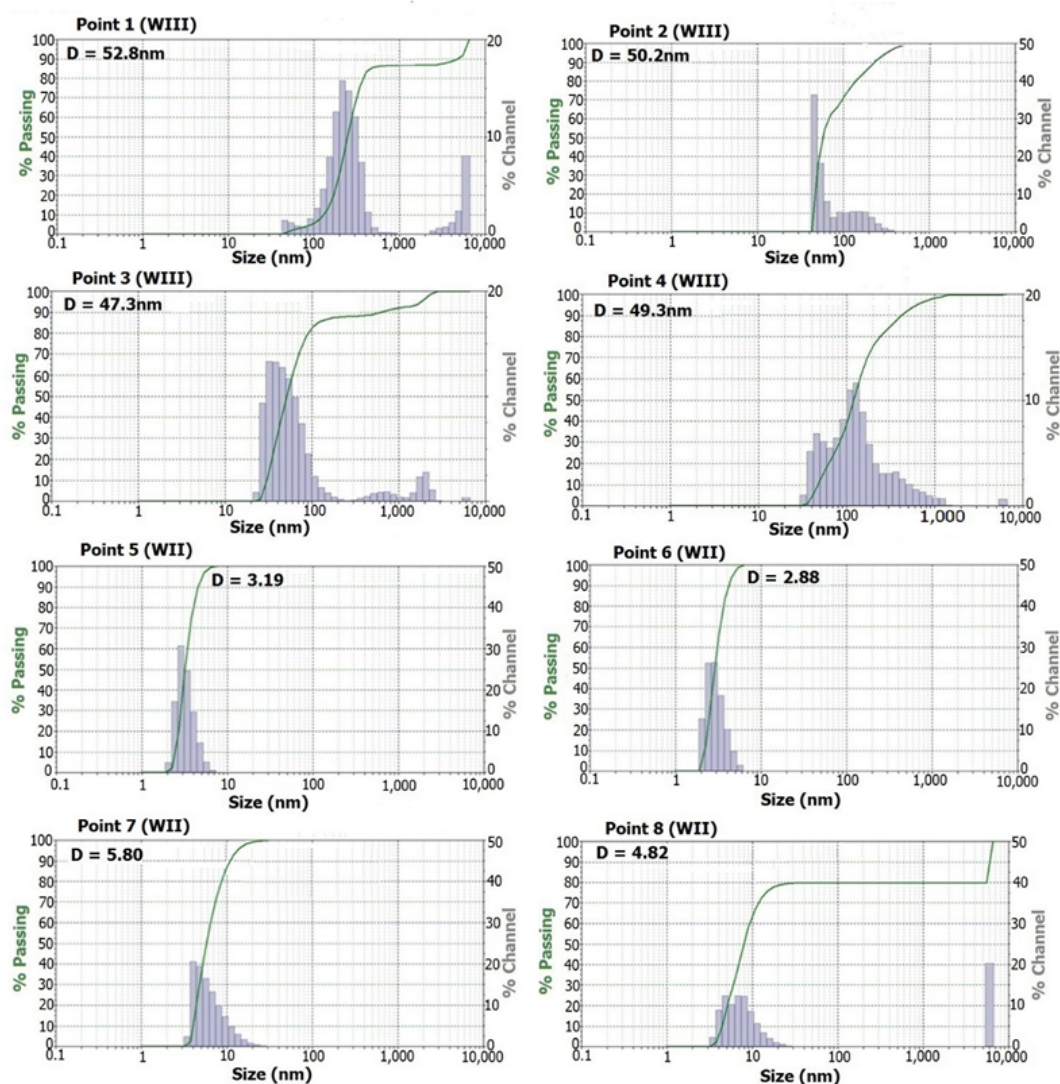
**Figure 2: Droplet diameters and their distribution for all studied systems.**

Figure 2 shows that the micellar structures formed in WIII systems were larger than those formed in WII systems. For WII systems, with only reverse micelles, it was observed that the size of the droplets is more uniform. For points in the WIII region, with direct and reverse micelles, a wider distribution was observed.

Microscopic Study of Chromium Extraction Using Microemulsion Systems

In this study, to examine the behavior of chromium in microemulsion systems, a WII distilled water-based microemulsion (Figure 3a) was compared with one containing a digested acid solution (Figure 3b). Small well-defined spherical droplets were observed in the microemulsion with chromium. The location of chromium in the outer ring boundary of the droplets was due to the interactions between chromium ions and the surfactant molecule. In the water-based microemulsion, the small droplets had a

less intense boundary line. Comparing the Chromium extraction in WII (Figure 3b) with that in WIII systems (Figure 3c), one can observe that a greater amount of chromium-rich droplets appear in WIII system.

To monitor the behavior of the systems, a new study was performed adding 2 wt.% NaCl to the chromium solution. In this study, the active matter and the oil phase were placed in a Petri dish. The chromium solution was added to the Petri dish in pre-determined amounts to obtain WII (Figure 4a) and WIII systems (Figure 4b). The dynamic behaviors of the phases were examined microscopically when the solution was added. Analyzing Figure 4a, one can view the formation of two phases, as well as the presence of chromium-bearing microdroplets in the microemulsion phase. On the other hand, Figure 4b shows the formation of three microemulsion phases. The intermediate phase had a lower volume and presented chromium-bearing microdroplets.

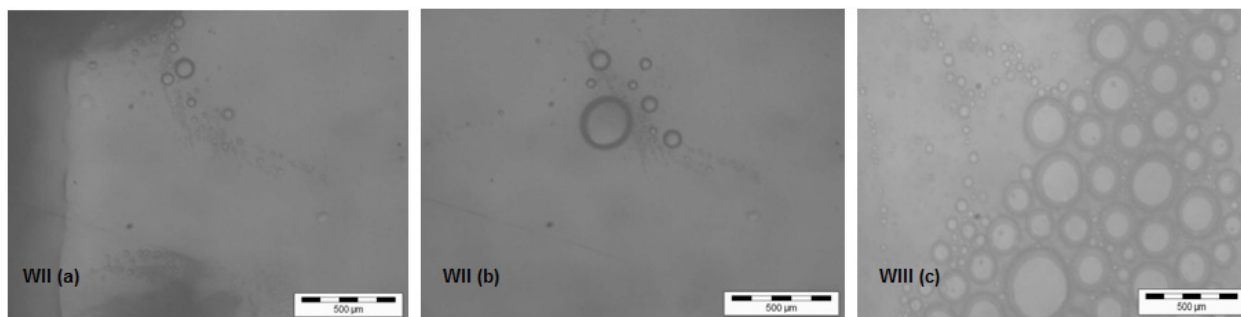


Figure 3: Optical microscopy photos, with a magnification of 50x (500 µm), for microemulsion systems: (a) WII with distilled water (27 °C), (b) WII with digested acid solution ([Cr] = 616 ppm, pH = 3.7, 27 °C), and (c) WIII with digested acid solution ([Cr] = 616 ppm, pH = 3.7, 27 °C).

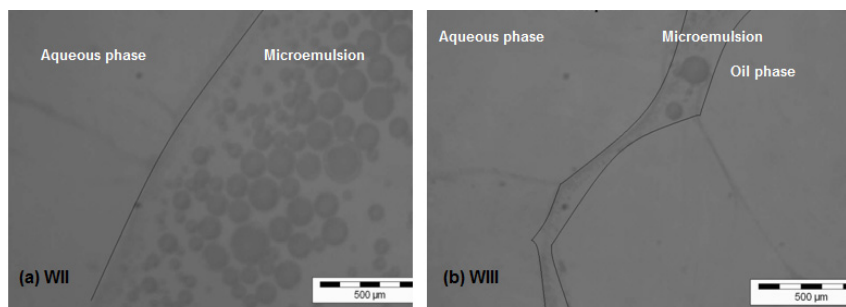


Figure 4: Optical microscopy photos, with a magnification of 50x (500µm), for WII (a) and WIII (b) microemulsion systems with 2 wt.% NaCl digested acid solution ([Cr] = 616 ppm, pH = 3.7, 27 °C).

CONCLUSIONS

Winsor II and Winsor III microemulsion systems were used to extract chromium from a tannery sludge solution. The main conclusions may be summarized as follows:

1. The pseudo-ternary phase diagram showed well-defined WII and WIII regions, which extended from the water-rich to the oil-rich side;
2. WII and WIII systems showed a very similar extraction behavior, with chromium extractions over 96%;
3. Systems in the Winsor III region were considered to be more appropriate due to the small presence of C/S, to the possibility of recovering the excess oil phase, and to the formation of a chromium-bearing microemulsion in lower volume;
4. Chromium recovery in the re-extraction stage showed a similar behavior for WII and WIII microemulsions, demonstrating the effectiveness of the stripping solution.
5. A microemulsion system containing 14 wt.% saponified coconut oil, 24 wt.% kerosene, and 62 wt.% tannery sludge solution (System 4) was very effective, representing the best choice.

NOMENCLATURE

AP	aqueous phase
C	co-surfactant
C/S	co-surfactant/surfactant ratio
C_{AP}	concentration of metal in the aqueous phase after extraction (ppm)
C_E	concentration of metal in the acid digestion solution (ppm)
C_{re}	concentration of metal in the aqueous phase after re-extraction
$C_{\mu E}$	initial concentration of metal in the microemulsion
D	droplet diameter (nm)
E_{Cr}	percentage of chromium extracted (%)
FAAS	Flame Atomic Absorption Spectrometry
M_{added}	total amount of metal in the acid digestion solution (g)
$M_{aqueous\ phase}$	total amount of metal in the aqueous phase after extraction (g)
M_{re}	total amount of metal in the aqueous phase after re-extraction (mg)
$M_{\mu E}$	total amount of metal in the microemulsion phase (mg)
OP	oil phase
RE_{Cr}	Chromium re-extraction (%)
S	surfactant

SCO	Saponified Coconut Oil
V_{AP}	volume of aqueous phase after extraction (mL)
V_E	volume of acid digestion solution used in the system (mL)
V_{re}	volume of aqueous phase after re-extraction
$V_{\mu E}$	volume of microemulsion used in the re-extraction process
WI	Winsor I (a microemulsion phase in equilibrium with an organic phase in excess)
WII	Winsor II (a microemulsion phase in equilibrium with an aqueous phase in excess)
WIII	Winsor III (a microemulsion phase in equilibrium with both excess aqueous and organic phases)
WIV	Winsor IV (only a single microemulsion phase)

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REFERENCES

- Adriá-Cerezo, D. M., Llobat-Estellés, M., Maurí-Aucejo, A. R., Preconcentration and speciation of chromium in waters using solid-phase extraction and atomic absorption spectrometry. *Talanta*, 51(3), 531-536 (2000).
- Castro Dantas, T. N., Dantas Neto, A. A., Moura, M. C. P. A., Barros Neto, E. L., Forte, K. R., Leite, R. H. L., Heavy metals extraction by microemulsions. *Water Research*, 37(11), 2709-2717 (2003).
- Castro Dantas, T. N., Oliveira, K. R., Dantas Neto, A. A., Moura, M. C. P. A., The use of microemulsions to remove chromium from industrial sludge. *Water Research*, 43(5), 1464-1470 (2009).
- Dantas Neto, A. A., Castro Dantas, T. N., Moura, M. C. P. A., Gurgel, A., Barros Neto, E. L., Extraction of heavy metals by microemulsions: A novel approach. In: Warey, P. B. (Editor) *New Research on Hazardous Materials*, Nova Science Publishers, v. 10, USA, p. 311-345 (2007).
- Dantas Neto, A. A., Castro Dantas, T. N., Moura, M. C. P. A., Barros Neto, E. L., Gurgel, A., Microemulsions as potential interfacial chemical systems

- applied in the petroleum industry. In: Fanun, M. (Editor) *Microemulsions: Properties and Applications*, CRC Press, Surfactant Science Series, v. 144(15), USA, p. 411-450 (2009).
- Dantas Neto, A. A., Fernandes, M. R., Barros Neto, E. L., Castro Dantas, T. N., & Moura, M. C. P., Alternative fuels composed by blends of nonionic surfactant with diesel and water: Engine performance and emissions. *Brazilian Journal of Chemical Engineering*, 28(3), 521-531 (2011).
- Gayathri, R., & Senthil Kumar, P., Recovery and reuse of hexavalent chromium from aqueous solutions by a hybrid technique of electrodialysis and ion exchange. *Brazilian Journal of Chemical Engineering*, 27(1), 71-78 (2010).
- Haroun, M., Idris, A., Omar, S. R. S., A study of heavy metals and their fate in the composting of tannery sludge. *Waste Management*, 27(11), 1541-1550 (2007).
- Kiliç, E., Font, J., Puig, R., Çolak, S., Çelik, D., Chromium recovery from tannery sludge with saponin and oxidative remediation. *Journal of Hazardous Materials*, 185(1), 456-462 (2011).
- Kotás, J., Stasicka, Z., Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution*, 107(3), 263-283 (2000).
- Lofrano, G., Meriç, S., Zengin, G. E., Orhon, D., Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review. *Science of Total Environment*, 461-462, 265-281 (2013).
- Mant, C., Costa, S., Williams, J., & Tambourgi, E., Studies of removal of chromium by model constructed wetland. *Brazilian Journal of Chemical Engineering*, 22(3), 381-387 (2005).
- Moulik, S. P., Paul, B. K., Structure, dynamics and transport properties of microemulsions. *Colloid and Interface Science*, 78(2), 99-195 (1998).
- Parks, J. L., McNeil, L., Frey, M., Eaton, A. D., Haghani, A., Ramirez, L., Edwards, M., Determination of total chromium in environmental water samples. *Water Research*, 38 (12), 2827-2838 (2004).
- Qiu, Z., Texter, J., Ionic liquids in microemulsions. *Colloid and Interface Science*, 13(4), 252-262 (2008).
- Selvi, K., Pattabhi, S., Kadirvelu, K., Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon. *Bioresource Technology*, 80, 87-89 (2001).
- Sharma, S., Adholeya, A., Detoxification and accumulation of chromium from tannery effluent and spent chrome effluent by *Paecilomyces lilacinus* fungi. *International Biodeterioration & Biodegradation*, 65(2) 309-317 (2011).
- Sripriya, R., Raja, M., Santhosh, G., Chandrasekaran, M., Noel, M., The effect of structure of oil phase, surfactant and co-surfactant on the physicochemical and electrochemical properties of bicontinuous microemulsion. *Journal of Colloid and Interface Science*, 314(2), 712-717 (2007).
- Stasinakis, A. S., Nikolaos, S. T., Mamais, D., Karivali, M., Lekkas, T. D., Chromium species behaviour in the activated sludge process. *Chemosphere*, 52(6), 1059-1067 (2003).