

Evaluation and optimization of chromium removal from tannery effluent by microemulsion in the Morris extractor

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Abstract

In this research a surfactant derived from a vegetable oil (coconut oil) was used to remove chromium from a tannery effluent. In the extraction process, a Morris extractor was used. Important variables used in assessing the optimization of the process included agitation speed, solvent rate and total flow rate. The experiments were conducted using a 2^3 factorial design. According to the response from the experimental design, the effects of each variable were calculated and the interactions between them determined. Response surface methodology was employed to study the effects of the studied variables. The optimum operational conditions were: agitation speed, 428 rpm; solvent rate, 0.37; total flow rate, 2.01 h^{-1} . After extraction process, a re-extraction study was accomplished and the obtained results showed that chromium could be removed from the microemulsion phase by hydrochloric and sulphuric acidic solutions, what allows its reuse in the leather manufacturing process.

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1. Introduction

Heavy metals are toxic substances that have been discharged into water bodies as industrial wastes, causing environmental damage. They are not biodegradable and tend to accumulate in living organisms, causing serious diseases and disorders [1–3]. Chromium has received a great deal of attention. Chromium-laden wastewater can be originated from leather tanning, dyes and pigments manufacturing, wood preserving, and electroplating [4–5].

Tanning industries, due to the complexity of the animal hide (or skin) transformation into leather, are industries that use a great number of chemical agents and produce an enormous volume of residual waters and solid residues.

The production of wet blue (chrome leather) occurs in a number of stages. The tanning process uses an acidic solution of chromium and during the process Cr(III) forms

crosslinks between the collagen fibers. The effluent from the chromium stream consists primary of a saline solution of spent chromium and residual fungicide at a pH between 3 and 5 [6–9].

The industry is quite interested in efficient effluent treatment processes to reach the standards established by environmental agencies. The modern tanneries have satisfactory treatment processes, but the effluents of several small or/and old leather industries do not receive the convenient treatment for the reduction of the chromium content to the levels established by the legislation [8].

In the world, the most usual technology for the treatment of the liquid residues generated by the leather industries is constituted of physical–chemical treatment, for the precipitation of chromium and sulfide oxidation, followed by units of biological treatment, usually activated sludge or aerated lagoons systems, being a process that represents high capital and/or operational costs [9].

The development of new technologies is the main objective of this research that intends to develop and use an

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unconventional process of liquid–liquid extraction using a microemulsion as solvent. Previous works [10–14] demonstrated that the microemulsions are quite efficient in metallic ions recovery processes.

A microemulsion is defined as a system formed by the dispersion of microdroplets of two immiscible liquids, stabilized by an interfacial membrane formed by surfactant and cosurfactant. They are thermodynamically stable, homogeneous and optically isotropic solutions. In excess of oil, the microemulsion coexists with one oil continuous phase (Winsor I) and in excess of water it coexists with one aqueous continuous phase (Winsor II). In Winsor III system three phases are present, where the microemulsion is in equilibrium with both excess aqueous and organic phases, and in Winsor IV only a microemulsion phase is formed [15–18].

In this study, the optimization of chromium recovery process from tannery effluents in the Morris extractor was performed. A factorial design 2^3 was carried out in order to determine the effects of agitation speed, solvent rate, and total flow rate. Re-extraction studies were accomplished seeking chromium reuse in the leather manufacturing process.

2. Materials and methods

2.1. Chemicals

The chemicals used in the experimental procedure were analytical grade except the surfactant (derived from a coconut oil of regional production saponified using NaOH in a

stoichiometric reaction) and kerosene (Petrobrás – chemical composition: paraffinic hydrocarbons – minimum 70%, aromatic hydrocarbons – maximum 20% and olefinic hydrocarbons – maximum 5%; density <1; viscosity 2.7 cSt at 20 °C; distillation range 150–300 °C at 760 mmHg), and were used without previous purification. The heavy metal concentrations in aqueous samples were analyzed by flame atomic absorption spectroscopy (FAAS) using a VARIAN SpectrAA-10 PLUS in an air–acetylene flame. When required, pH was adjusted by using 1N HNO₃.

2.2. Microemulsion (μE)

The extraction system was composed basically by a microemulsion in equilibrium with an aqueous phase in excess (Winsor II). The used microemulsion was composed by 3.3 wt.% surfactant (saponified coconut oil – SCO); 57.0 wt.% aqueous phase (tannery effluent); 13.2 wt.% cosurfactant (*n*-butanol – 99% P.A.), and 26.5 wt.% oil phase (kerosene). This composition was based on a previous work [14] of heavy metal extraction using microemulsions. The pseudoternary phase diagram showing the Winsor's regions and the chosen point is represented in Fig. 1. In this study, was used as aqueous phase distilled water containing 2% NaCl (pH = 3.5) to simulate tannery effluent salinity and pH.

2.3. Microemulsion load capacity

The study of microemulsion load capacity, that is, the maximum of chromium extracted by the same microemulsion,

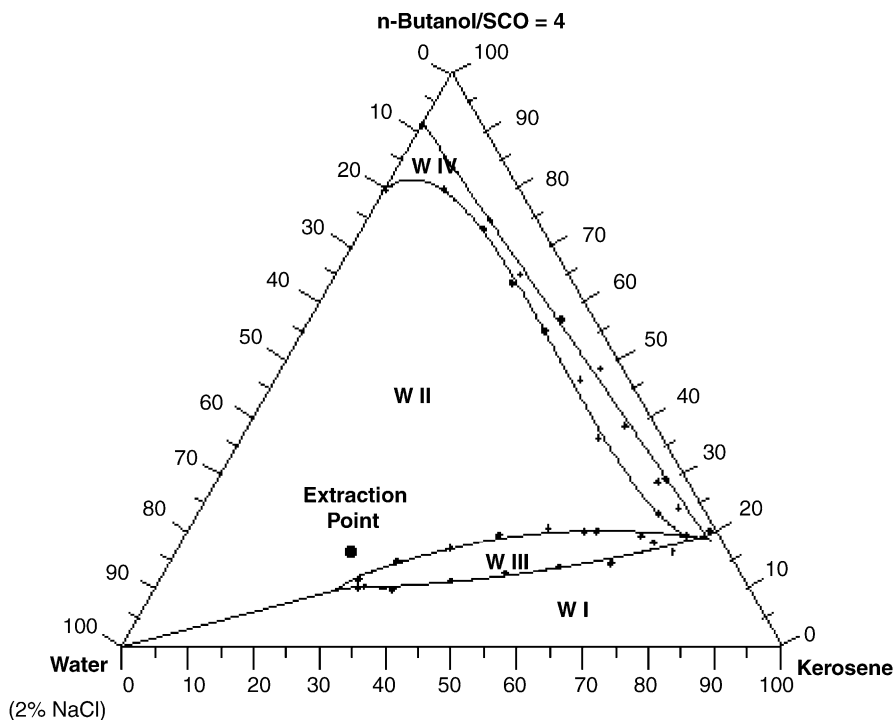


Fig. 1. Winsor's regions for the system composed by water/kerosene/SCO + *n*-butanol ($T = 27\text{ }^{\circ}\text{C}$; C/S ratio = 4.0; aqueous phase pH = 3.5).

Table 1
Microemulsion load capacity ($V_{\mu E} = 23 \text{ mL}$)

Stage	$V_{SS}(\text{mL})$	$\sum V_{SS}(\text{mL})$	$C_{R_{ADDED}}(\text{mg})$	$C_{R_{REMOVED}}(\text{mg})$	Extraction(%)	$[C_{\mu E}](\text{g Cr L}^{-1})$
1	28.16	28.16	44.51	44.42	99	1.78
2	6.00	34.16	9.50	9.49	99	2.16
3	6.00	40.16	9.50	9.47	99	2.53
4	6.00	46.16	9.50	9.48	99	2.91
5	6.00	52.16	9.50	9.46	99	3.29
6	6.00	58.16	9.50	9.34	98	3.67
7	6.00	64.16	9.50	1.13	11	3.71
8	6.00	70.16	9.50	0.00	0	3.71

was accomplished with the purpose of obtaining information about the solvent rate to be used in the Morris extractor. To obtain the microemulsion, the constituents were mixed forming a Winsor II system, taken as calculation base 50 g, where was used 28.16 mL of a chromium synthetic effluent (1.58 g Cr L^{-1} ; pH 3.5; 2% NaCl). The system was stirred during 10 min and after that maintained in rest (1 h) for complete phase separation (Winsor II – microemulsion phase = 23 mL). The aqueous phase in excess, poor in chromium, was removed using a syringe. The extraction percentile was calculated through the following equations:

$$C_{R_{ADDED}} = V_{SS} C_{SS} \quad (1)$$

$$C_{R_{AP}} = V_{AP} C_{AP} \quad (2)$$

$$\% \text{ Extraction} = [(C_{R_{ADDED}} - C_{R_{AP}}) / C_{R_{ADDED}}] \times 100 \quad (3)$$

where $C_{R_{ADDED}}$ is the total amount of chromium added to the system, $C_{R_{AP}}$ is the amount of chromium present in the aqueous phase after extraction process; V_{SS} is the chromium synthetic solution volume added and C_{SS} is its chromium concentration; V_{AP} is the volume of aqueous phase formed after extraction process and C_{AP} its chromium concentration.

Chromium synthetic solution (6 mL) was again added to the microemulsion phase (Table 1) and the system was shaken and maintained in rest during 1 h, being the new aqueous

phase formed removed. The process was repeated several times until the microemulsion phase saturation was observed.

2.4. Tannery effluent

The wastewater from chromium stream was collected from the tannery rotating drum. The effluent is a saline solution of spent chromium (1.65 g Cr L^{-1} – pH 3.54). It was analyzed for Cr by FAAS.

2.5. Chromium extraction from tannery effluent

The Morris extractor [19] was used in the extraction process (Fig. 2). The experiments were carried out at room temperature ($30 \pm 3 \text{ }^\circ\text{C}$) using in one side of the extractor a mixture composed by cosurfactant, surfactant, and oil phase (CSO mixture) and in the other side the tannery effluent.

As can be seen in Fig. 2, the extractor extremities have two great settler vessels. The vessel near to the CSO mixture feeding has an opening in the lower part where the chromium poor aqueous phase is removed (raffinate phase – after extraction process), while the other one, close to the effluent feeding, has an opening in the upper part, where the microemulsion phase, loaded with chromium, is removed (extract phase). In this countercurrent extraction process the two phases, microemulsion and chromium wastewater, flow from stage to stage in

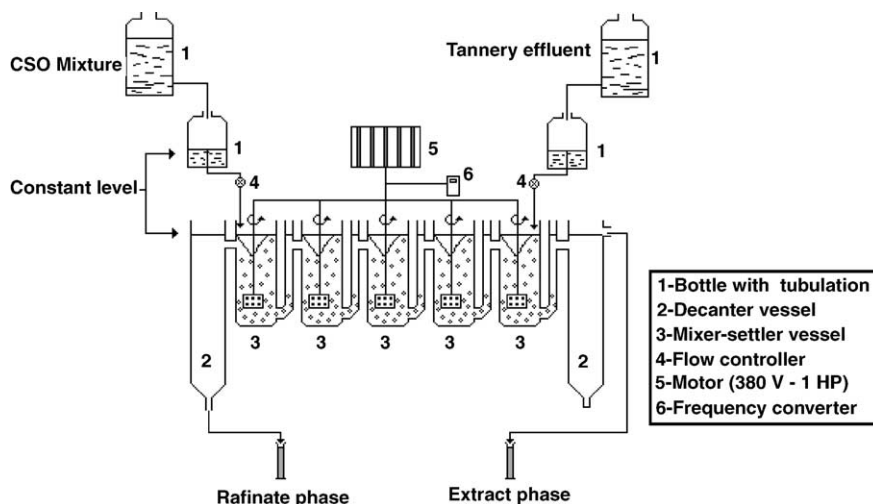


Fig. 2. Extraction apparatus – Morris extractor.

opposite directions. The continuous phase was composed by tannery effluent and the dispersed one by the microemulsion, passing as liquid droplets. The operational conditions (agitation speed, effluent flow rate, CSO mixture flow rate, and solvent rate) were varied seeking to evaluate its influence in the extraction process. In all the experiments five mixer-settler vessels were used. To place the extractor in operation, tannery effluent was supplied with the flow rate adjusted to the wanted value. As soon as the extraction operation level was reached, the CSO mixture feeding was introduced in a desired flow rate.

2.6. Re-extraction process

After the extraction stage in the Morris extractor, the microemulsion phase, rich in chromium, was placed in contact with a concentrated acidic solution promoting a new Winsor II system. The addition of the acidic solution causes the passage of the heavy metal ions, present in the microemulsion, to a new aqueous phase, turning it more concentrated than the feeding solution. The microemulsion from the extraction process was used for the choice of the acid to be used in the re-extraction process. Re-extraction agents tested included the hydrochloric acid (HCl; 8 and 10 M – Merck) and the sulphuric acid (H₂SO₄; A.G. – Merck) and the process was carried out at 28, 40 and 50 °C. Each set consisted of 12 samples with 8 mL of microemulsion and 3 mL of acidic solution. The samples were stirred during 5 min and left in rest for the desired time interval (15 min to 48 h). After each contact time, the aqueous phase formed was collected by a syringe and analyzed in FAAE.

2.7. Factorial design

A factorial design 2³ was performed in order to study the effects of the following variables: agitation speed (*A*; rpm), solvent rate (*B*), and total flow rate (*C*; L h⁻¹). To carry out the experimental design, eight experimental runs were performed (all in duplicate). The response is the chromium extraction percentile. Table 2 shows the choose levels for each variable and Table 3 shows the recorded data with the levels coded, so that for the quantitative variables a minus sign represents the low level and a plus sign the high level. The main effect and interaction effects were evaluated. The contribution of main and interaction effects on the obtained extraction percentile can be easily understood and visualized through the interaction diagrams. For the construction of these diagrams two factors were took and all the possible level combinations

Table 2
Variation domain for each studied variable in the chromium extraction process

	High level (+)	Low level (-)
Agitation speed (rpm)	490	365
Total flow rate (L h ⁻¹)	2.0	0.7
Solvent rate	0.50	0.25

Table 3
The design matrix and the obtained responses (*Y*)

Run	Main factors (design matrix)			<i>Y</i> ₁ (%)	<i>Y</i> ₂ (%)	\bar{Y} (%)
	<i>A</i>	<i>B</i>	<i>C</i>			
1	-	-	-	86.9	85.1	86.0
2	+	-	-	98.4	98.5	98.4
3	-	+	-	98.6	98.1	98.4
4	+	+	-	98.1	97.4	97.3
5	-	-	+	95.2	96.7	96.5
6	+	-	+	57.1	58.1	57.6
7	-	+	+	99.3	98.9	99.1
8	+	+	+	99.4	99.3	99.4

A – agitation speed (rpm); *B* – solvent rate; *C* – total flow rate (L h⁻¹).

accomplished, that is (+, +), (-, -), (-, +), and (+, -). Each diagram quadrant represents the average of the obtained results by two factors in the pre-established levels, as can be seen in Fig. 3 [20]. All data were treated with the aid of SAS System Software, version 6.12.

3. Results and discussions

3.1. Microemulsion load capacity

The microemulsion load capacity, or the maximum amount of chromium that the same microemulsion is able to extract, was accomplished with the purpose to obtain information about the solvent rate to be used in the Morris extractor. Table 1 shows the obtained results and through its analysis can be verified that the microemulsion presented a high extraction power and load capacity, being efficient up to a synthetic solution volume of 58 mL. With the addition of more synthetic solution its capacity decreased abruptly and was observed the formation of a precipitate. After this volume the chromium extraction process, that was practically immediate, became slow, justified by the loss of microemulsion efficiency.

The results obtained with the microemulsion load capacity study make possible the calculation of the solvent rate (ρ):

$$\rho = S/F = 23/58.16 \cong 0.4 \quad (4)$$

where *S* is the amount of solvent used (microemulsion – mL) in the extraction process and *F* is the chromium synthetic solution feeding (mL). The solvent rate adopted in the Morris extractor was varied from 0.25 (low level) to 0.5 (high level).

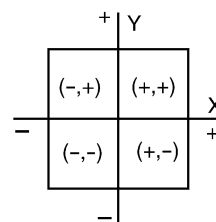


Fig. 3. Two-factor interaction diagram in a 2ⁿ factorial design.

It is important to point out that the microemulsion load capacity study was accomplished in batch and in the Morris extractor the chromium extraction occurs in a countercurrent process, under constant agitation, what favors phase contact, implying a probable reduction in solvent rate.

3.2. Chromium extraction from tannery effluent

The Morris extractor was used to perform chromium extraction process from a tannery effluent. The levels from total flow rate and agitation speed were selected based on preliminary studies, taking into account the contact between the phases and emulsion formation. The experiments in the Morris extractor were accomplished according to a factorial design 2^3 , whose variation domains of the selected factors are shown in Table 2.

The optimization process seeks to evaluate, in a quantitative way, among important variables of an experimental planning, its influences on the answers of interest, as well as its possible interactions. To obtain important information with a minimum of experiments, reducing the operational costs, the researcher can use a factorial design that will give a global answer about the behavior of the studied process.

Each experimental run took approximately 2 h to place the Morris extractor in a working flow rate. To analyze the evolution of the extraction process, samples were collected at each 30 min up to 5.5 h. The collected samples (aqueous phase) were analyzed in FAAS to evaluate chromium removal.

Table 3 shows the design matrix and the obtained responses (Y). It was taken the average response (\bar{Y}) to calculate the interaction and main effects; being used a statistical model (SAS System Software, version 6.12) and a confidence level of 95%, where all factors were considered in the statistical significance test.

The empirical model obtained, it means, the model that describes chromium extraction process behavior based on the experimental conditions, is given by the following equation, where Y represents the response function.

$$Y = 91.57 - 3.29 A + 7.08 B - 3.58 C + 3.19 AB - 6.24 AC + 4.16 BC + 6.46 ABC \quad (5)$$

with an standard error of 0.17.

Based on the obtained result, some important points can be noticed: agitation speed (A) exerted a negative effect (-3.29) in the extraction process due to the fact that an increase in the agitation speed can cause emulsion formation and, consequently, a decrease in phase separation process, resulting in a reduced efficiency, solvent rate (B) produced a very significant positive effect (7.08) because an increase in solvent rate will enhance solute transference between the phases and, total flow rate (C) exerted a negative effect (-3.58) due to an increase in the flow of the phases which results in a reduction in the contact time.

Fig. 4 presents two-factor interaction diagrams related with the chromium extraction percentile response (Y). Its analysis allows to conclude that the best results were ob-

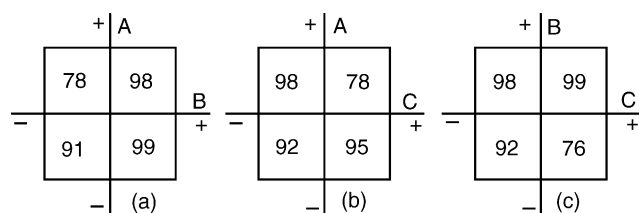


Fig. 4. Interaction diagrams for chromium extraction process (%): (a) total solvent rate (B) \times agitation speed (A); (b) total flow rate (C) \times agitation speed (A); (c) total flow rate (C) \times total solvent rate (B).

tained in the high level of the solvent rate ($B = 0.5$) with the low level of agitation speed ($A = 375$ rpm) and high level of total flow rate ($C = 2$ L h $^{-1}$), corresponding to the following combinations: $A (-) B (+) = 99\%$, $A (+) C (-) = 98\%$, and $B (+) C (-) = 99\%$.

With the purpose of exemplifying, the calculation of the answer (Y) for the interaction among total flow rate (C) and solvent rate (B) in the positive levels (+, +) is shown in Eq. (6):

$$Y(\%) = 91.57 + 7.08(+1) - 3.58(+1) + 4.16(+1)(+1) \cong 99 \quad (6)$$

3.3. Analysis of isoresponse surfaces generated by the obtained empirical model

The isoresponse surface is the geometrical representation, in a two-dimensional space, of the studied variables, and they clearly indicate a tendency in the response that should be analyzed in detail. After the determination of the region where was obtained the relevant aspects of the situation of interest, the experimenter can detail this particular area in order to obtain the conditions where the process yield will be better.

For chromium extraction process, the search of the region of high yield can be made through the interpretation of the isoresponse surfaces presented in Fig. 5. These curves allow knowing and optimizing the extraction process in the entire variables domain studied.

The model allows building two different response surfaces for each variable in study, that is, one for the high level and other for the low level. Through the analysis of Fig. 5 can be observed that it was chosen among the studied variables the variable A for presenting the smallest individual effect (-3.29) and variable B for presenting the greater statistical significance (7.08). The analysis of the obtained results shows that: for the same flow rate value (C) an increase in total solvent rate value (B) leads to an enhancement in chromium extraction percent; however at the low level of agitation speed value (A) the maximum extraction percentile values were obtained (98%) even when the high level of solvent rate (B) was reduced in 25% (Fig. 5(a) and (c)).

For intermediate values of total flow rate and agitation speed (Fig. 5(b)) the variation among high and low levels

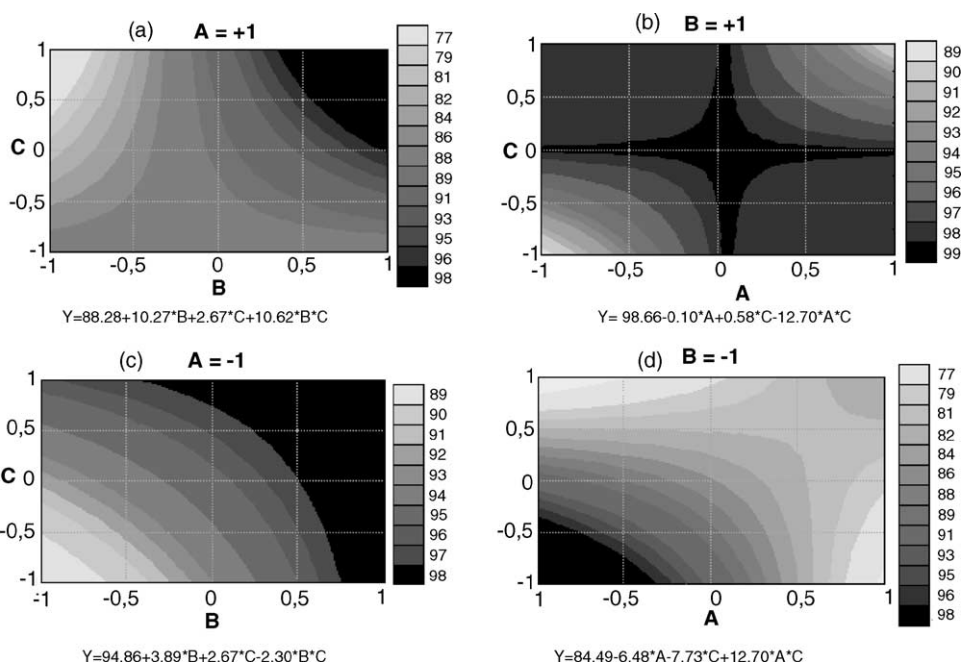


Fig. 5. Isoresponse surfaces representing the relationship between: (a) high level of A (+) and C and B ; (b) low level of A (-) and C and B ; (c) high level of B (+) and C and A ; (d) low level of B (-) and C and A .

does not interfere in chromium extraction process (99% extraction).

Through the analysis of Fig. 5(d) was observed that for the low level of solvent rate the obtained results for extraction percentiles, when the flow rate value was in a maximum, were not good (72%). The conclusions obtained in these analysis are in complete agreement with those obtained of the two-factor interaction diagrams. From the analysis of the isoreponse curves can be concluded that the best yields can be obtained with high level of total flow rate (2.0 L h^{-1}), an intermediate agitation speed (428 rpm) and with 25% reduction in the high level of solvent rate (0.37).

3.4. Re-extraction process

The re-extraction study was performed with the purpose to reuse chromium and/or the microemulsion phase. For the optimization of the process, some parameters were an-

alyzed, such as: acid type (HCl 8 and 10 mol L^{-1} and H_2SO_4 8 mol L^{-1}), temperature (28, 40 and 50°C), and re-extraction percentile. Figs. 6–8 show the obtained results.

In Fig. 6 can be observed the temperature influence in the re-extraction process using hydrochloric acidic solution at 8 mol L^{-1} . It can be noticed that an increase in temperature causes an increment in re-extraction percentile. It is important to point out that the rise in temperature represents an increase in energy expense but the process at 50°C (96%) is made possible due a reduction in re-extraction time.

In Fig. 7 can be noticed that with an increase in hydrochloric acidic solution concentration (10 mol L^{-1}) the best results were obtained at 40°C (93%). It is important to verify that this reduction in temperature (10°C) implies a little decrease in re-extraction percentile and an increase in reagent consumption.

When a sulphuric acidic solution was used (Fig. 8) the best re-extraction percentile was obtained with a contact time of

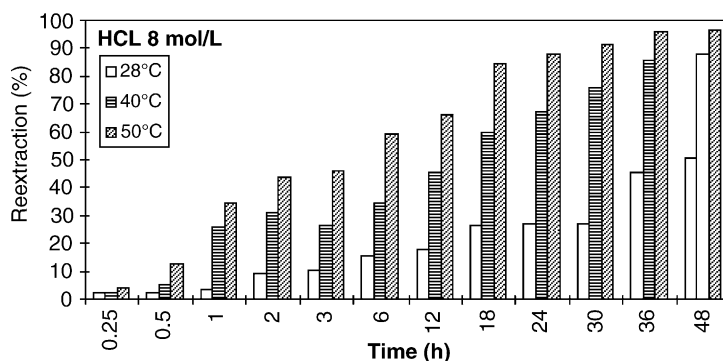


Fig. 6. Re-extraction percentile as a function of time using HCl 8 mol L^{-1} .

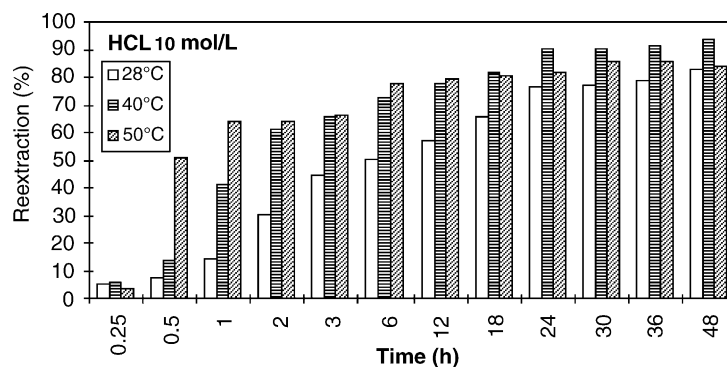


Fig. 7. Re-extraction percentile as a function of the time using HCL 10 mol L⁻¹.

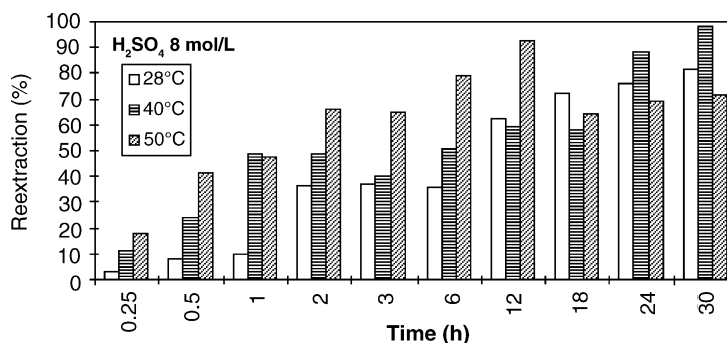


Fig. 8. Re-extraction percentile as a function of time using H₂SO₄ 8 mol L⁻¹.

30 h at 40 °C (98%). In higher temperatures, the re-extraction percentile reaches a maximum and begins to decrease maybe due the presence of interfering ions present in the tannery effluent (organic matter).

4. Conclusions

The results obtained in this research allowed understanding and improving chromium extraction process from tannery effluent using microemulsions in the Morris extractor. It is concluded that the microemulsion is an efficient solvent with best results being obtained in the following operational conditions: agitation speed, 428 rpm; solvent rate, 0.37; total flow rate, 2.0 L h⁻¹; with the Morris extractor configured with five stages.

As explained, wastewaters from tannery industries contain high levels of chromium. These levels are normally reduced by precipitation. The steps include reduction of the hexavalent to the trivalent form at an acidic pH followed by precipitation at pH 9.5, which generates a large amount of sludge that are usually disposed in landfill. The microemulsion process can be applied soon after chromium wastewater stream, after tanning rotating drum, and its effluent can pass to the conventional biological treatment process employed to the full stream wastewater of all process steps.

The re-extraction study showed that chromium could be removed from the microemulsion phase by hydrochloric and

sulphuric acidic solutions, which allows its reuse in the leather process. The microemulsion phase, after re-extraction process, was not efficient in chromium removal process due to pH reduction in the re-extraction process. The surfactant, which is derived from a weak fat acid and a strong base, will be decomposed in oil and salt portions, implying in the break of the microemulsion phase, making necessary the accomplishment of other studies for its reuse.

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