NOVEL COMBINED METHOD FOR LANOLINE RECOVERY FROM SHEEPSKINS TANNERIES WASTEWATERS♦

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Abstract: The paper presents a two-stage method for the fast and high- yield recovery of lanoline from spent woolen sheepskin scouring liquors. Through its characteristics, the resulting waxy matter allows a straightforward and efficient purification of lanoline. The first stage involves the selective removal of hydrophilic and medium hydrophobic non-lanoline constituents of the spent liquor, using conventional Al-pillared clays (Al-PILCs). The second stage consists in electrochemical separation of crude waxy matter in electro flotation cells operated in pulse-width-modulated regime, at constant current density.

Keywords: *lanoline, recovery, wastewater, pillared clays, electro flotation.*

INTRODUCTION

Lanoline, naturally occurring in sheep wool, consists of a complex mixture with high compositional polydispersity and breed-depending variability, in which the main constituents are the esters of fatty acids with sterols and with higher aliphatic mono-

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alcohols. Due to lanolin's high affinity for both hydrophobic and hydrophilic species, wool chemical scouring results in highly impurified lanoline emulsions associated with micelles including various chemicals and with fine particles. The medium content of chemical scouring wastewaters after plain settling and filtration is as it follows: 0.15 ... 0.6 g/L waxy matters; 0.7 ... 1.2 g/l triglycerides, 0.3 ... 1.4 g/L protein fractions, 0.1 ... 0.3 g/l carbohydrates, 1.5 ... 3.5 g/L anionic surfactants, 0.2 ...1.2 g/l nonionic surfactants, 1.2 ... 3.5 g/L inorganic salts, 0.4 ... 1.3 g/l colloidal suspended solids, together with a fluctuant but high microorganisms charge. From a physicochemical point of view, these waste liquors represent colloidal mixed systems, including emulsions, suspensions and solutions. They present limited time stability and undergo bioenzyme-induced chemical alteration and emulsion destabilization through physical associations.
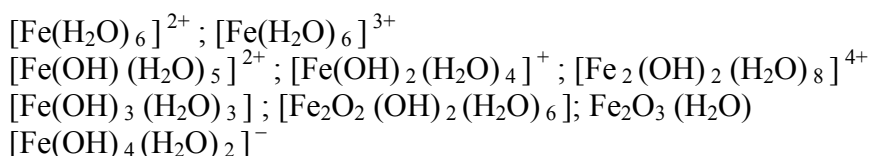
Separation with the purpose of high-yield recovery of low-concentration useful products found in liquors with such various and fluctuating composition can not be efficient through classical coagulation/flocculation treatments, because it results in mixtures of organic species that are hard to fractionate, and are amenable to chemical interactions, thus making the purification even harder. In order to become feasible, a separation addresses to systems like this must discriminatingly operate upon the constituents and be conducted in successive steps, implying distinct processes and mechanisms. Such an approach is motivated in this paper.

The principle of the proposed method consists in the efficient separation of the small waxy and triglycerides fractions through bipolar electro flotation applied to a colloidal system whose compositional polydispersity and physicochemical stability had been previously diminished through a selective coagulation / flocculation treatment addressed both to the other chemical species and to the tenside micelles in excess. This latter mentioned treatment resorts to a class of functionalized smectites with selective affinity for hydrophilic and weakly hydrophobic compounds.

First stage – **Treatment with intercalated smectites.** Selective coagulation / flocculation of organic species is achieved by contacting the spent liquor, previously freed of settling solids through screening and plain sedimentation, with a modified smectite, that, when dispersed in the liquor to be treated, generates a colloidal system able to provide extended active surfaces amenable to adsorption and associations with the above mentioned species from the aqueous system. The selective coagulation / flocculation agent is in fact a conventional Al-pillared clay, resulting from the intercalation of poly-oxo-hydroxo-aluminum polynuclear cations, from which the Al-Keggin or Al_{13} ion $[AlO_4 Al_{12} (OH)_{24} (H_2O)_{12}]^{7+}$ is the most representative [1], in the interlayers of expandable smectite clays. The Keggin ion insertion between the phylosilicate platelets results in a layered nanostructured material, in which the increase of the basal spacing from 14 Å in the natural clay to 17.9 – 20.3 Å in the intercalation product leads to spaced structure, amenable to retain other molecules and/or aggregates with similar sizes.

Second stage – **Electrochemical treatment.** Since the chemical wool cleaning uses mainly anionic surfactants, the emulsion resulting from the coagulation treatment contains micelles with anionic charge, that can be neutralized by the cationic species generated during the electrochemical process on the surface of the sacrifice electrode. The anodic oxidation products are particularly efficient, as they rapidly transform into

short-life complexing cations, which turn into colloidal hydroxides. The electrochemically generated colloidal hydroxides are much more smaller in size than the chemically generated ones, which result in remarkable electrostatic sorption affinity [2]. Thus, the anionic micelles whose peripheral charge is efficiently neutralized will be easily destabilized and extracted from the colloidal system. The resulting flocks are smaller, retain less water and have higher mixing strength than those resulting from the chemical process [3]. Actual work conditions in electro flotation cells with steel and aluminum electrodes enable electrode processes that generate a wide range of oxolated and olated ionic species with high complexing potential, among which the following are representative (according to [4]):

$$[Fe(H_2O)_6]^{2+} ; [Fe(H_2O)_6]^{3+}$$
$$[Fe(OH)(H_2O)_5]^{2+} ; [Fe(OH)_2(H_2O)_4]^+ ; [Fe_2(OH)_2(H_2O)_8]^{4+}$$
$$[Fe(OH)_3(H_2O)_3] ; [Fe_2O_2(OH)_2(H_2O)_6]; Fe_2O_3(H_2O)$$
$$[Fe(OH)_4(H_2O)_2]^-$$

As the species generated by aluminum and other alloy metals have similar structures, only the iron complexes are presented.

Acid wastewaters saturated with CO_2 contain variable amounts of complexes including large acidic ligands, which are very active in the coagulation of anionic particles and micelles and in promoting the electrostatic aggregation of submilimetric solid impurities. When the electro flotation cell is operated in electrolysis regime with gas generation, both flocks and solid aggregates are attached to the oxygen and hydrogen bubbles and carried in the flotation froth. Subsequently, the collected froth can be subjected to physical disintegration / selective dissolution / chemical splitting / chemical hydrolysis, for the recovery of useful constituents.

EXPERIMENTAL

Obtaining of functionalized smectite

The substrate was a native Na-bentonite from Valea Chioarului deposits, 91.6 % purity, with a cation exchange capacity (CEC) of 65 meq/g and Methylene Blue Index (MBI) of 352.5 mg/g, thoroughly swelled/hydrated in a 5% w/w suspension. ***The intercalation agent*** was prepared through controlled hydrolysis of $AlCl_3$ with NaOH, so that the resulting Al-based pillaring solution had a concentration of 0.11M Al and OH/Al molar ratio 2.5, which corresponds to 83% basicity and a maximum Keggin ions concentration. ***The masic combination ratio*** was 22.083 mg Al_2O_3 /g bentonite, equivalent to 200% of the CEC compensation degree. ***The functionalization.*** The smectite suspension was slowly added to the pillaring solution, under vigurous stirring; the reaction mass was then heated to 70 ÷ 80 ºC and stirred for 3 hours. After cooling down, the reaction product was separated through vacuum filtration and thoroughly washed. The aluminum content in the washings was null. The reaction product had the appearance of a stable gel, provided its water content did not exceed 83%, and was kept in wet state.

The electro flotation device

Constituent parts: a lab-scale electoflotation cell equiped with two sacrifice electrodes: one cast aluminum alloy electrode (Al 97 %, Mg 1.2 %, Si 0.8 %, Mn 0.8 %, Zn 0.2 %) and one fashioned stainless steel (1MoCr260 brand) electrode (Al 97 %, Mg 1,2 %, Si 0,8 %, Mn 0,8 %, Zn 0,2 %). *Operating regime.* Pulsed direct current with controlled frequency and impulse width, under constant current density. ***The electric and working parameters control scheme*** is presented in Figure 1, where the electrodes polarities, corresponding to the three operating regimes are also given. The current density on the electrodes surface is kept constant by an electronic regulator, while the applied potential changes as a function of the electrochemical system impedance variation, throughout the electro flotation process.
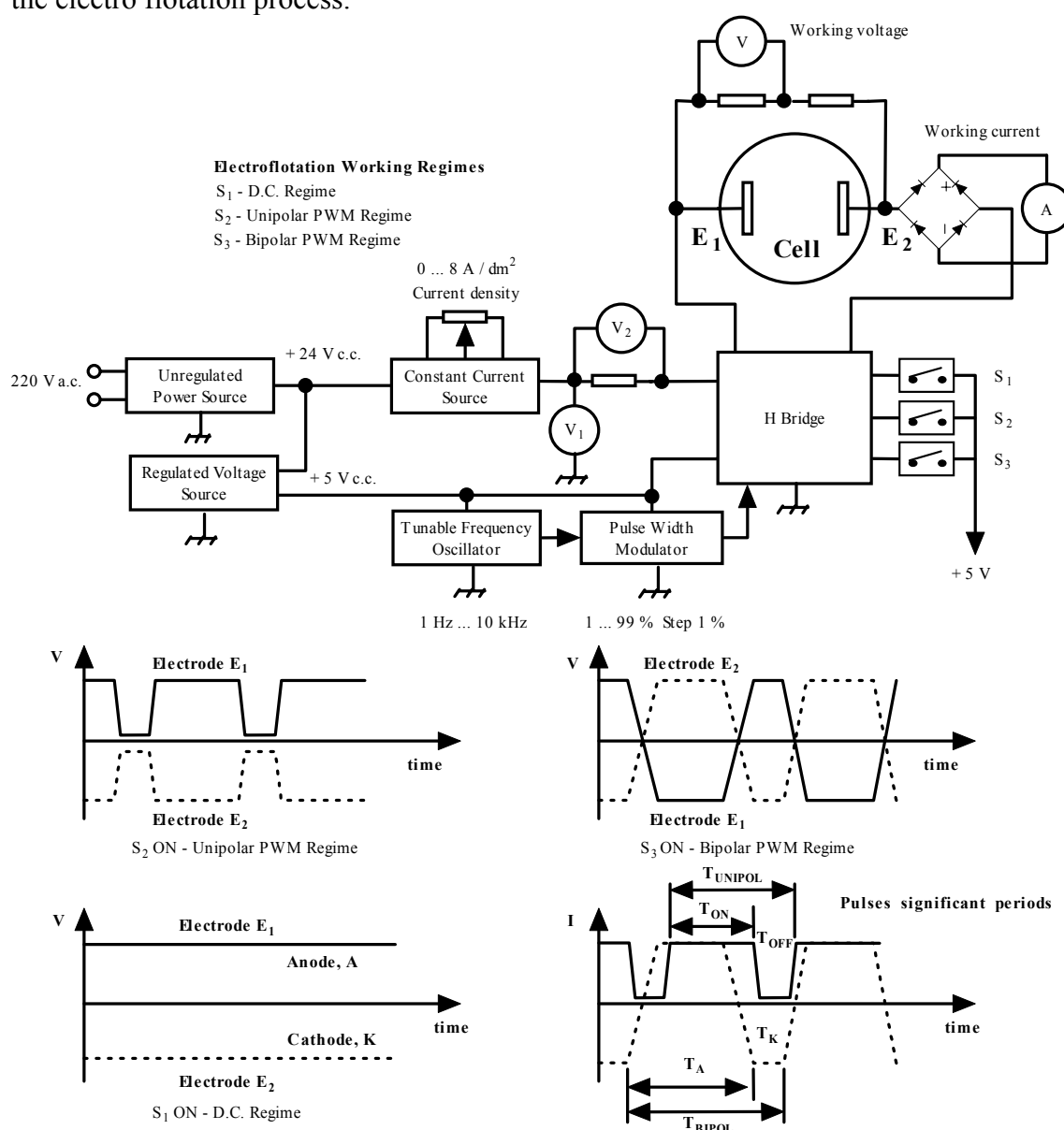

Figure 1. *Electro flotation unit electronic block diagram and working regimes*

Tested aqueous systems. Laboratory - scale experiments comprising selective coagulation / flocculation and electro flotation treatments were performed on two different lanoline-containing aqueous systems: (**1**) a highly stable "synthetic" emulsion prepared from 0.4 g/L pure lanoline (pharmaceutical grade), emulsified in a laboratory ultrasonic bath with 0.02 g/L nonionic surfactant; (**2**) an individual scouring spent liquor from woolen - sheepskins processing, subjected to plain settling for three hours, screened and settled again for two hours.

The coagulation / flocculation treatment was performed according to the classical "jar test" procedure, with coagulating agent dosages ranging between 0.2-3 g/L and pH values between 4 and 9. The main pollution indices - suspended solids, COD, greasy matters, proteic matters and Cr_2O_3 - before and after the selective coagulation treatment were determined through conventional laboratory techniques.

Electro flotation treatment. The electrochemical processes induced in aqueous media can be narrowly controlled, if the electrodes work under pulsed current density, either in unipolar regime (when each electrode keeps its individual electrochemical function) or bipolar regime (when the electrodes temporarily shift their electrochemical function). The working parameters allowing the optimization of electro flotation in pulsed regime are: *pulse current density J_P* , *pulse frequency f*, and *duty cycle d*; the significant durations of pulse: working time T_{ON} and relaxing time T_{OFF} for the unipolar regime, and anode function time T_A and cathode function time T_K, for the bipolar regime, respectively, are derived from the duty cycle. The actual current density in electroflotation is calculated as the average value per pulse, J_{AVRG} , from the following relationships :

$$J_{AVRG\_UNIPOLAR} = J_P \cdot \frac{T_{ON}}{T_{ON} + T_{OFF}} = d \cdot J_P = f \cdot T_{ON} \cdot J_P \text{ [A/dm}^2] \tag{1}$$

$$J_{AVRG\_BIPOLAR} = \frac{J_P \cdot T_A + J_P \cdot T_K}{T_A + T_K} = J_P \text{ [A/dm}^2] \tag{2}$$

in which the time significances are those given in Figure 1. This average value dictates the electrode processes intensity, expressed as the discharged metallic ions "flow" and the evolved gases "flow", into the liquid medium. The working parameters of the electro flotation cell are given in Table 1.

Table 1. Operating parameters of pulsed regime electroflotation

Parameter	Symbol	UM	Operating regime	
			unipolar	bipolar
Imposed current density per pulse	J_P	A/dm^2	0,9	1,2
Pulse frequency	f	kHz	0,3 ... 3	0,01 ... 1
Duty cycle	d	--	0,1 ... 0,5	0,3 ... 0,9
Inter-electrode distance	x	mm	30	100
Anode / Anodic leading electrode	A / E_1	--	steel	aluminum
Cathode / Cathodic leading electrode	K / E_2	--	aluminum	steel

Under these circumstances, owing to the mutual position of the two electrodes, *i.e.* the aluminum electrode placed at the bottom of the cell, unipolar operation regime results in massive generation of iron ions, while the bipolar regime permits the adjustment of the iron-to-aluminum ratio.

The theoretical volume of gases evolved during water electrolysis results from:

$$V_{T\_UNIPOLAR} = \frac{R \cdot J_{AVRG\_UNIPOLAR} \cdot T \cdot T_{ON}}{F \cdot p \cdot z} \ [\text{m}^3/\text{dm}^2] \tag{3}$$

$$V_{T\_BIPOLAR} = \frac{R \cdot J_P \cdot T \cdot (T_A + T_K)}{F \cdot p \cdot z} \ [\text{m}^3/\text{dm}^2] \tag{4}$$

where:

R, universal gas constant, 8.314 J/(mol K) ;

T, absolute temperature, K ;

F, Faraday's constant, 96485 C/mol ;

p, atmospheric pressure in the working conditions, approx. 10^5 Pa = 10^5 J/m^3;

z, number of electrons implied in the gas generating electrode reaction ; $z = 2$ for H_2 generation from the cathode and $z = 4$ when O_2 is generated from the anode ; if the overall evolved gas is considered, $z = 6$.

The efficiency of gas evolvement in electro flotation is calculated as the ratio between the actual and the theoretical evolved gas volumes. This parameter depends on the current density, the working frequency and the duty cycle in respect with the pulses, and can be associated with the rate and efficiency of the colloidal species separation from the treated liquor.

RESULTS AND DISCUSSIONS

The initial composition of the spent wooled skin scouring liquor was: 0.32 g/L waxy matters, 0.82 % triglycerides, 2.1 g/L anionic surfactants, 0.77 g/L nonionic surfactants, 1.2 g/L other organics, 1.63 g/L submilimetrical solid impurities.

The coagulation experiments allowed the following observations: (**1**) working chemical dosage ranges between 0.6 – 2 g/L as dry matter; (**2**) working pH ranges between 5 and 8; pH values below 5 render the product ineffective; (**3**) the coagulant addition does not significantly change the pH of the original aqueous medium; (**4**) vigorous mixing is required in order to achieve complete dispersion of functionalized smectite in water and intimate contact with suspended matters; (**5**) settling is very fast and results in a stable, dense sludge, even without polyelectrolyte flocculent addition. The effect of the chemical coagulation treatment upon the pollution parameters of the treated liquors is given in Table 2.

Due to the complex composition and particular physical structure, the functionalized smectite product exhibits a dual action when dispersed in a lanolin emulsion: coagulant due to the presence of oligomeric oxo-hydroxo Al-species and microflocculant, due to the presence of bentonitic clay. The selective sorption of colloidal and dissolved matters and inability to break the emulsion must be related to the decrease of aluminum oxo-hydroxo-cations hydrophilicity due to immobilization between clay platelets and to steric hindrance in the PILC porous matrix. Voluminous emulsified grease drops can not compete with the colloidal proteic fractions for active sites in the adsorbent. Chrome Cr(III) cations are retained *via* cation exchange reactions.

The dependence between the residual greasy matter content in the electrochemically treated liquors and the pulsed current parameters for the two operating regimes of the

electro flotation cell are depicted in Figures 2 and 3, respectively. The gas evolvement efficiency as a function of the same parameters is given in Figures 4 and 5.

Table 2. *Effects of selective chemical coagulation upon the pollution parameters*

| Pollution parameter	„Synthetic" emulsion			Individual effluent		
	before treatment	after treatment	% removal	before treatment	after treatment	% removal
Suspended solids, mg/L	--	--	--	1635	1139	30.33
COD, mg O_2/L	--	--	--	256	187	27
Cr_2O_3, mg/L	--	--	--	267	ND*	100
Extractable greasy matters, mg/L	4012	3863	3.71	1140	1092	4.2
Total nitrogen	--	--	--	25.2	5.78	77.06
Proteic matters mg/L				160.7	36.8	77.1

* - ND means "non detectable".
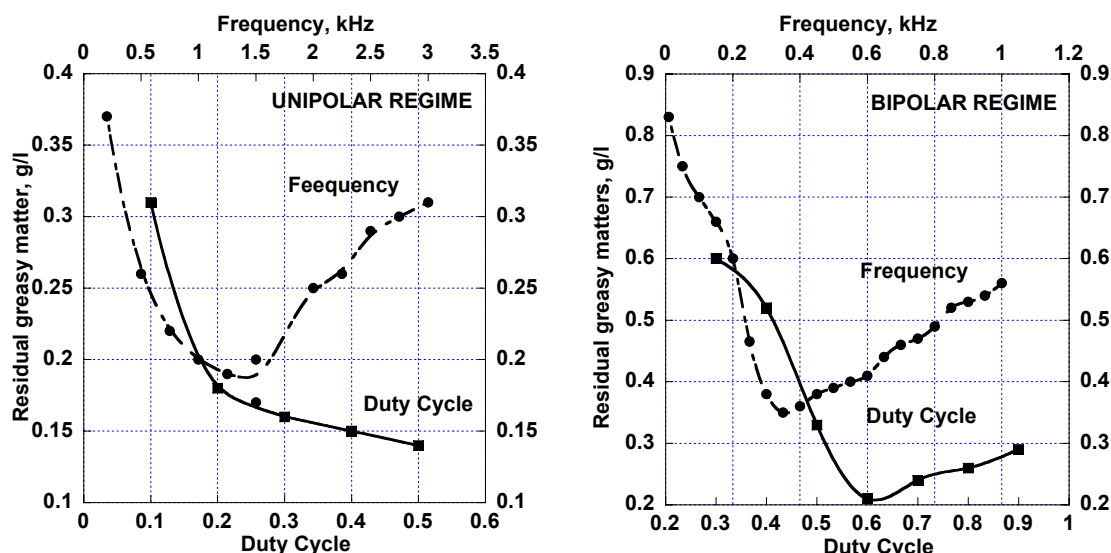
Figure 2. *Variation of residual grease concentration in the "synthetic" lanoline emulsion with the electro flotation regime and working parameters*

All the electro flotation experiments were conducted under constant current density, at values that avoid temperature rising during the electrochemical process (see Table 1). The duration of the electrochemical treatment was 60 minutes in all cases, even though in the bipolar regime the separation seemed to be finished after 30 minutes.

Significant differences are noticed between the efficiency of the greasy matter separation depending on the operating regime and pulsed current parameters, when the two kinds of treated liquors are comparatively analyzed. Higher levels of residual greasy matters in the spent scouring float may be the consequence of the presence of other interfering chemical species.
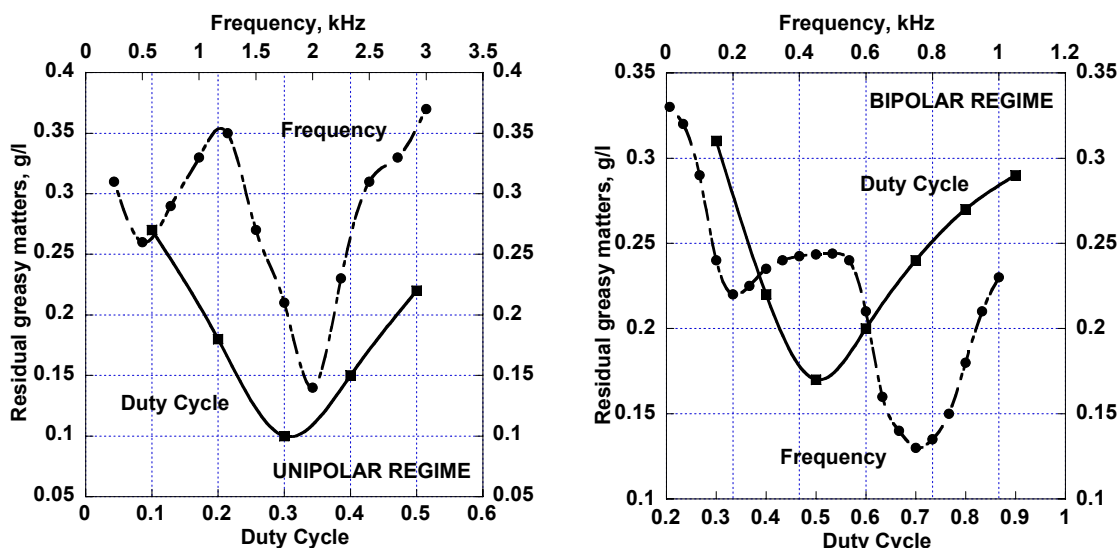
Figure 3. *Variation of residual grease concentration in the previously purified float with the electro flotation regime and working parameters*
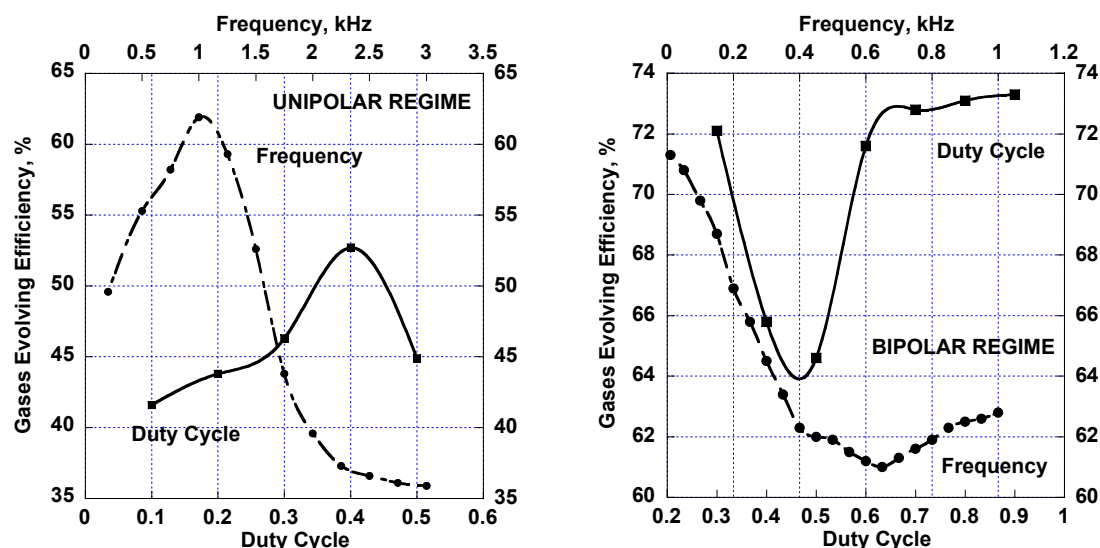

Figure 4. *The dependence between the gases development efficiency and the electro flotation process parameters, for the "synthetic" lanoline emulsion*

CONCLUSIONS

The couple of treatments discussed in the paper provide high efficiency of lanoline recovery from wastewater resulting from wooled skins chemical scouring, with minimum supplemental impurification, comparing with the classical recovery procedures. The pulse current parameters at which the electro flotation cell is operated are of major importance, as they dictate the separation quality, defined by the flocculating species and the volume of gases generated during the electrochemical process.
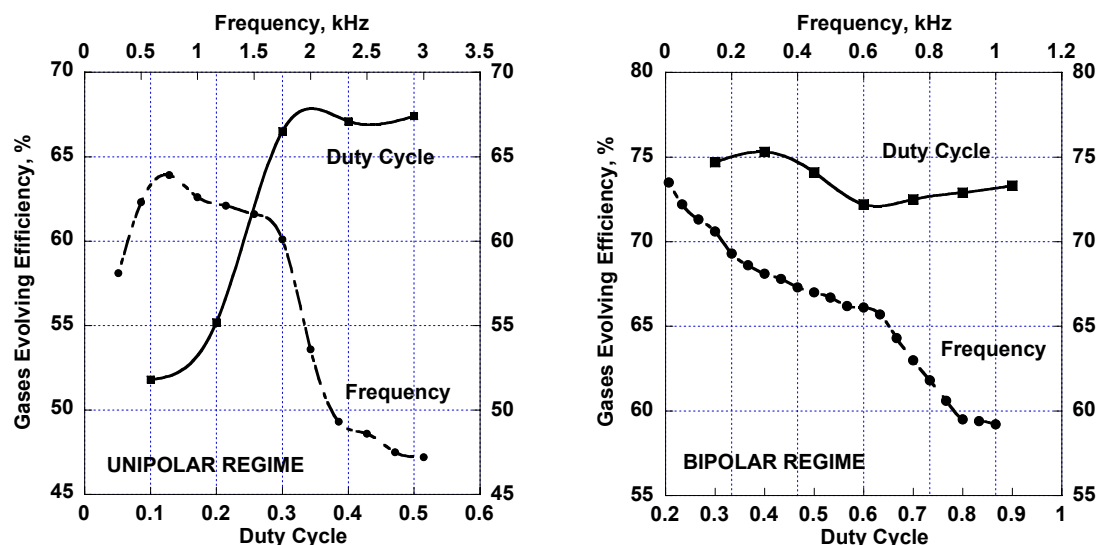
Figure 5. *The dependence between the gases evolvement efficiency and the electro flotation process parameters, for the scouring liquor previously treated with the smectite-based coagulant.*

Owing to the particularities of the supplying source electronic scheme (modulated constant current using a pulse operated H bridge) and of the manner in which the operating parameters are controlled (the variation of T_{ON}, T_{OFF}, T_A and T_K times) the impact of the electrolyte impedance modification during the electrochemical treatment was significant and could not be counteracted. For this reason, Figures 2 to 5 depict paradoxical evolutions of the greasy matter separation and gas evolvement efficiencies. In both unipolar and bipolar regime, there is a strong dependence between the pulse frequency and the duty cycle. Thus, even if the frequency increase results in a decrease of soluble chemical species and of gas "flows", this reduction can be balanced by the duty cycle growth. As a consequence, the optimal working ranges, which provide an advanced separation of greasy matters with fast kinetics, as established at the laboratory scale for the "synthetic emulsion" are:
-   in unipolar regime: frequency of 0.8 ... 1.2 kHz, duty cycle of 0.3 ... 0.5;
-   in bipolar regime: frequency of 0.2 ... 0.6 kHz, duty cycle of approx. 0.5.

The optimal working ranges for the treatment of spent wooled skins scouring are:
-   in unipolar regime: frequency of 1.5 ... 2.5 kHz, duty cycle of 0.2 ... 0.4;
-   in bipolar regime: frequency of 0.6 ... 0.9 kHz, duty cycle of approx. 0.5.

Working at the highest frequency values is to be preferred, because the generated bubbles are very fine and evenly distributed, and have the best efficiency in attaching and lifting the flocks and micelles present in the colloidal system.

Energies implied in the destabilization of the tested colloidal systems were calculated from the pulses parameters and range between 2 ... 12 J, with smaller values for the bipolar regime.

An improved control of the electro flotation performance is possible provided pulse current sources with high energy supply are used. Such sources are used in the electroporation cells, in which great changes of cell impedance do not decrease the pulse shape and amplitude so drastically, even if the density current is kept unchanged.

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