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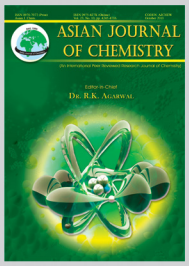

Characterization of An Effluent of An Algerian Oil Mill

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This work concerns to characterize the effluent, a by-product of an Algerian oil mill, for its valorization. A microbiological study certified the healthiness of the effluent, followed by various means of analysis such as their observation under the microscope, water chemistry, thin layer chromatography, infrared and the ultra-violet spectrophotometry. The results of analyses suggest that the effluents is biodegradable (86.54 %) and present in form of an emulsion of type I *i.e.*, oil-in-water mouthful of soap (15.5 g/L), bathing in conservatives. The results of a traditional analysis inherent in the soap corroborated these results. Moreover, a viscoplastic rheology was surrounded by the determination of various viscosities of the effluent, whose stability is ensured by the presence of contaminants, revealed by atomic absorption spectrophotometry.

Key Words: Ecoproducts, Valorization, Emulsion, Emulgator, Tensionactive, Biolubricants.

INTRODUCTION

The use of the effluents and the wastes must be the official information object which leads to the creation of environmental labels of the companies for the protection of nature[1]. This must represent the motive of any company production ready to deal with its waste, but any contrary action exposes it to its definite extinction.

The vegetable origin and the chemical structure of the products of the lipochimy and its derivatives are harmless with respect to the human and the environment, biodegradable, non-toxics and renewable. The vegetable resources and their derivatives in solvents had not been explored earlier and less studied[2]. In fact, it is possible to formulate these products with the surface-active or solvents of other origins to confer them other properties[3]. The undertaken works in this field give a positive report for the lubricants of natural origin.

Nevertheless, biotechnologies are seldom competitive if the economic study does not take account of the factors such as the cost of income (essential criterion), as well as the impact on the environment or the valorization of the products of agricultural industry[4]. In fact of their biodegradability, their abundance and their availability, a new glance must be carried on the by-products of the lipochimy which constitute 'green layers', a biomass insufficiently exploited. In past an interesting research was already accomplished on the rational valorization of the by-product of the greasy alimentary substances and on the possibility of making use of raw material for manufacturing lubricating products[5].

At present, it is a possible promising way of valorization concerning the biolubricants, resulting from plant oils and their derivatives. This work aims at reducing the rejections of the pollution which reaches the alarming proportions.

This work carries on the characterization of effluent resulting from the traditional refining of alimentary plant oils. At the stage of neutralization with soda, free fatty acids (FFA) are transformed into soap which is eliminated. This soap will be released at the stage of washing. The effluent are presented under an emulsion full of soap involving neutral oil.

EXPERIMENTAL

The samples of the effluent was obtained from an Algerian oil mill, located within the port of Bejaia, in the Algerian east coast. Sampling was carried out during winter (2007-2008). The homogeneous effluent required a presence at the washing stage where they are evacuated on the sea (*via* sewer) at 80 to 90 °C. Their volume is dependant on the quantity of crude oil to be refined. Thus it is difficult to find out the exact figures. However, an approximation can be given 10 to 15 % of treated oil. Their conservation required for setting them at -4 ºC.

Microbiology of the effluents: A reactivation of the bacterial strains in two pressure-sealed Erlenmeyers at 120 °C were carried. Each one filled with 30 mL of standard medium

HS culture and sown with 10 mL of the effluents. One Erlenmeyer is incubated at ambient temperature and the second under cold at -4 °C (as the conservation of the effluent is supposed to be) during 15 days. The microscopic observation (under enlargement: GR. 400*0.75, the apparatus is a ZEISS AXIOPLAN coupled to a camera OLYMPUS OPTICAL ZOOM), is considered to translate into image the possible presence of micro-organism in the effluents.

Determination of the emulsion type: It is chekced by observation of the effluents under microscope of the same type as the precedent.

Physico-chemical studies of the effluents: Relative with the raw material to be refined and the consumable matters, the parameters determined according to standard NF T90 are: phosphates (PO_4^{3-}: mg/L), nitrates (NO_3^-: mg/L), sulfates (SO_4^{2-}: mg/l), soap (mg/L), greases (mg/L), suspended matters (SM: mg/L), salinity (mg/L) and electric conductivity (EC: ms cm^{-1}, turbidity (NTU, the turbidimeter is a 21000 HACH), the demand for biological oxygen (DBO: mg/L, DBO meter is a OXITOP BOX) and the demand for chemical oxygen produced by chemical reaction (DCO: mg/L, DCO meter is a ACH LECTUR DR. 2000 coupled with an engine HACH). These last two parameters lead to the determination of the biodeterioration of the effluents[6-8]. The fractionation of the effluents is studied by thin layer chromatography. The infrared spectrophotometer used is Perkin-Emer GAN 1000 PC in range of 4000 to 400 cm^{-1}. The spectrophotometer used is a UNICAM UV2 UV/visible V2.04 with quartz premiums. Measurements were carried out in hexane solution after separation to chloroform.

Soap in the effluents analyzes: Essentially, the analysis is determined by the glycerol content, the caustic alkali content (free and total), the salt content (NaCl) and the water content, normalized as AFNOR NFT 60.

Proportioning of the impurities of the effluents: The principal impurities of the soaps (unsaponified-unsaponifiables and free alkali) are given according to standard of AFNOR NF T60 and sodium sulfates; it is generally proportioned by traditional gravimetry with barium chloride.

Rheological properties of the effluents: Rheological properties were determined according to cinematic viscosity (C_P:V20), dynamic viscosity (C_P:V20); the viscometer is a HVU 90 HERZOG, normalized ASTMD 4052, apparent viscosity (C_P: μa), plastic viscosity (C_P: μp) and the yield value or point value (γv or γp: Pa); the rheometer is a FANN, the electrokinetic potential ZETA (ξ: mv); the apparatus is a ZETASIZER 3000 HS HALVERN, the density (20 °C/eau/20 °C g/cm^3: D20), the densimeter is a DMA 48A P PAA and the index of refraction (n_{20}); the refractometer is an ABBOT 60 normalized ASTMD 445.

Analysis of metals present in effluents: The presence of certain metals was studied by atomic absorption spectrophotometry using Perkin-Elmer 1000-100B.

RESULTS AND DISCUSSION

Physical aspect of the effluents: These effluents of hydrocolloïdal stable aspect, of ochre yellow colour, dense, viscous, saponaceous, sticky, slightly foaming of consistent rheology have a manifest odour of the Marseille's soap, which enables to suppose the presence of soap. This is confirmed by the fact that the washing of oils after neutralization gives a hydro-soapy colloid.

Microbiological study of the effluents: Figs. 1 and 2 show that the effluents are virgin of microorganisms, explained by an asepticized environment and by the presence of soap with the bactericidal properties.

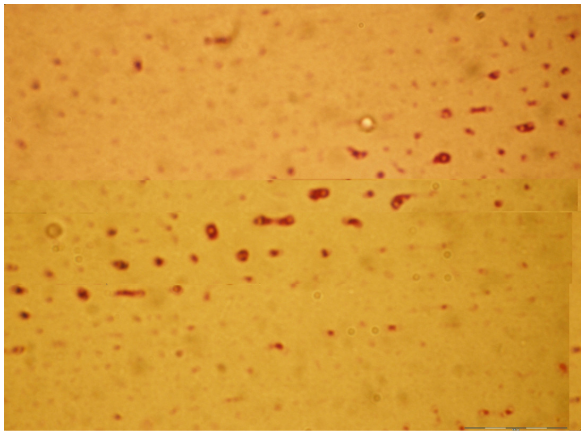

Fig. 1. Microbiological study of the effluents at ambient temperature

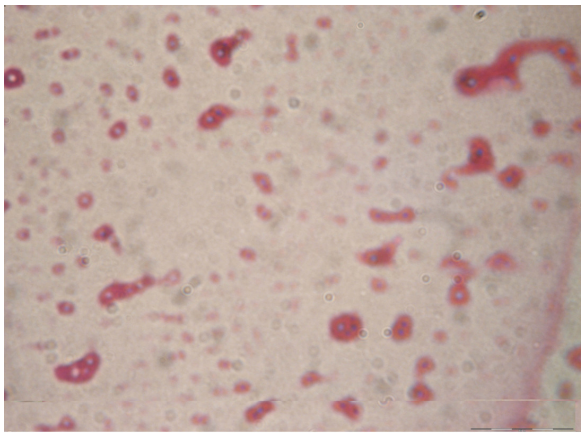

Fig. 2. Microbiological study of the effluents at -4 °C

Determination of the emulsion type: Fig. 3 showed that the effluents form a stable dispersion of oil-in-water type. This system is of technological interest since it makes it possible to encapsulate hydrophobic species in water and thus to control the velocity.

Physico-chemical analysis of the effluents: The water chemistry offers about on the physico-chemical contents of the effluents. Table-1 shows the results of analysis.

TABLE-1
PHYSICO-CHEMICAL ANALYSIS OF THE EFFLUENTS

PO_4 (mg/L)	SO_4 (mg/L)	NO_3 (mg/L)	Soap (mg/L)	Oil (mg/L)	Salinity (mg/L)	SM (mg/L)	DCO (mg/L)	DBO (mg/L)	pH	Turbidity NTU	Conductivity (ms cm^{-1})
24	191	2	15500	2582	3800	1.65	16.4	18.95	12	422	1.049

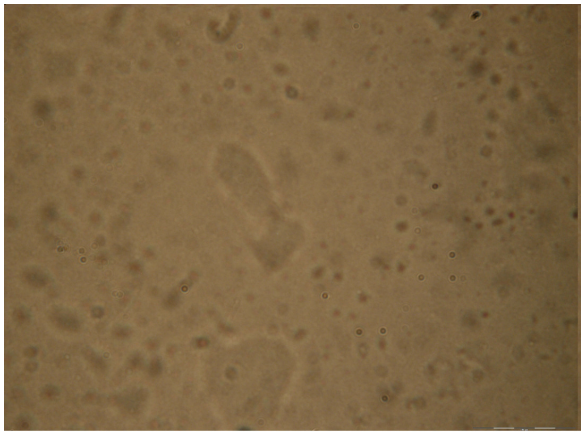

Fig. 3. Determination of the emulsion type

The presence of soap 15,500 g/L and of oil 2,582 g/L suggesting that the effluents a emulsifying character, gelling, stabilizing, lubricant and bactericide. Their presence is explained by neutralizating of the free fatty acids in crude oil which during the refining gives soap and by lipophilia brings neutral oil. This is worth an arrangement in waste water in mixed matte. The pH value 12 confirms the presence of soap and that it is about an emulsion oil-in-water of great stability. The presence of phosphates, sulfates and nitrates are neutralizing agents which ensure the longevity of the effluents and prove their exaggerated turbidity (422 NTU). The values of the DCO 18.95 and the DBO5 16.40 lead to a good biodegradability: (K) of 86.54 %.

Fractionation of the effluents: After preliminary extraction with ethanol of the active matter, thin layer chromatography allowed to detect two components: R_f 0.346 and R_f 0.339. It is without any doubt that the first R_f (apolar for oil) and the second R_f for (less polar for soap).

Soap in the effluents analyzes: The soap abundance in the effluents requires a specific analysis of the liquid soaps. Table-2 present the presence of products (glycerol, alkali and salt) resulting from a fatty-acids salt.

TABLE-2
AMOUNT OF THE EFFLUENTS IN PERCENTAGE

Glycerol	Free alkali	Total alkali	NaCl	Water
0.6	0.1	1.80	0.02	79

Infrared spectra of effluents: The spectrum essentially translates the revealing vibrations of soap, of fatty acids and of alcohol. (i) Beyond the absorption of 3500 cm^{-1}, a prominent band of the OH shows the presence water. (ii) Vibration of valence ν(C-C) in CH-CH, is met around 3016 cm^{-1} characteristic of the fatty-acids. (iii) Vibration of valence ν(CH), CH_2, CH_3,is met around 2069-2960, 2356, 2315 and 2069 cm^{-1} characteristic of a salt of carboxylic acid. (iv) Vibration of valence ν(C-O) in ester is shown around 1740 cm^{-1}. (v) Vibration of valence ν(C=C) in -CH=CH- is shown around 1650 cm^{-1}. (vi) Vibration of valence ν(R-COO-) characteristic of the carboxylate ions is shown around 1500 cm^{-1}. (vii) Vibration of deformation δ(CH) in CH_2 is shown around 1475 and 1420 cm^{-1}. (viii) The band of valence ν(C-H) in esters appeared at *ca.* 1350, 1306, 1270, 1220 and 1163 cm^{-1}. (ix) Vibration CO in alcohols appeared at 1035 and 994 cm^{-1}. (x) Vibration of valence ν(C-H) in *trans* CH=CH appeared at *ca.* 938 cm^{-1}. (xi) Vibration $\nu(CH_2)_n$ with $n \geq 4$ characteristic of an aliphatic chain of the fat contents meets at 770 cm^{-1}.

Ultraviolet spectrophotometry of the effluents: UV spectra expresses two extinctions which absorb in the vicinities of 268 nm (minotory) and 210 nm (majoritory) relative to two tension-actives.

Proportioning of the impurities of the soaps: The results of analyses are collected in Table-3.

TABLE-3
PRINCIPAL IMPURITIES OF THE SOAP (%)

Unsaponified	Unsaponifiables	Sodium sulfate	Alkali free
0.158	1.229	0.2	0.1

The presence of impurities such as unsaponified-unsaponifiables, free alkali and sodium sulfate confirm the presence of soap in the effluents.

Rheological properties of the effluents: The rheological results are present in Table-4.

The rheological results qualify a flow close to a model Bingamien. This nature is related to a macromolecular characteristic of the components of the effluents. They also determined the influence of the additives present on the texture non-thixotropic of the fluid at low consistency. The soap acts on plasticity and oil on viscosity, hence, the traditional name of viscoplastic to indicate the lubricants.

Contaminants in the effluents: One understands by contaminant, the metals (Cu, Pb, Cd, Li, Fe, Ni, Co, Cr mg/L) whose results of analysis are given in Table-5. Their negligible presence of metal ions in the effluents is explained by their drive during the extraction of the seed oil. They contribute effectively to the stability of the emulsions and support their colloidal properties by ensuring their detergent capacity.

TABLE-5
CONCENTRATION OF THE METAL CONTAMINANTS PRESENT IN EFFLUENT (mg/L)

Cu	Pb	Cd	Li	Fe	Ni	Co	Cr
<0.04	<0.01	<0.01	<0.01	<0.30	<0.06	<0.05	<0.05

Conclusion

The microbiological study certified the healthiness of the effluents whose microscopic observation shows that it is a stable emulsion of type I. The water chemistry confirms a total biodeterioration (86.54%) doubled with very good biocompatibility of the effluents. The results of analysis suggest an

TABLE-4
RHEOLOGICAL PARAMETERS OF THE EFFLUENTS WITH 20 ºC

Kinematic viscosity (Cst: V_{20})	Dynamic viscosity (C_P: V_{20})	Density (20 ºC/eau 20 ºC g/cm^3: D_{20})	Index of refraction (n_{20})	Viscosity apparent (C_P: μa)	Viscosity plastic (C_P: μp)	Yield value (γv or γp: Pa)
1.50	1.51	1.0034	1.3406	2.5	2	1

increased presence of soap related to a negligible lipidic phase which makes of the effluents an activate tension of the vegetable origin. The phosphates, the sulfates and the nitrates by their antioxidant properties are good conservatives stabilized by the presence of certain metals. This confers to the effluents effluents viscoplastic properties of the effluents allowing to it a contribution to a real progress in the field of the formulation of lubricant by new molecules. In front of the excessive prices of the lubricants, this is a natural emulgator (effluents) of a considerable source (emulsifier, gelling, stabilizing, peptising, lubricant, bactericides and antifoaming). This raises certainly a lively interest for user industries such as surfactant in the cattle food, coatings products, cosmetic, pharmacy, production of oil, construction materials, the foundry in minerals, the polishing of metals, in the plastics (plasticizing and lubricating) in various employment (joined, candles), detergents and particularly paper, textile, leather. This study proves to be conclusive with their identity in the capacity as surfactants and encourages their exploitation with multistage.

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