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Treatment and Modeling of Industrial Liquid Effluent adsorption isotherm on plant-based materials

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ABSTRACT/RESUME

Abstract: *Margins are not degradable due to the presence of substances (phenols, volatile fatty acids, etc.), which pose problems for the environment. In order to protect our environment, and currently know various treatment pathways such as adsorption, we studied the effects of diethylaminoethyl-cellulose (DEAE-ellulose) on the constituents of a gem and studied the adsorption power of DEAE-cellulose of phenolic compounds present in the gills of Tadmait willaya Tizi-Ouzou. The latter showed that the best adsorption conditions are simple to achieve: temperature of 22°C, direct use of the margin (Vm = 10 ml, pH = 4.5) in rather large quantities compared to that of the adsorbent (mass ratio = 10) and that the Freundlich model better represents the adsorption of the phenolic compounds of the margin on the DEAE cellulose. Infrared spectroscopy analyzes showed the complex composition of the margin in various organic constituents. MEB- EDS microscopy analyzes revealed amorphous morphologies of the cellulose and the dry matter of the margin.*

I. Introduction

Originally, the margines are presented as an aqueous residual liquid, of reddish brown color, which transforms reddish brown, which turns into black margine, foul-smelling, cloudy appearance and a specific smell of olive oil. They are characterized by an acid pH of 4 to 5 [1, 2,3] and a very high electrical conductivity due mainly to potassium ions (4 g/l), chloride, calcium and magnesium ions [4,5]. Its black color results from the presence of polyphenols [6,7].
The margins are a serious environmental problem. Their harmful effects derive largely from their content in polyphenolic compounds, some of which are very difficult to biodegrade [8]. When these are released into the wild without any control, it is then necessary to foresee contamination of groundwater, pollution of surface and groundwater, clogging of the soil and the release of foul odors. Therefore, Prior treatment would be necessary. These considerations led several researchers to develop decontamination processes. These techniques, physical, chemical and even biological, involve treating these effluents in order to reduce their impact on the environment.
[9] The uncontrolled discharge of the Algerian olive industry (TiziOuzou) leads to pollution that can have negative impacts on human health and the environment [10]. In this paper we studied one of the processes that consist of the elimination of polyphenols present in the margins where DEAE-cellulose was selected as adsorbent.

II. Results and Discussion

The adsorption power of DEAE-cellulose, phenolic compounds, was studied by assessing the effects of the parameters: Initial pH of the margin, temperature, mass ratio (mass of the margin / mass of the adsorbent) and volume of the parent margin concentrated by 10 ml of the margin in contact with the cellulose. To investigate the influence of these parameters and their interactions,

. The operating conditions and results of adsorption tests of phenolic compounds on DEAE-cellulose are given in Table 1.

We used a complete factor plan of 24.These experiments were carried out in a 2-minute period, corresponding to the time sufficient to reach the adsorption balance.

The grapes used are from a modern oil mill in the region of Tadmait willaya Tizi-ouzou.It is black in color and originally contains a solid phase which is separated by filtration on sintered glass.
The resulting margin is then stored at a temperature of 4 C°. It is then characterized by: Measurement of acidity (PH), Dry matter (MS) (g/l), Volatile matter (MV) (g/l), determination of phenolic compounds: Experimental tests were carried out over a period of 2 minutes to study the adsorption power of diethylaminoethyl-cellulose (DEAE-cellulose) screw the constituents of a magneto. Different analytical techniques were used to characterize adsorbate (margine) and adsorbant (DEAE-cellulose) and Infrared Spectroscopy (FTIR).

II.1. Characterization of adsorbent (DEAE-cellulose):

The samples of DEAE-cellulose fine powder pure and loaded with adsorbate, shall be analyzed by:
Infrared spectroscopy (FTIR) analyzed with a device of type PERKIN-ELMER-ONE SPECTRUM, at room temperature with a number of scans equal to 60 and a resolution of 2 cm-1. Spectrum analysis and processing was carried out using the computer software GRAMS 386. , Electronic scanning microscopy (MEB) with the Using the Philips ESEMXL30 scanning electron microscope with tungsten filament and the analyzes (EDS) were made with an EDS device from oxford SDD detector instrument Xmax 50mm2.

II.2. Characteristics and composition of the margins

The main characteristics of the gears are given in the table below [1]

Table 1. *Feature of the Margins Used*

Parameters	Values	Unit
pH	4.5	
Dry matter (DM)	76.7	(g/l)
Volatile matter (VM)	54.6	(g/l)
Phenolic compounds (PC)	3.73	(g/l)
CDO	6.35	(g/l)
Refraction index	1.32	

In general, the margins contain a variety of organic and inorganic compounds of different concentration and nature. Several factors may affect their quantity, quality and chemical composition during extraction and/or after release to the receiving environment, including: the variety of olive, the maturity of fruit, climatic conditions [2, 3] the nature of the soil, the agronomic practices of cultivation and harvesting,the age of olive trees and the methods of extraction [11].
The measure of PH of margine indicates that the margine used is acid in nature, because of the organic acids it contains [12].
The organic matter of the margins consists of two fractions: an insoluble fraction consisting mainly of olive pulp and a soluble fraction containing various compounds such as sugars and phenolic compounds [13]. The latter are considered among the most important constituents of the margins, in fact they are largely responsible for the polluting power of the margins [14]. The organic matter content expressed as COD is in the order of 6.35 g of O2/l, which is still less important than that recorded for other types of releases.

II.3. FTIR Spectrum of the Margin

The FTIR spectra of the dried parent and treated material are virtually identical, indicating the following figure 1.1:

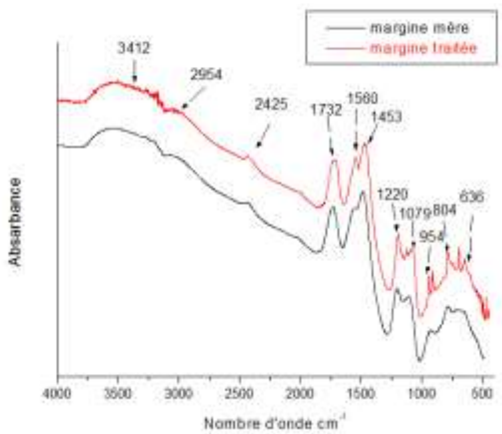

Figure 1. *Infrared spectra of the parent and treated margin.*

Examination of the spectra of the two margins would reveal the IR absorption bands mentioned in Table 2:

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Table 2. *IR bands characteristics of the margin*

Number of waves cm^{-1}	Assignment
Broad and intense band at 3412	O-H bond elongation (phenol)
band at 2954	Sature and aromatic C-H elongation vibration
peak at 2425	elongation C=O
Intense band at 1732	C=O elongation of ketones
1560 strip	C=C elongation of alkenes (aromatic)
peak at 1453	deformation - CH3 in plane
Peak at 1079-1220	C-O Alcohol Extension (secondary)
Peak at 636-804	deformation out of plane C-H (adjacent 2H).

Figure 1 shows the infrared spectrum of the crude and cellulosic-treated margin. This figure shows a great resemblance in all adsorption bands, but it is noted that the adsorption bands of the crude margin have slightly higher intensities than those of the treated margin, and this is due to the elimination of some compounds initially present in the margin.

II.4. microanalysis by EDS

EDS microanalysis gives the chemical composition according to the mass and atomic percentages (see Figures 2 and Table 3). the EDS spectrum of the margin, tells us the high presence as a proportion of carbon, which confirms that the margin is rich in organic matter.
Other elements have been detected, with different proportions such as: oxygen; potassium, chlorine, magnesium and calcium.

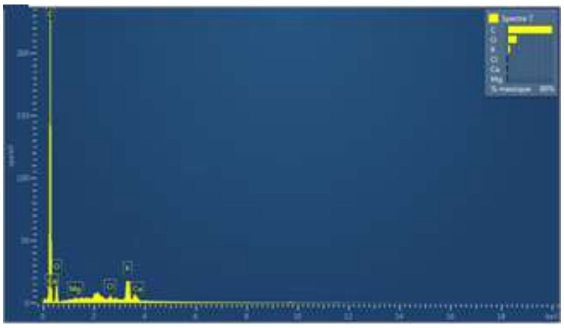

Figure 2. *Spectrum EDS of the dry matter of the parent margin*

Table 3. *Microanalysis by EDS based on the mass and atomic percentages of the parent margin.*

Element	% Mass	% atomic
C	78.21	84.81
O	16.43	13.37
Mg	0.11	0.06
Cl	0.26	0.10
K	4.77	1.59
Ca	0.22	0.07
Total	100.00	100.00

II.5. Scanning electron microscopy (MEB)

Scanning electron microscopy (MEB) observations could give us an insight into the morphology of the parent margin, and provide information on the homogeneous or non-homogeneous dispersion of our solid (aggregate formation). Figure 3 shows the MEB scanning electron microscopy micrograph of the parent margin dry matter obtained after 1000 times magnification.
According to this micrograph, the dry matter of the parent margin appears in an irregular and heterogeneous granular form over the entire surface analyzed. Two distinct parts appear: one dark with a melted aspect, probably corresponding to the organic fraction of the dry matter, the other brighter and grainier because it is richer in heavier elements, constituting the mineral part.

II.6. Cellulose characteristics and composition

Fourier Transform Infrared Spectroscopy (DEAE-cellulose FTIR:
IR analysis was performed for pure and charged DEAE-cellulose obtained after adsorption of the margin

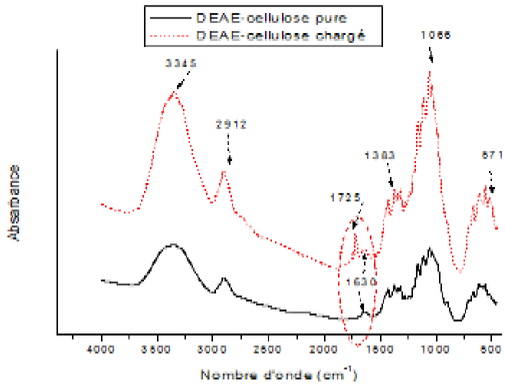

Figure 3. *Infrared spectra of pure and charged DEAE-cellulose.*

Figure 3 shows the infrared spectra of pure and charged celluloses.Based on both spectra, the 3345 cm-1 band, characteristic of the OH bond of the celluloses, is shown. Phenol and water in the case of charged cellulose; the appearance of a new peak at 1725 cm^{-1} in the FTIR spectrum of the charged cellulose. This means that cellulose adsorbed polyphenols and other compounds containing in the margin.

The following table (4) shows the different peaks a nd bands that characterize pure cellulose and after treatment (loaded).

Table 4. *Attribution of the characteristic bands and peaks of the cellulose FTIR.*

Number of waves cm^{-1}	Assignment
Widespread and intense peak at 3345	O-H elongation
peak in 2912	Sature and aromatic C-H elongation vibration
1725	C=O extension of ketone
1630 cm^{-1}	C=C elongation of alkenes (aromatic) deformation.
1383 band	deformation. C-H in the plane (CH_2- CH_3).
pic 1066	C-O Alcohol Extension (Secondary)
571-994	deformation. off-plane C-H (benzene. (4Hadjacent).

II.7. Microanalysis by EDS on DEAE-cellulose

EDS analyzes of pure DEAE-cellulose show that it consists of three atoms, respectively:

Oxygen, carbon, and chlorine given (Figure 5 and Table 5), and this of the charged DEAE-cellulose shows that, in addition to the elements already present in pure DEAE-cellulose, other elements are found, in this casepotassium and calcium which fall within the constitution of the margine (Figure 6 and Table 5).
It is also noted that there is an increase in the mass percentage of carbon, which is explained by the adsorption of organic constituents of themargine by DEAE-cellulose.

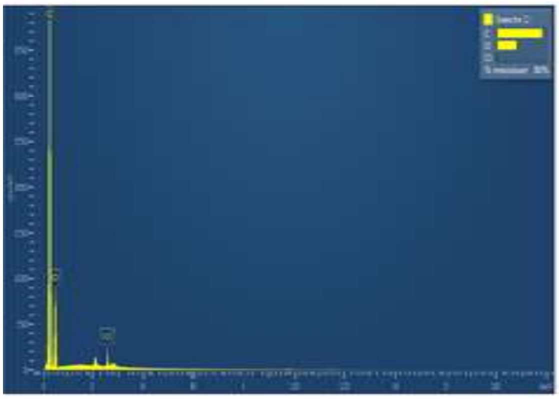

Figure 4. *DEAE-pur EDS Spectrum*

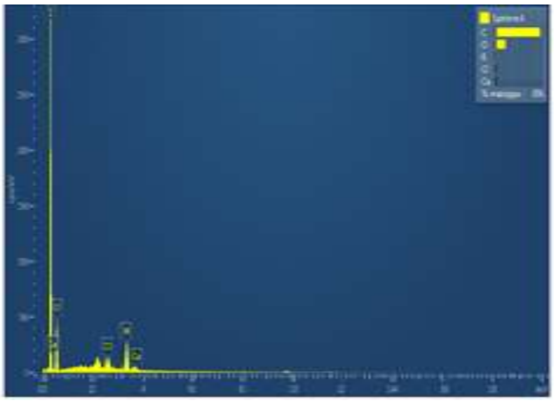

Figure 5. *Filled cellulose DEAE EDS Spectrum*

Table 5. *Microanalysis by EDS based on mass and atomic percentages of DEAE-cellulose*

Element	% Mass	% atomic
C	71.79	77.49
O	27.41	22.21
Cl	0.80	0.29
Total	100.00	100.00

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Table 6. *Microanalysis by EDS based on mass and atomic percentages of DEAE-cellulose loaded.*

Element	% Mass	% atomic
C	76.00	81.68
O	21078	17.58
Cl	0.54	0.20
k	1.54	0.51
Ca	0.14	0.04
Total	100.00	100.00

II.8.Scanning Electronic Microscopy (MEB)
Figures (6 and 7) show, respectively, the micrograp hs of MEB scanning electron microscopy of pure ce llulose and charged cellulose obtained after 1000 m agnification.

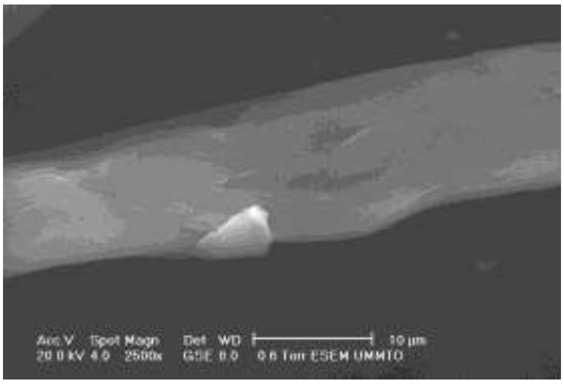

Figure 6. *Pure DEAE-cellulose MEB images*

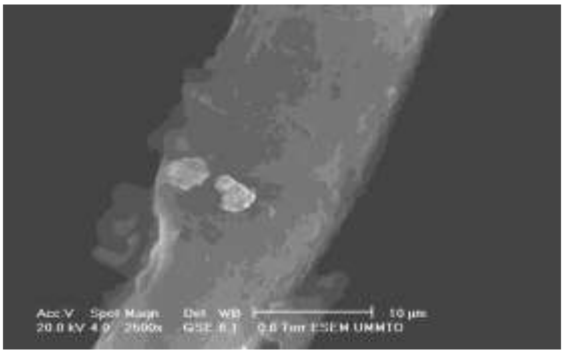

Figure 7. *DEAE-loaded MEB Images*

C.Study of the adsorption power of DEAE-cellulose The operating conditions and the results of the adsorption tests of phenolic compounds on DEAE-cellulose are listed in the following table:

Table 7. *Operating conditions and results of adsorp tion testing of phenolic compounds*.

ExpN°	Coded Values (Experience Matrix)				Response
	X_1	X_2	X_3	X_4	Δ Cp (g/l)
1	-1	-1	-1	-1	0.67
2	1	-1	-1	-1	0.62
3	-1	1	-1	-1	2.58
4	1	1	-1	-1	2.46
5	-1	-1	1	-1	0.62
6	1	-1	1	-1	0.60
7	-1	1	1	-1	1.96
8	1	1	1	-1	2.05
9	-1	-1	-1	1	1.23
10	1	-1	-1	1	1.23
11	-1	1	-1	1	2.02
12	1	1	-1	1	3.03
13	-1	-1	1	1	1.13
14	1	-1	1	1	1.28
15	-1	1	1	1	2.30
16	1	1	1	1	0.80

II.9. Parametric study
The parameter effects diagram [10,11,12] shows that the coefficient b2, corresponding to the volume Vm, is clearly the most important (Figure 9). This i ndicates the dominant effect of this factor on the ad sorption power of phenolic compounds.

Figure 8. *Effects diagram.*

bi: Main effect of factor i.
bij: Effect of interaction between factors i and j.

The interaction [13,14] of the first order Vm-R (b_{2-4}), comes second with an effect that appears to be relatively less important than that of the Vm parameter.
These results are confirmed by the Late approach (Table 8).

***Table 8.** Late End Outcomes*

Iteration Count	1	2
Median	0.133	0.112
So	0.200	0.168
Limit Value	0.501	0.419
texp	2.64	
ddl	4.67	

So: standard deviation.
text: t experimental.
ddl: degrees of freedom.

Taking only this interaction between the two ratio factors and Vm into account, the best adsorption power is obtained with a mass ratio of 10 and 10 ml Vm. Temperature and pH do not appear to have much influence. Therefore, it is more interesting to choose the ambient temperature and natural acidity of the Margin (T ± 22°C and pH = 4.5) for adsorpti on operations of phenolic compounds.

III. Adsorption isotherm

The adsorption isotherm curve of the phenolic compounds of the margine represents the variation in the equilibrium adsorbate concentrations, respect ively in the Ce solution (g/l) and in the Qe adsorbent (g/g cellulose).

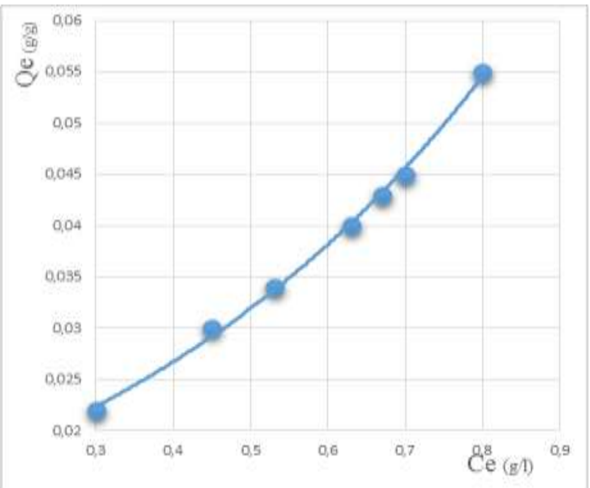

***Figure 09.** Isotherm of adsorption of phenolic Compounds*

With reference to the classification of Gil and al, this isotherm is of type S group 1, which means that the Adsorption of the phenolic compounds of the margin is a vertical adsorption, with solute molecules clinging to the solid through a single group and the adsorption of the solvent is appreciable.

III.1. Modeling of adsorption isotherm

The description of the adsorption isotherm was carried out using the Langmuir and Freundlich models.
The plots of the 1/Qe curves according to 1/Ce (Langmuir) and ln Qe according to ln Ce (Freundli ch) are shown in the following figures.

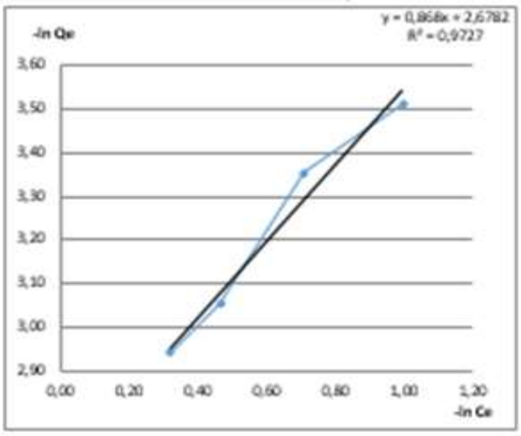

***Figure 10.** Linear form of the Freundlich isotherm*

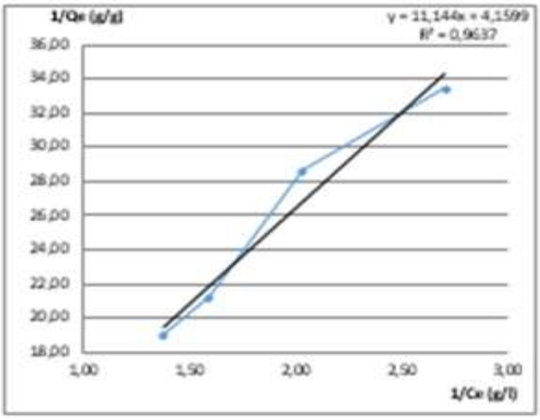

***Figure 11.** Linear form of the Freundlich isotherm*

The parameter values for both models (Langmuir an d Freundlich) are given in Table 9.

***Table 9.**parameters characterizing the adsorption i sotherm models of phenolic compounds.*

Isotherme Model	parameter		**R^2**
Langmuir équation 1	Q_m	0.24	0.963
	K_L	0.36	
	R_L	0.88	
Freundlich	K_F	14.55	0.972
	n_F	1.15	

Qm: maximum adsorption capacity g/g,
KL: Langmuir equilibrium constant,
RL: equilibrium parameter of Langmuir,
KF and nF: Freundlich constant,
R^2: coefficient of determination, R: correlation coeff icient.

We note that the values of the coefficients of determination R^2 obtained are greater than 0.95 for the two models, they are close to unity The adsorption of phenolic compounds from vegetable water on DEAE-cellulose follows:

¬ The Langmuir model with a maximum quantity of adsorption of 0.24 mg.g-1, The intensity of the adsorption, evaluated by the parameter RL, also indicates that the adsorption is favorable because 0< RL (0.36) <1.

¬ The Freundlich model is found when there is heterogeneity of the surface of the adsorbent and that of the interactions between the adsorbed species, The value of the Freundlich heterogeneity factor n =1.15, the phenolic compounds are there fore favorably adsorbed by the DEAE-cellulose

IV. Conclusion

The physicochemical characterization of themargins studied shows that it is a polluting acid effluent. The study of the adsorbent power of cellulose for the phenolic compounds that make up margine revealed essentially that:

¬ Margin is acidic in nature and contains various constituents of different kinds (organic compounds and minerals).

¬ Infrared spectroscopy, EDS microscopy, and ME B analysis revealed the binding of gem particles to cellulose

¬ The operating conditions and results of the adsorption tests of phenolic compounds on DEAE-cellulose show that the best adsorption power is obtained with a mass ratio of 10 and 10 ml Vm. Temperature and pH do not appear to have much influence. Therefore, it is more interesting to choose the ambient temperature and natural acidity of the Margin (T ± 22°C and pH = 4.5) for adsorption operations of phenolic compounds.

¬The appearance of the adsorption isotherm of the phenolic compounds of the gem on cellulose is of type S

¬ The Langmuir and freundlich model better represents the adsorption of phenolic compounds on thecelleulosebecause the value of the coefficient R^2 is closest to the unit.

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