

Optimization of the Electrocoagulation Process by Central Composite Design for Olive Mill Wastewater Decolorization and Removal of Polyphenols

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Abstract— Olive oil extraction processes generate three phases: Olive oil, solid residue (pomace), and aqueous liquor Olive Mill Wastewater (OMW). OMW causes serious environmental deteriorations such as coloring of natural waters, alteration of soil quality, phytotoxicity, and odor nuisance. The direct discharge of this effluent into the soil brings various negative effects on the environment, due to its high load of organic matter and phenolic compounds. Coagulation, flocculation, and their combined processes are among the most widely applied processes for wastewater treatment. In this study, electrocoagulation (EC), alone or in combination with precipitation or centrifugation, was evaluated as a potential pretreatment method for OMW, which is an effective solution to reduce COD and phenolic compounds from OMW. It is a low-cost treatment, using fewer chemicals and less sludge production. CCD (Central Composite Design) optimization has been established for the electrocoagulation process to achieve OMW decolorization and polyphenol removal. The min and max values selected for the pH (X_1) [4 to 9], the intensity of the current user (X_2) [0.5 to 1.5 A], the distance between the electrodes (X_3) [1 to 3 cm], and the amount of salt added (X_4) [1 to 5 g/l]. With 30 min of electrolysis, a voltage of 20 volts ($250 \text{ A} / \text{m}^2$), the decolorization of OMW diluted five times is between 22 and 37%, the reduction in chemical oxygen demand (COD) is approximately 80 to 85%. The values for the six responses determined (theoretical and practical) are respectively, Decolorization (23.16.16%), final pH (4.02, 4.4), final conductivity (12.02, 12.04 ms/cm), Purification (80.9, 84.42%), Separated mass (0.61, 0.56g), Rate of polyphenols removed (72.59, 67.03%). We remove up to 70% of the polyphenols which are a source of toxicity in OMW and have a clarified effluent.

Keywords— OMW, decolorization, DOE, Optimization, electrocoagulation, hydroxytyrosol, polyphenols.

I. INTRODUCTION

During the previous decade, the electrochemical wastewater treatment process initiated to be grown as an environmentally friendly technique that produces minimum footprint without compromising the quality of the treated water, minimum sludge generation, and requires no chemical additives [1]. In the present study, electrocoagulation (EC), alone or in combination with precipitation or centrifugation, was assessed as a potential pre-treatment method for Olive mill wastewater. The Electrocoagulation process is economical as it produces a relatively less amount of sludge in comparison with conventional processes [2]. EC technology is a treatment

process to treat wastewater by applying electric current as the main power source [3]. In an EC process, the dissolute metal hydroxide ions are capable enough to eliminate solvable inorganic contaminants. The foremost reactions in the EC procedure are iron/aluminum dissolution from the anode and hydroxyl ion production at the cathode [4]. OMW is an environmentally problematic effluent, on the other hand, it is a rich source of bioactive compounds with promising biological properties. Consequently, both treatment and valorization of this wastewater have been the focus of research during the past two decades [5]. In fact, OMW is characterized by high concentrations of several organic compounds including sugars, tannins, pectins, lipids, and phenolic substances. Furthermore, the process allows for the recovery of olive mill wastewater that is enriched particularly in bioactive components of interest, of a varied nature and composition, which can be extracted and used for industrial purposes [6].

However, these by-products present a complex physicochemical composition and the recovery of target compounds from these sources require several steps (i.e., coagulation and precipitation of impurities, adsorption on resins) based on the use of chemicals, solvents, and high temperatures, which increase the total production costs [7]. For example, OMW typically is a phenolic-rich industrial effluent that contains 98% of the total phenols in the olive fruit [8]. Accordingly, during the last two decades, many publications describe polyphenols removal by electrocoagulation as a single treatment process or as a process integrated into a combined treatment system [9]. The olive tree is a tree that belongs to the subphylum Angiosperms, the dicotyledonous class, the asteridae subclass, the order *Scrophulariaceae* and the family *Oleaceae*. There are several species distributed in the world, one in particular the species *Olea europaea* cultivated in the Mediterranean world. In Tunisia, depending on ripening, olive trees are cultivated in all regions starting with the island of Kerkena passing through Cap Bon and Sousse to end in the steppes of Kasserine and, in the South, around Zarzis and the island of Djerba.

Thanks to the geographical location, several varieties have emerged: the two main varieties are "Chemlali" and "Chetoui" and the other secondary varieties are "Chemcheli", "Zalmati", "Zarrazi", "Gerbouli" and "Sayali". There are also varieties,

which give table olives such as "Meski", "Besbesi", "Beldi" etc. Tunisia is therefore an olive grove by excellence [10]. In terms of olive oil production, Tunisia is the sixth largest producer in the world, but it can reach, when the harvest is good, the fourth place in the world. Tunisian production is characterized by high variability since yields are largely influenced by rainfall. In Tunisia, olive oil is a very important export product for the economy. Tunisia is the third largest exporter of olive oil in the world after Italy and Spain.

The process of turning olives into olive oil is called crushing. In this step, we collect the olives, then the leaf stripping and washing take place and finally we move on to extracting the oil. There are three olive oil extraction processes: by press, continuous 3-phase system and continuous 2-phase system.

These methods generate toxic vegetable waters (very concentrated in chemical elements) with a volume of (40 to 60 L/100 kg olives since water is added in small quantities for 1 to 2 phases extractions and 80 to 120 L/100kg for 3 phases extractions process [11].

In addition, the chemical oxygen demand (COD) and biological oxygen demand (BOD₅) are very high, the pH is very acidic and several other parameters described in Table I show this toxicity [12].

TABLE I. Some characteristics of OMW raw sample compared with others samples

Settings	Our OMW Raw sample	Interval for other research	References
Organic material (%)	52.3 - 59.4	57.2 - 62.1	[13]
pH	4.2 - 5.5	2.2 - 5.9	[14]
Lipid level (%)	0.007 - 3.9	0.003 - 4.25	[15]
Total polyphenols (g/l)	7.09 - 7.42	0.63 - 5.45	
COD (g/L)	45.23-106.80	30 - 320	[16]
BOD ₅ (g/L)	17.64- 41.72	35 - 132	

Indeed, olive oil has several advantages other than nutritional value. It is used in the prevention of diseases such as cardiovascular disease, atherosclerosis, high blood pressure, diabetes, digestive system dysfunction, and certain cancers. In addition, it is used in several cosmetic products for the hair, the skin, and against wrinkles. During production, leaves, pomace, and vegetable water are inevitable by-products and we notice poor management of these by-products. Indeed, these elements are valued in several areas. The fresh olive leaf consists of dry matter (50% by weight), cellulose, proteins, lipids, minerals, a low level of polyphenols and tannin. They are used for animal feed, but also in herbal medicine to treat certain diseases (hypertension, for example) and to maintain health [17]. Research shows that the extract of these leaves has antimicrobial activities, antiviral activities and anti-oxidant activities [18]. In addition, the extraction of compounds of interest such as mannitol, sterols, fatty alcohols, phenolic, flavonoids and mainly oleuropein compounds [19].

Pomace is made up of 25% water. The dry matter is composed of mineral matter (3%), nitrogenous matter (5%), cellulose (35%) and fat (8 to 15%) but these proportions vary according to the variety of olives. This pomace is used as fuel (after drying) and in the wood industries. The residual oil is

chemically extracted to give a secondary oil, which requires refining. Pitting allows the pomace to be used for livestock feed [20]. Combustion allows the ash to be used as a fertilizer [21].

Olive Mill Wastewater (OMW), the subject of our study, may be the most valuable by-product according to its composition. The vegetation water and OMW of the olives remains after decantation or centrifugation (during the extraction of olive oil). They are usually brown colour, with a bad odour, bitter taste, and cloudy appearance (fig 1).



Fig. 1. Storage of vegetable waters (OMW) in basins

OMW is defined as the vegetation water oilseed plants recovered as by-products during the extraction of their oil. Olive's vegetable waters contain several valuable substances depending on the variety of the olive tree, maturity, and the oil extraction process [22]. The composition of vegetable waters is an asset for scientific research as a by-product containing several molecules of interest [23]. However, the concentration of its elements is very dangerous on the soil and the plants when this effluent is spread in nature without treatment. Several techniques are used for the treatment of vegetable waters, among which we can cite: ultrafiltration [24], flocculation [25], coagulation [26-13], and composting [27].

OMW are generally composed of 88% water, 10.5% organic matter, 1.5% mineral matter, 1.25% nitrogenous matter, 0.1% fat and 1% polyphenols. This composition varies depending on several factors such as the extraction technique used and the maturation of the crushed olives [22]. The mineral matter is composed of potassium salts and phosphates. OMW is acidic (pH 4.5 to 5) and contain poorly biodegradable polyphenols. The conductivity of OMW is of the order of 10-12.5 mS/cm thanks to the presence of minerals such as potassium, chloride, calcium, magnesium. The chemical oxygen demand (COD) can vary from 50 to 220 g/l [28].

These characteristics show the richness of OMW, which can be valued in different areas:

- Irrigation of certain plants,
- Use of polyphenols for their antioxidant power. The result was favorable to the use of synthetic antioxidants,
- Production of methane by anaerobic fermentation of organic matter [29].
- Fertilization of the soil due to mineral content,
- Spreading in arid soils [30].
- Natural biodegradation by storage in ponds shown in fig. 1 if the COD is low [31].

In addition, the pollutants in the OMW infiltrate towards the subsoil that exceeding the standards for discharge in the natural environment [22]. Our major concern is to treat the

OMW before their release into nature, so it is imperative to find solutions in order to minimize the harmful effects of this effluent. Tunisia has put several laws, decrees and standards to be observed before dumping an effluent either in nature or in the sewerage network. Table II gives the limits cited in the Tunisian standard NT 106.02. [32].

TABLE II. Some discharge limits given by Tunisian standards

Characteristics	In the natural environment	In the sanitation network
pH	6,5	6,5 à 9
COD (mg/l)	90	1000
BOD ₅ (mg/l)	30	400
Phenols (mg/l)	0,002	1
Fat (mg/l)	10	30

These limits are intended to require manufacturers to apply an effective treatment to remove as many pollutants as possible. The manufacturer is always trying to minimize the cost hence the emergence of several treatments.

New techniques have appeared with the aim of optimizing the detoxification of OMW, including treatment by adsorption [33], and the coupling of treatment processes (Ultrafiltration, Nanofiltration, Evaporation, Coagulation, Flocculation) with electrocoagulation as an electrochemical treatment being the subject of our work.

Electrocoagulation is a technique derived from coagulation-flocculation. Its advantage is that it allows ions to be generated in situ, which can provide electrostatic destabilization at acidic or neutral pH. It also has the advantage of eliminating certain pollutions (turbidity, colloidal matter, color, heavy metals) by adsorption on the metal hydroxide flocs which form when the pH is basic [34]. The main advantages of the electrocoagulation process highlighted by several authors are the compactness of the installations, the lower volume of sludge, and the elimination of colloidal particles [35].

Our goals are

- The treatment of OMW by electrocoagulation considered as a new electrochemical process.
- Optimization of electrocoagulation for a possible separation and characterization of biomolecules of interest.
- Promotion of OMW in order to reduce environmental pollution,

In addition, this electrocoagulation treatment solution facilitates subsequent separation and further minimizes their chemical oxygen demand (COD) and their biological oxygen demand (BOD₅) and therefore their toxicity.

II. MATERIALS AND METHODS

2.1. Olive Mill Wastewater Effluents

This study focused on wastewater from olive mills called vegetable waters from an industrial olive oil unit MEDGOLD located in Menzel Kamel - Monastir central Tunisia, during the 2020-2021 olive season. No chemical additives are used during the production of olive oil. The samples are taken in plastic jars, tightly closed, and stored at (-4°C) until use. Before electrocoagulation, the samples are decanted then the supernatant is filtrated through Whatman paper. After thawing

at room temperature these samples are ready for electrochemical treatment.

2.2 Delipidation

The raw OMW effluent requires delipidation because the lipid fraction hinders EC treatment. The delipidation of the OMW effluent is carried out according to De Marco et al [36], by adding 1.5 liters of hexane to 1.5 liters of OMW, then a decantation is carried out for the separation of the lipid fraction shown in Fig. 2 thus we recover the delipidated phase.



Fig. 2. Delipidation of OMW effluent

The delipidated OMWs are placed in a centrifuge at 6000 rpm for 15 min. This operation removes all solid impurities by precipitation and the liquid phase will be recovered.

2.3. Experimental techniques

In this study, we are interested in electrochemical treatment by electrocoagulation since it is the least expensive and the most effective, according to recent research [37]. An electrocoagulation reactor consists of an electrolytic cell with an anode and a cathode, equivalent to pairs of conductive metal plates. The plates are connected to an electric voltage generator by conductive wires [38]. The electrocoagulation cell shown in fig. 3, with a volume of 100 ml, has two aluminum electrodes (Al-Al), one serving as a cathode and the other as an anode. The electrodes are 45 mm x 40 mm and an inter-electrode distance was chosen. Direct current is applied to the electrodes by a current generator (4A, 30V).

A magnetic stirrer mixes the solution in the electrolytic cell. The agitation is fixed at 200 rpm. After EC treatment, the solutions are allowed to settle and then the supernatant will be filtered on Watmann paper.

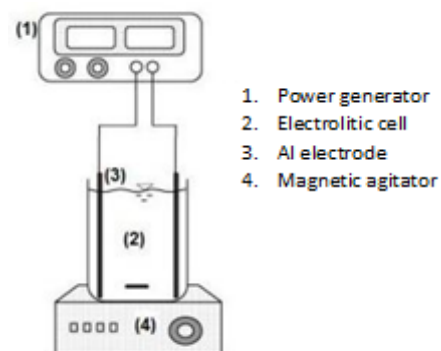
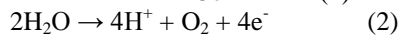
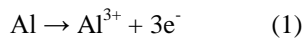


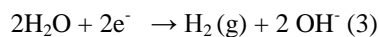
Fig. 3. Process of electrocoagulation [39]

When an electric current is introduced into the solution, the positive side undergoes anodic reactions, while cathodic reactions are encountered on the negative [40]. We find several types of materials used as electrodes such as iron, copper, zinc and aluminum. The most widely used and efficient electrodes in electrocoagulation process are aluminum ones [41]. The reactions that take place in the anode produce Al^{3+} ions and oxygen according to the two equations 1 and 2:

At the anode:



At the cathode in a basic medium, the reaction that takes place is the formation of hydrogen bubbles according to equation 3:



Due to the pH, aluminum does not remain in cationic form. The cations formed react with water to form complexes of the type $Al_2(OH)_5^+$, $Al_2(OH)_2^{4+}$, or the poorly soluble hydroxide $Al(OH)_3$.

These species play the role of coagulant by neutralizing the negative charges on the surface of the colloids.

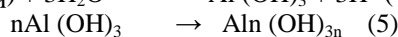
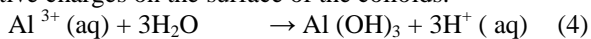


Fig. 4 illustrates the three reactions and the fate of each ion formed in the anode and in the cathode. The metal ions sacrificed in the liquid medium (Al^{3+}) tend to eliminate unwanted contaminants (pollutants) either by chemical reaction and precipitation, or by causing the colloidal materials (flocs) to melt, then to be removed by electrolytic flotation (arrow up) thanks to the hydrogen H_2 formed with the cathodic reaction [42].

The electrocoagulation process is therefore favorable for the removal of metals, solids, colloidal particles, and soluble inorganic pollutants. It has a number of advantages, such as reduced sludge production (compared to other treatments) and no requirement to use chemicals, which makes the choice of this treatment better [42].

Among the elements eliminated by this process, we are interested in phenolic compounds. A study shows that OMW contain a soluble fraction resulting from tannins, anthocyanins, and aromatic monomers. Despite the toxicity of this fraction, it can be eliminated spontaneously by biodegradation reactions. The problem is represented by the polyphenols, which give the black coloring to the OMW. It is true that these elements are not very toxic, however, their biodegradation is difficult [43].

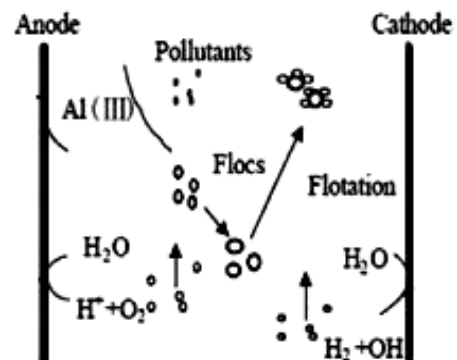


Fig. 4. Mechanism of electrocoagulation [44].

2.4. Extraction of Polyphenols from OMW Effluent

Polyphenols are secondary metabolites of plants that are produced in perfect synergy with the Mediterranean climate exerting stress on these plants. "Polyphenols" designates compounds having a benzene ring carrying one or more hydroxyl groups (free, esterified, or etherified). Polyphenols can bond with other molecules (carbohydrates, fats, proteins or other phenolic compounds). They represent almost 800 different compounds [45]. Fig. 5 shows representations of the main elements of these compounds with the numbering of carbon numbers. We can see that the benzene ring formed by six carbon atoms is the common form among different polyphenols.

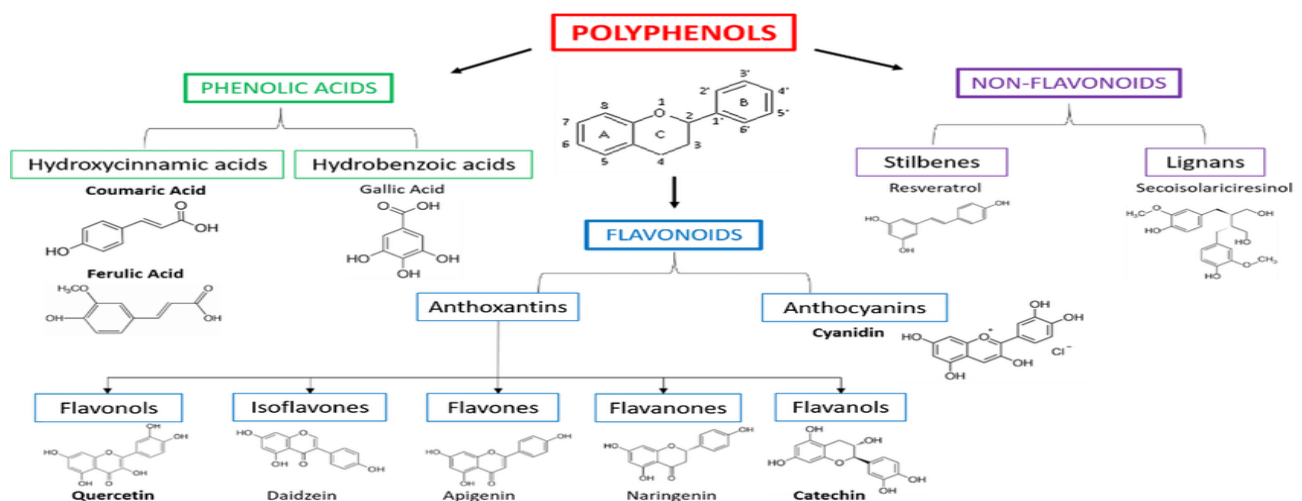


Fig. 5. Some classes of polyphenols [46]

Polyphenols exist in vegetables, fruits, teas, etc. They can prevent degenerative diseases and certain types of cancer by

their antioxidant action and/or by the modulation of several protein functions [45].

TABLE III. Polyphenols Classification [47]

Carbon skeleton	Class	Example
C ₆	Simple phenols	Catechols
C ₆ -C ₁	Hydroxybenzoic acids	p-hydroxybenzoic
C ₆ -C ₃	Hydroxycinnamic acids	Caffeic acid
C ₆ -C ₄	Naphthoquinones	Juglone
C ₆ -C ₂ -C ₆	Stilbenes	Resveratrol
C ₆ -C ₃ -C ₆	Flavonoids	Cyanidine
(C ₆ -C ₃) _n	Condensed forms	Lignins
(C ₆ -C ₃ -C ₆) _n		Tannins

According to the Table III there are several classifications according to the structure, the synthetic route and the degrees of modification of the basic skeleton of polyphenols (degree of oxidation, hydroxylation, methylation). Among these different choices, the classification according to the structure is the most used. It is based on the number of carbon atoms that make up the backbone of the molecule. Usually, six carbon atoms form a cyclic nucleus and the rest connects these nuclei to each other or between the nucleus and another molecule (can be another phenol or a polysaccharide).

2.5. Polyphenols Content Determination

The determination of total polyphenols is carried out by the colorimetric method using the Folin-Ciocalteu reagent. The Folin Ciocalteu reagent consists of an acid yellow solution; containing polymeric complex ions formed from phosphomolybdic and phosphotungstic heteropolyacids. It oxidizes phenols to phenolate ions in an alkaline medium and partially reduces these heteropolyacids resulting in the formation of a blue molybdotungsten complex. The bluish coloration obtained is proportional to the quantity of phenols present. The polyphenols are determined by the colorimetric technique of Folin Ciocalteu.

The resulting blue coloration gives maximum absorption around 750-760 nm wavelengths. This absorption is proportional to the amount of oxidized phenolic compounds present in the sample. The measurement is carried out by a UV/visible spectrophotometer [48].

This method helps us to determine the level of polyphenols in our samples (OMW). For a test portion of 2 g we add 5 ml of the extraction solution (80% methanol, 20% water), we stir with an ultra-turax for 30 sec at a speed of 13000 rpm. Then, a 10 min centrifugation is carried out at a speed of 3800 rev/min and at 4°C. 400 µl of the supernatant is recovered to which 1.6 ml of water is added with the addition of 10 ml of Folin-Ciocalteu reagent (diluted 1/10) and 8 ml of sodium carbonate NaCO₃ (7.5%) After stirring, the mixture is left to settle for 20 min. The blank test contains 400 µl of methanol instead of the supernatant obtained after centrifugation. Compliance with this procedure makes it possible to read the level of total polyphenols in parts per million (µg of polyphenols per g of sample) with computer software at a wavelength equal to 725 nm. The Lambda25 software each time displays the polyphenol content in the sample to be measured.

2.6. Biochemical and Chemical Oxygen Demands

The biochemical oxygen demand (BOD) is measured by the consumption of oxygen at 20°C in the dark for 5 days of incubation of a sample previously inoculated, the time necessary for the biological oxidation of carbonaceous organic matter [49]. The BOD₅ of our samples was measured by a respirometric method using a BOD meter (BOD Sensor 6, VELP Scientifica) [49]. The results are expressed in mg O₂/l.

Chemical oxygen demand (COD) is the measure of the amount of oxygen required for the chemical degradation of all organic matter that is biodegradable or not contained in water. It was carried out by the small-scale closed-tube method [50-51]. To 2 ml of the tube, the sample is added the COD reagent heated for two hours at 150°C. The COD reading is taken directly with a DR 930 spectrophotometer. It is expressed in mg of O₂/l.

The phenolic fractions of vegetable waters were identified by high-pressure liquid chromatography (HPLC). These analyzes were performed using a UV detector (280 nm) and a C-18 column (4.6 x 250 mm). Twenty µL of extract were injected and eluted by solvent gradient (Mobile phases: H₂O + H₃PO₄ (0.1%), Acetonitrile/Water (7/3) for 60 min with a flow rate of 0.8 ml/min.

2.7. Statistical and Experimental Design

Minitab is software that uses statistical laws and enforces them for our purposes. It is used to find a regression in a point cloud, to optimize the phenomenon studied by performing a minimum number of targeted experiments, to control the various parameters (or factors) influencing the process phenomenon, and to highlight the interactions between the variables. For each factor, we assign an optimal response interval (according to previous or preliminary scientific research). Thus, we use a fractional design to further minimize the experiments and based on subsequent research to set the ranges of variation for each factor. The acquired data were processed to calculate statistical values such as the mean and standard deviation (SD). The assumptions of normality and constant variance were checked and confirmed. DOE design analysis and analysis of variance (ANOVA) were used to determine the regression coefficients, the statistical significance of the model terms, and to fit the mathematical models of the experimental data that aimed to optimize the overall region for all response variables. A second-order polynomial model was used to predict the response variables as shown in Eq 6.

$$Y = \beta_0 + \sum_1^4 \beta_i X_i + \sum_1^4 \beta_{ij} X_i X_j + \sum_1^4 \beta_{ijk} X_i X_j X_k + \sum_1^4 \beta_{ijkl} X_i X_j X_k X_l \quad (6)$$

Y is the predicted dependent variable; β₀ is a constant regression coefficient, β_i are the regression coefficients for the linear effect terms, and β_{ij}, β_{ijk}, and β_{ijkl} are the regression coefficients of two, three, and four factor interactions effect terms, respectively. X₁, X₂, X₃, and X₄ are the factors (independent variables).

The influence of the various independent variables for all measurement was studied using one-factor at a time to select the significant ones, and to determine their preliminary range. Based on our previous experimental results (data not shown)

and other previous research intervals are set depending on semi-industrial or even industrial feasibility [39]. For this electrocoagulation process, the minimum/maximum values selected for the DOE design experiment as following, for the pH of OMW X_1 [4 to 9], the intensity of the current used X_2 [0.5 to 1.5 A], the distance between the electrodes X_3 [1 to 3 cm] and the amount of salt added X_4 [1 to 5 g/l].

The adequacy of the model was predicted through the regression analysis (R^2) and the ANOVA analysis.

Therefore, the combined effect of these four variables on the achieved Response (Y_i) for six responses values as following : Optical density for decolorization, mass of filtrate separated, Final conductivity, final pH, Turbidity and Eliminated rate of polyphenols was studied using central composite design (CCD) following a fractional factorial design $2^{(4-1)}$ or 2^3 so 8 experiences. In this design, the experimental points are generated on a sphere around the central point. It is assumed that the central point is close to an optimal position for the different responses. The experimental trials were randomized to minimize the effects of unexpected variability in observed responses.

The relationship between the independent variables and the response variables was demonstrated by the contour graph. Multiple graphical and numerical optimizations of the experimental data were done to identify the optimum conditions to achieve the desired optimum of all studied response. Verification of predicted response conditions that would give the desired response was determined based on the superimposed contour graph of different responses.

A detailed description of the mathematical expressions used to calculate the design distribution and to decode and code the ranges of the tested variable can be found in Table I. Once the optimal conditions (X_1 , X_2 , X_3 and X_4) have been found for a better rate of elimination of polyphenols and giving a treated effluent as clear as possible, tending to maximize the efficiency of degradation and separation of the desired target molecules. Table IV gives the matrix of the different experiments offered by the Minitab software as a fractional experimental design.

TABLE IV. Experimental matrix and values for the different experiments

Sample	Factors			
	Initial pH	Current intensity (A)	D _{electrodes} (cm)	Added salt (g/l)
Run 1	4	0,5	1	1
Run 2	4	0,5	3	5
Run 3	4	1,5	1	5
Run 4	4	1,5	3	1
Run 5	9	0,5	3	1
Run 6	9	1,5	3	5
Run 7	9	0,5	1	5
Run 8	9	1,5	1	1

The results of responses such as Separated Mass (g), Decolorization (%), Final Conductivity (mS/cm), Final pH, Purification (%), Rate of polyphenols removed (%) were expressed according to the response format (Y_i): which was specifically determined in the form of a mathematical model as a function of the variables and their interactions.

2.8. Electrocoagulation Process

For 8 programmed experiments, each beaker contains 100 ml of the delipidated OMW. Sadif et al describe the method used with some modifications [52]. The choice of electrodes and their materials are justified by Inoussa Zongo [41]. Two flat aluminum electrodes are immersed in the sample. The electrodes are linked to an electric voltage generator with a voltage set at 20V and variable intensity. The contact time is fixed at 30 minutes. The choice of these fixed values is based on experiments previously established in our Common Service and Research Unit Food InnLab Innovative Bioprocess – Environmental Bioprocess and Biotechnology -ISBM institute. Fig. 6 is a good illustration of the result of the electrocoagulation showing a good change in colour and the effervescence caused by this electrocoagulation.



Fig. 6 : Montage du procédé au laboratoire

2.8.1. Decolorization

Electrocoagulation oxidizes substances contained in OMW samples, including anthocyanins and polyphenols giving them their corresponding colors. Consequently, the intensity of the color decreases, and therefore the absorbance decreases. The lower this decolorization value, the more the medium loses its color due to electrocoagulation, and therefore the treatment will be more effective. We will calculate this response by the relationship described by Abu Ghalwa et al [53] in Eq.7.

$$D (\%) = \frac{(DO_{initial} - DO_{final})}{DO_{initial}} * 100 \tag{7}$$

Initial OD = absorbance of the stock solution before treatment
Final OD = absorbance of the sample after treatment

2.8.2. Final pH

It is the potential of the hydrogen is measured at the end of the electrocoagulation, this measurement of the pH aims to confirm the transformation of the various phenolic, hydroxybenzoïc, hydroxycinnamic, caffeic Acids present and thus to modify the final pH of the solution [54]. The pH is determined by a pH meter with an electronic display from 100 ml of vegetable waters.

2.8.3. Final conductivity

Conductivity provides information on the state of molecules in the medium. The higher the conductivity value, the more molecules the medium contains in ionic forms (positive cations and negative anions). These ions, in their presence, can improve the current conductance between the anode and the cathode. At the end of the treatment, the

electrical conductivity is measured by a conductimeter and the results are expressed in mS/cm at 20 °C.

2.8.4. Purification

Turbidity (measured by the turbidimeter, its unit is NTU) provides information on the existence of suspended matter in the medium which should be eliminated in one way or another to further clarify the OMW effluent. The purification is calculated by the following ratio in Eq.7:

$$\text{Purification (\%)} = \frac{(\text{Control sample turbidity} - \text{Sample turbidity})}{(\text{Raw sample turbidity})} * 100 \quad (8)$$

It is measured using a HACK-Lange brand multi-parameter TM + MM150 model and is expressed in g/l The higher this value is, the more the electrocoagulation process eliminates more the suspended matter proving the efficiency of the electrocoagulation and interest of this step in the purification and the separation or the extraction of the molecules of interest.

2.8.5. Separate mass

After a certain period of the electrocoagulation process (five days), a new solid bottom forms (although we have centrifuged the vegetable waters). This phenomenon proves the theorem of the oxidation of pollutants by electrocoagulation and of the transformation of soluble pollutants into a solid mass by precipitation [42]. Separation of the resulting solid phase is accomplished by filtering each sample through Wattman paper to collect the bottom as a filtrate. The separated mass is calculated as follows in Eq.9:

$$M \text{ (g)} = \text{Mass of paper after drying (g)} - \text{Mass of paper before drying (g)} \quad (9)$$

The higher this value, the more electrocoagulation promotes the elimination of pollutants, which has shown us the effectiveness or efficiency of this treatment.

2.8.6. Eliminated rate of polyphenols

OMW contains a very high amount of polyphenols which is the cause of their toxicity. In this work, we want to show that it is possible to remove a large phenolic fraction by electrocoagulation. To achieve this objective, we will find the quantity of polyphenols initially present in OMW and the quantity remaining after treatment. The level of polyphenols removed is calculated according to the following ratio in Eq.10:

$$\text{Eliminated rate of polyphenols (\%)} = \frac{(Z_{\text{initial}} - Z_{\text{final}})}{Z_{\text{initial}}} * 100 \quad (10)$$

Z_{initial} : Amount of polyphenols in the raw sample

Z_{final} : Amount of polyphenols in the treated sample

The higher this value, the more the electrocoagulation reduces or eliminates phenolic substances in the sample or the effluent to be treated.

III. RESULTS AND DISCUSSION

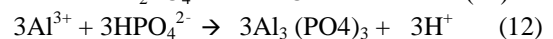
3.1. Electrolysis Effect on Decolorization and Removal of Polyphenols

According to Hanafi et al [42] At a voltage (20 V corresponds to 250 A/m²) causes a reduction of 75 to 80% of the COD, polyphenols, and the decolorization of vegetable waters and the formation of 6 to 7 kg/m³ of mud, for a time of 15 min. This is attributed to the fact that at this electrical

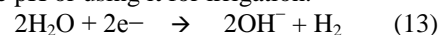
voltage, the current density within the cell also rises, the level of aluminum-oxidized increases, causing a large amount of precipitate, and the removal of more and more pollutants. In addition, it has been shown that the density of bubbles increases, and their size decreases with increasing current density, resulting in a large increase in fluxes, faster removal of pollutants and sludge flotation [55].

We also note that at the start of electrocoagulation the color of the vegetable waters becomes darker and darker, from reddish-brown to black; this can be explained by non-total oxidation of organic molecules, consequently the formation of other intermediate molecules [56-57-58]. With this electrical voltage, the decolorization becomes more and more distinct. The variation of the current intensity favors the formation of the rapidly produced aluminum ions, compared to the coagulation processes, which leads to a decrease in purification efficiency. In addition, the rapid removal of aluminum hydroxide from the solution by flotation leads to a reduction in the probability of collision between pollutants and coagulants.

Our results suggest that 250 A/m² is the optimal current density for OMW water treatment, as it provides a rapid removal rate at the lowest cost. These conditions can only be favorable for the reduction of phosphates. Orthophosphates are initially in the form H₂PO₄⁻ or HPO₄²⁻ they are probably eliminated by precipitation with aluminum ions according to the following reactions Eq.11 and in Eq.12 :



The initial pH of vegetable waters before treatment is around 4.2; after electrocoagulation, the pH increases with the voltage applied to the cell, so there is a drop in acidity until neutralization at 20 V. This is mainly due to OH⁻ ions produced by electrolysis of water with release of hydrogen on the cathode according to the reaction in Eq.11, this has been observed by other researchers [59-60]. The final pH tends towards neutral pH, making it possible to discharge the effluent directly into natural receiving environments without adjusting the pH or using it for irrigation.



The heavy metals Zinc and Iron present in the cationic state can react in the reaction medium in different ways.

They can undergo either reduction, oxidation or adsorption to aluminum hydroxide flocs.

3.2. Results of the Different Responses

After each electrocoagulation treatment, we note that at acidic pH (pH= 4), we collect the solution from samples 1 to 4 shown in Fig. 7 and we can distinguish the difference in colour intensity (between treated samples and the raw sample) which proves the effectiveness of the electrocoagulation treatment.

At basic pH (pH=9) we notice the ineffectiveness of the Electrocoagulation treatment for samples 5 to 8 shown in fig. 8 and there is not a significant difference between the samples in comparison with the raw sample . The color is dark like the raw sample. We will review the effectiveness of the

electrocoagulation treatment by analyzing the result and looking for the optimum of each of the six different responses one after one: Discoloration, Final pH, Separated mass, Final

conductivity, Purification and Rate of polyphenols removed. The greater the number of responses, it is easily to converge towards the optimum of the optima.

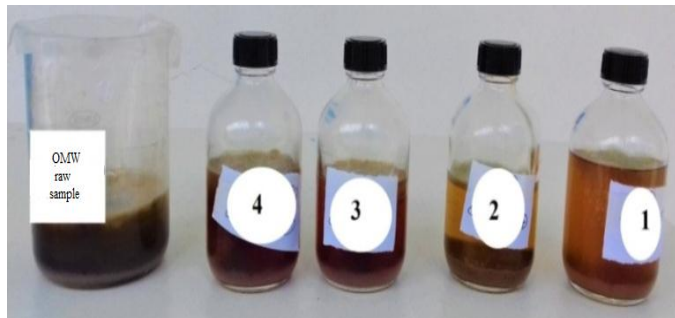


Fig. 7. Decolorization of acidic pH samples 1 to 4

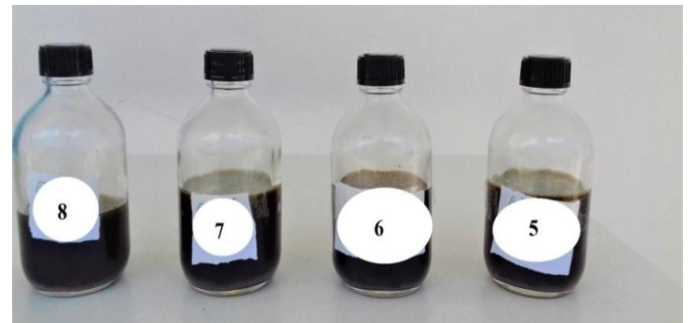


Fig. 8. Ineffective treatment for basic pH samples 5 to 8

TABLE V. Measurements taken at the end of treatment

Run	Separate mass (g)	Decolorization (%)	Final Conductivity (mS/cm)	Final pH	Purification (%)	Rate of eliminated Polyphenols (%)
1	0.18	37.57	3.96	3.4	79.30	78.16
2	0.56	16.10	12.04	4.4	84.42	67.03
3	0.67	16.67	12	4.2	83.11	49.63
4	0.39	22.32	6.04	4.1	77.04	46.33
5	0.27	2.26	5.5	5.3	55.65	39.97
6	0.22	5.08	12.62	5.01	37.22	52.19
7	0.20	2.82	12.33	5.2	57.74	44.02
8	0.17	4.24	6.4	4.9	1.57	50.38

These measurements are made for the different experiments according to a well-established experimental design based on the four variables according to Table IV.

This result approved by Hanafi et al. [42] during the effective treatment of OMW effluent with a pH ranging from 4 to 6.

3.3 Pareto Diagram Representation

Using the Pareto chart helps determine the size and magnitude of the effects on which the bars that intersect the baseline are statistically significant. For example, the horizontal bars that represent factors X_i and X_iX_j intersect the red reference line at 1.943 in fig. 9 for example. These factors are statistically significant at the 0.05 level with the terms of the current model. Since the Pareto chart shows the absolute value of the effects, you can determine which effects are important, but not which ones increase or decrease the response; it allows factors to be appreciated and compared with each other and with their interactions two by two. If the broken red line crosses the blue rectangle that represents one of the factors or the intersection of two or more factors, it is evident that these factors are the ones that most influence the responses studied.

Table V summarizes the results of the experimental measurements of the six responses for each of the experiments while respecting the appropriate experimental values.

The Pareto diagram (fig. 9) allows us to deduce that the initial pH is the most involved factor in decolorization. Its effect is much greater than the other factors. It also shows us that the interactions between the initial pH and the added NaCl (AD) come in the second position in the importance of their

effect on the response then the added NaCl (D), which comes in the third position. This confirms also a better influence than the factors themselves. The distance between electrodes $D_{\text{electrodes}}$ and that of the intensity comes last in their effect on the response studied.

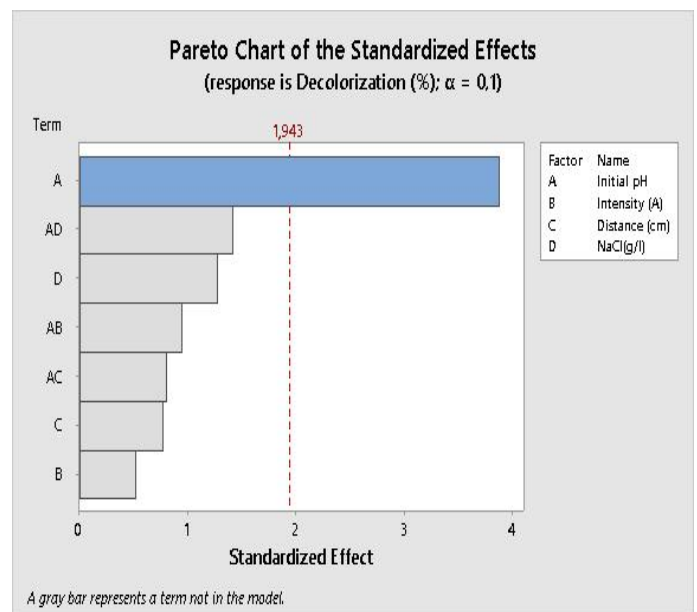


Fig. 9. Pareto Diagram of the decolorization response

This interpretation is justified because this diagram shows that the interaction between the initial pH and the added NaCl is more important than the added NaCl alone. These observations could never be verified and highlighted except by

DOE strategy of optimization of the plans of experiments and to highlight the effect of the interactions on a well-determined phenomenon, something that was not raised or treated by subsequent publications.

3.4 Discussion for Each Response

The Minitab software gives a representation of each response with coloured bands. Each colour represents an interval value. Our choice is for the 2-dimensional representation called contour plot to give us simple and understandable results. Then the contour plot is easily interpreted with other graphs: the Pareto chart, which notes the main factors to control to have the maximum value of the response, the factorial diagrams that explain this choice, and finally the equation of the proposed mathematical model. We will express the interpretations of these graphs for each of the six responses.

3.4.1 Decolorization

The contour graph (fig.10) shows that we can have a decolorization greater than 35% (dark green band) when the values of the parameters to be controlled are minimal. By increasing these values, the decolorization gradually decreases. If we set two parameters as maximum values, the decolorization exceeds 35% and only if the initial pH is minimum.

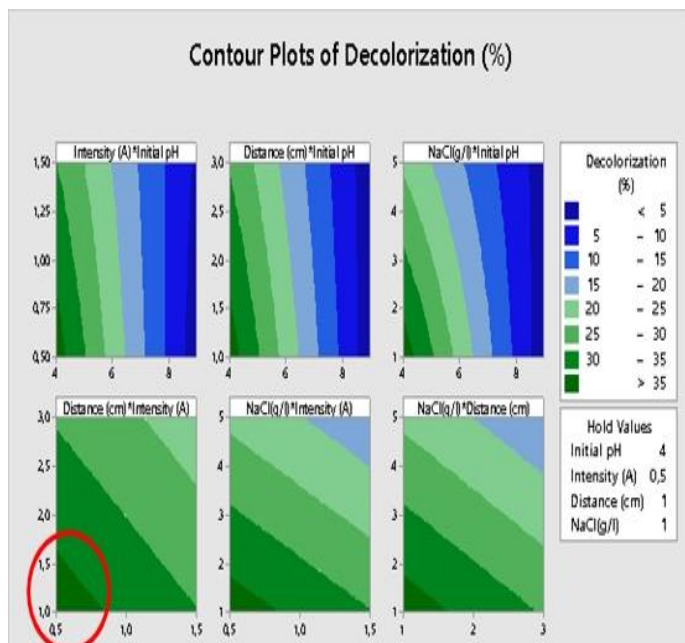


Fig. 10. Graphics of the decolorization contour

The main effects graph (Fig. 11a) shows the effect of each of the four factors alone on the decolorization effect. The initial basic pH equal to 9 gives a minimum decolorization of less than 5%. While the initial acidic pH equal to (pH=4) increases decolorization to over 24% after electrocoagulation treatment. The main effects graph gives us the evolution as a function of the variation for each parameter as the initial pH, intensity, distance between electrodes and the amount of NaCl added. We have chosen the initial pH alone as the main factor

in the mathematical model equation (Eq.14) depending on the affinity of the statistical calculations and their compliance with the statistical laws taken into account with a probability $P < 0.05$.

The intersection effects diagrams (Fig. 11b) also show the importance of the initial pH to expect a maximum decolorization value of up to 30%. Therefore, the other factors are not included in the model so their effect is negligible.

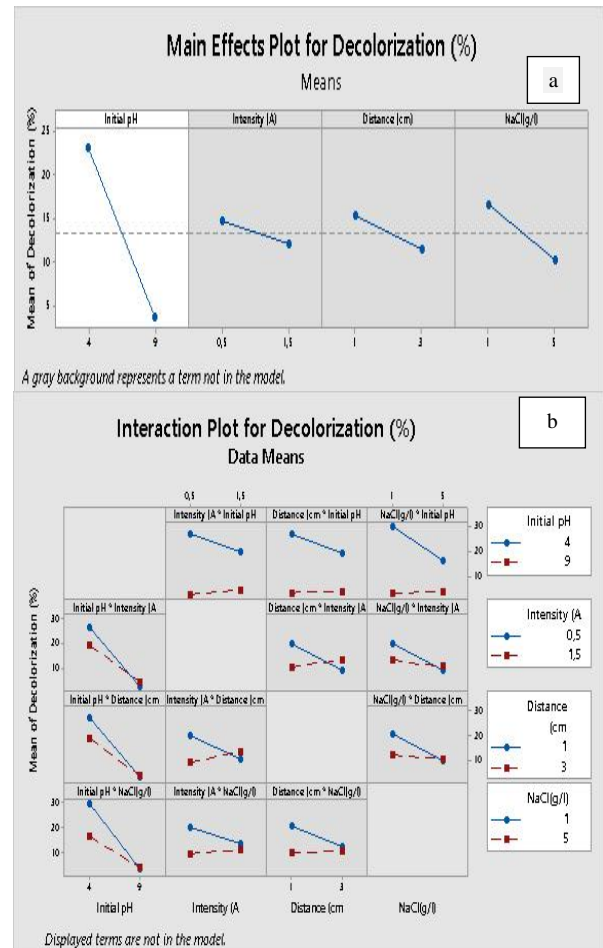


Fig. 11. Diagrams of the effects of interactions for decolorization (a and b)

$$\text{Decolorization (\%)} = 38.81 - 3.91 \text{ initial pH} \quad R^2 = 71.48\% \quad (14)$$

The higher is the initial pH, the lower the percentage of decolorization. Therefore, it is better to work with OMW at an acidic pH. The diagram of the interactions for the decolorization fig. 11b gives us the variation of this response according to the interactions two by two while specifying the decolorization on the ordinate and the variation of the parameters on the abscissa. This varies according to the parameters is given for the two limit values (maximum value and minimum value) for each parameter.

3.4.2 Final pH

For the contour graph (fig. 12), the final pH may exceed 5.2 if the intensity is minimum (0.5 A) and all other factors are maximum (initial pH = 9, Distance = 3 cm and NaCl = 5 g/l). According to the Pareto chart, shown in fig.13, the initial pH

is the main factor to control to have OMW effluent close to neutral after electrocoagulation treatment. The Pareto diagram makes it possible to deduce that the initial pH is the factor most involved in the effect on the second response (final pH) as on the decolorization as the first response.

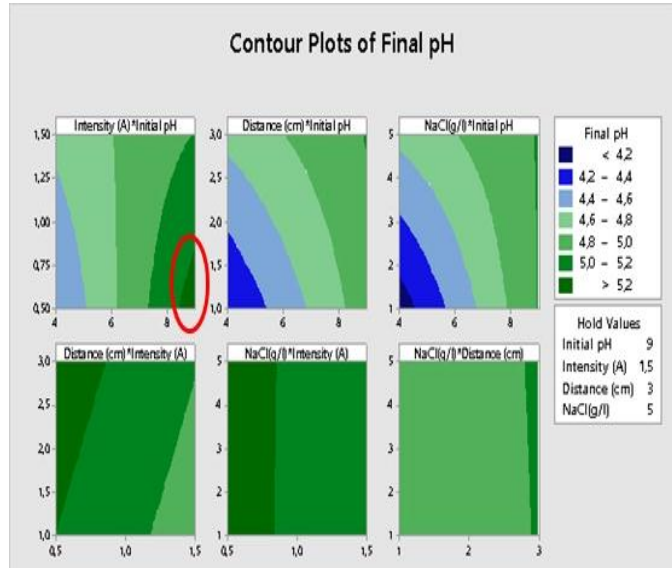


Fig. 12. Final pH contour graphs for each two by two interactions parameters

Its effect is much greater than the other factors. It shows us that the different interactions two by two interactions (X_1X_2 , X_1X_3 , and X_2X_3) come after the effect of the distance between electrodes and that of the concentration of added NaCl, the current intensity has the minimum effect indicated. The red reference line at 1.943 intersects only with the initial pH parameter mentioned as a decisive factor for this response.

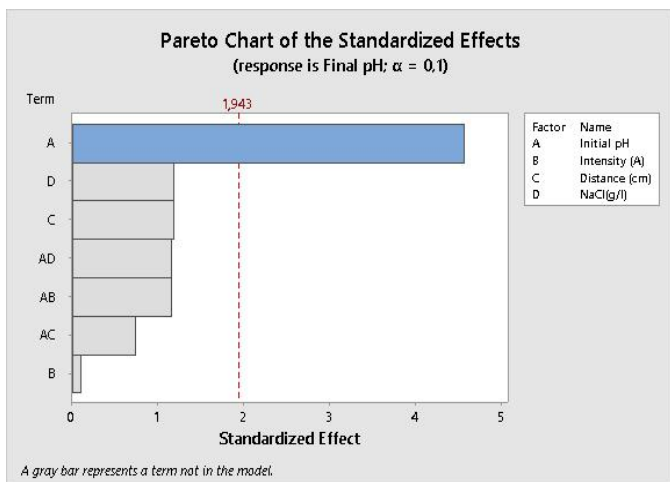


Fig. 13. Pareto chart for the second response Final pH

The effect of each factor on the Final pH response is illustrated in Fig. 14a that is increasing for the initial pH, low for the current intensity, and moderate for the distance between electrodes and the added of NaCl. We can see the importance of the initial basic pH to obtain a final pH closest to 7 value. While the acidic initial pH gives after the

electrocoagulation treatment at a final pH less than or equal to pH=4. The higher the initial pH value, the higher the final pH (as opposed to the effect on decolorization response)

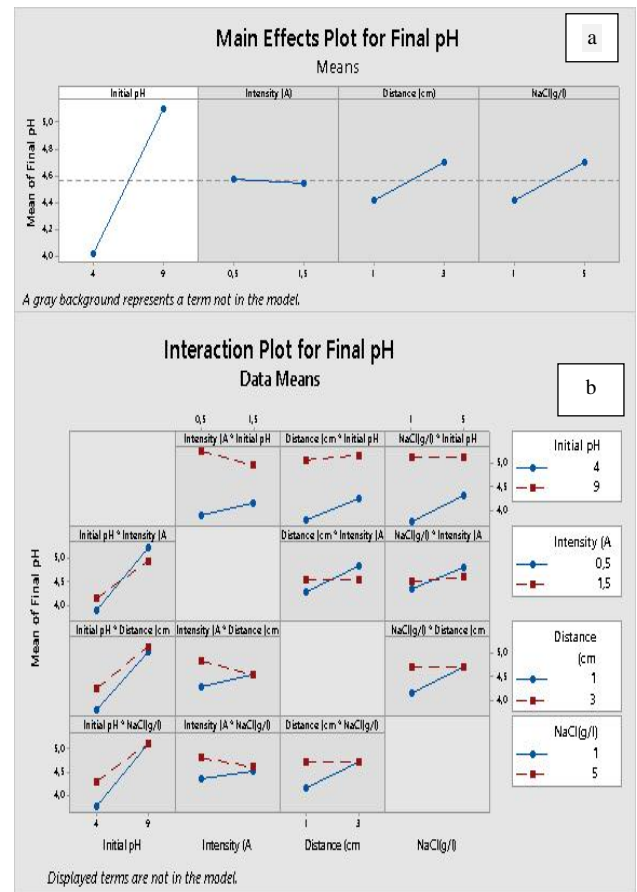


Fig. 14. the effects of interactions diagrams for final pH response (a and b)

The main effects graph (fig. 14a) gives us the evolution as a function of the variation for each parameter as the initial pH, intensity, distance between electrodes and the amount of NaCl added. We have chosen the initial pH alone as the main factor in the mathematical model equation depending on the affinity of the statistical calculations and their compliance with the statistical laws taken into account with a probability $P < 0.05$. The mathematical model in this case take into account only the initial pH as shown in Eq.15.

$$\text{Final pH} = 3.163 + 0.2155 \text{ initial pH} , R^2 = 77.72\% \quad (15)$$

The higher is the initial pH, the higher the final pH value. Therefore, it is better to work with OMW in a basic pH. The diagram of the interactions for the final pH response (fig. 14b) gives us the variation of this response according to the interactions two by two, by giving the final pH on the ordinate and the variation of the parameters on the abscissa. This varies according to the parameters is given for the two limit values (maximum value and minimum value) for each parameter.

3.4.3 Final Conductivity

For the third response, we want to have a Final Conductivity greater than 12 mS/cm, which is the maximum value that can be reached. According to the contours graph (fig. 15), the Final Conductivity can be greater than 12 mS/cm

if the NaCl content is maximum (5g/l). The other three factors do not have a significant effect. Since the intensity, the distance, and the initial pH have no significant effect on their variation intervals between their respective values hence the choice of the minimum values for and all other factors are minimum (initial pH = 4, Distance $D_{electrodes}$ = 1 cm, and NaCl = 1 g/l).

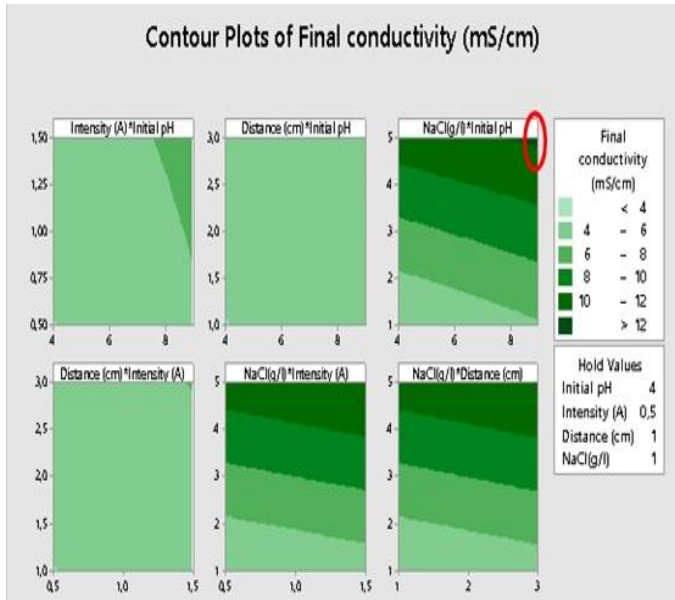


Fig. 15: Conductivity contour graphs for each two by two interactions parameters (on minimum value)

According to the Pareto diagram (fig.16), the concentration of NaCl is the main factor to have an OMW effluent close to neutral after an electrocoagulation treatment. The Pareto illustration allows us to have better conductivity than the concentration of NaCl, the current I is the second factor most involved in this effect and the initial pH comes in the third position. It shows us that the AC (Initial pH-Distance) interaction is very interesting as the distance factor and the other interactions come last. The red reference line at 2.92 intersects the distance between the Distance $D_{electrodes}$, the current I (A), and the AC interaction.

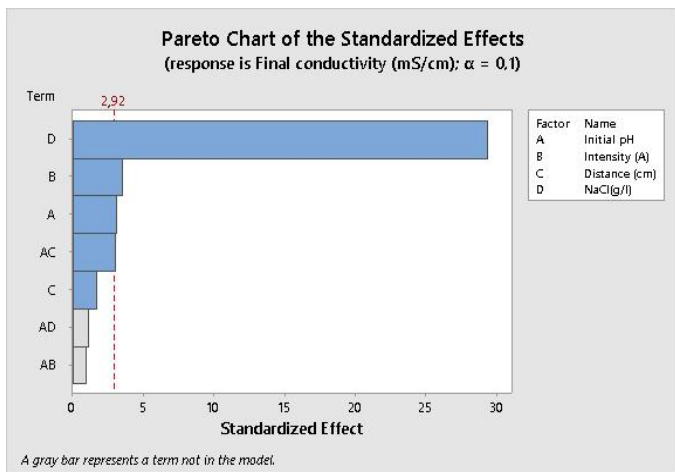


Fig. 16: Pareto Diagram of final conductivity

The main effects plots for the final conductivity as a function of the variation of the different factors (Fig. 17a), which is increasing for the NaCl concentration the initial pH and almost a null effect for the initial pH, current I (A), and the distance $D_{electrodes}$. The final conductivity can reach 12 mS/cm value with an addition of NaCl of 5 g / l.

For the diagram of interactions effect of on the above-mentioned response in fig 17b, we note that only for the addition of NaCl, which is very influential compared to the other factors.

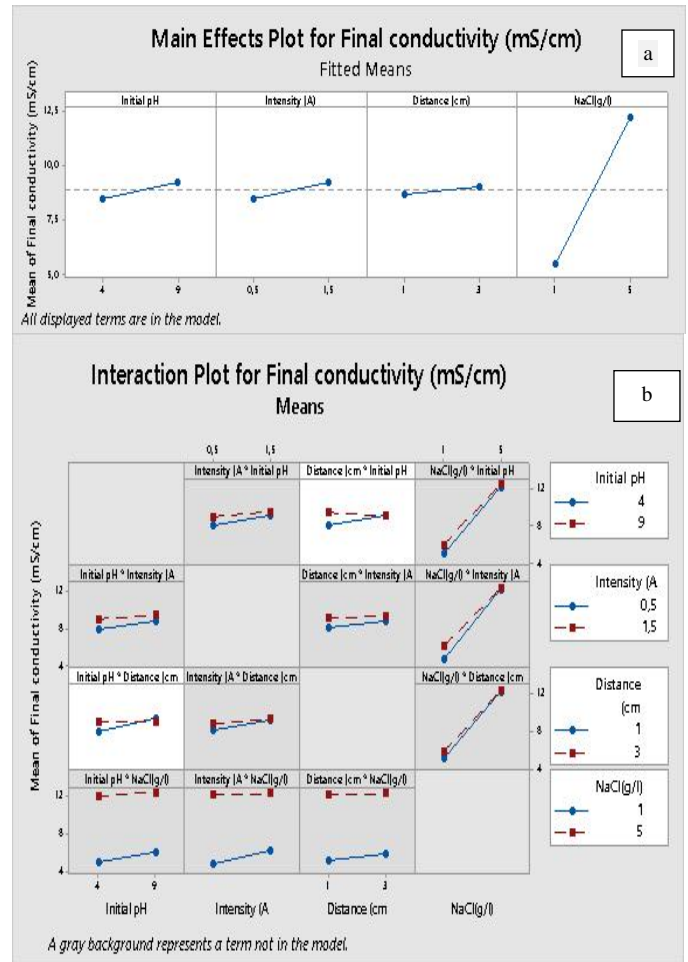


Fig. 17: Diagrams of the effects of interactions for final conductivity response (a and b)

The 4 factors and the interaction between distance and initial pH are significant and are mentioned in the mathematical model of final conductivity as following in (Eq.16)

$$\text{Final conductivity (mS/m)} = -0.091 + 0.413 \text{ initial pH} + 0.807 \text{ Intensity} + 1.076 \text{ Distance} + 1.6931 \text{ NaCl} - 0.1365 \text{ initial pH} * \text{Distance} \quad R^2 = 99.78\% \quad (16)$$

The final conductivity is important when all the factors of the electrocoagulation process are taken in maximum values.

3.4.4 Purification

For the fourth response, we want to have a maximum of purification and a clean sample.

When the initial pH is basic (fig. 18), the current intensity should be minimal to achieve the 75% purification percentage.

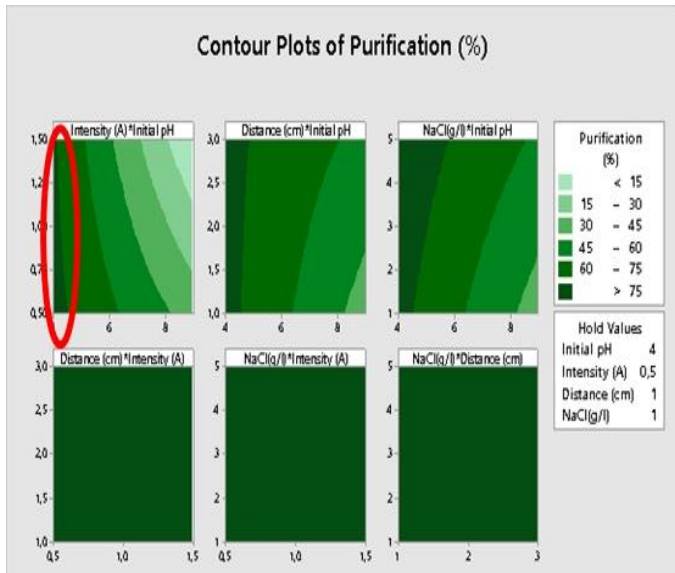


Fig. 18. Graphs of purification contours

The Pareto chart (fig. 19) shows the importance of the initial pH in achieving maximum purification after electrocoagulation treatment. The intensity of the current takes second place, yet it is not included in the mathematical model proposed by the experimental design. The red reference line at 1.943 intersects only with the initial pH parameter mentioned as a decisive factor for this response.

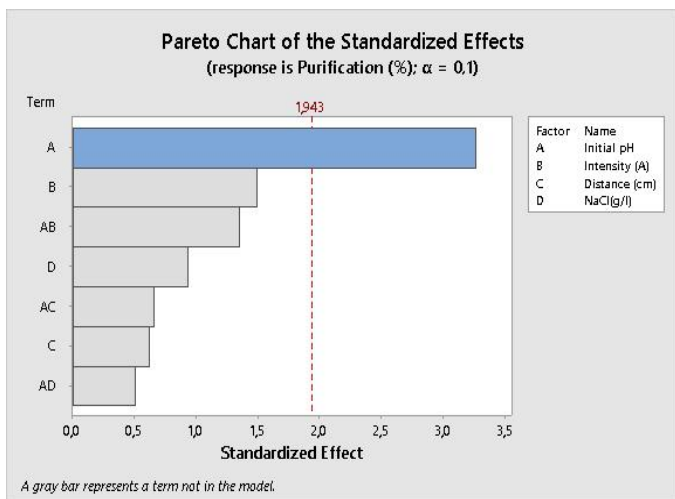


Fig. 19. Pareto chart for the purification response

Fig. 20a shows that purification decreases dramatically with increasing initial pH and current intensity while it increases with increasing the Distance $D_{\text{electrodes}}$ and NaCl added concentration.

The initial pH is the main factor included in the mathematical model proposed by the experimental design. The effect of the current I is considered small on Purification response, which is important when the initial pH is minimal.

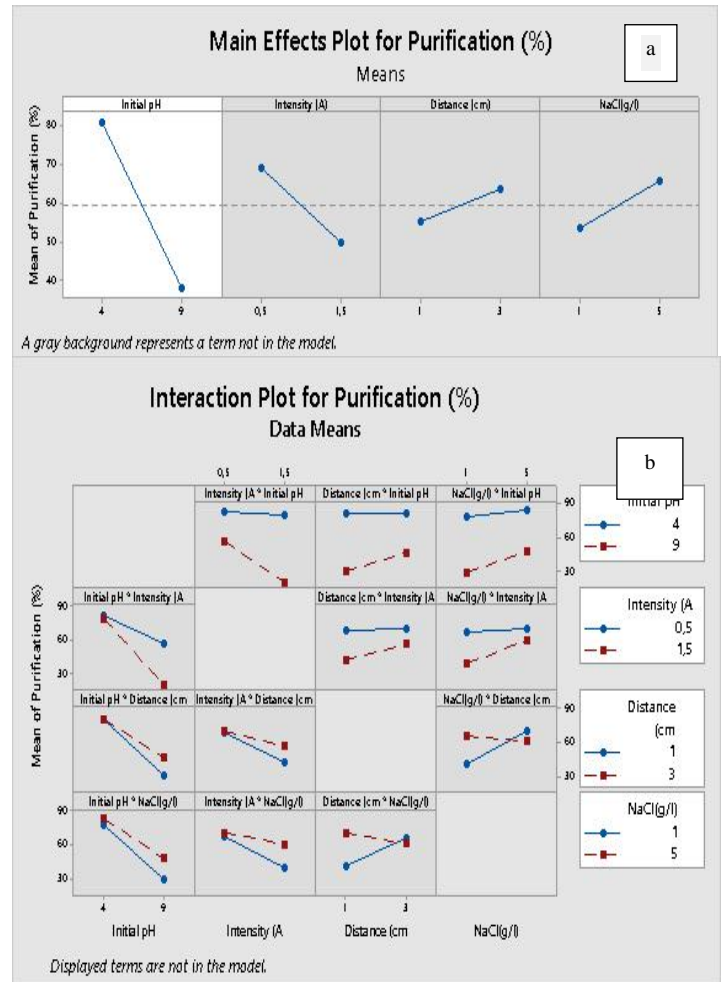


Fig. 20. Diagrams of the interactions effects of purification response (a and b)

For the diagram of interactions effect of on the above-mentioned response in fig 20b, we note that only for initial pH, which is very influential compared to the other factors. The other factors and their interactions are not very significant and are not mentioned and not taken into account in the mathematical model and the regression equation of the purification model is in Eq.17 :

$$\text{Purification (\%)} = 115.3 - 8.58 \text{ initial pH}, R^2 = 64.10\% \quad (17)$$

3.4.5 Separate Mass

Fig. 21 shows the plot of separate mass contours, which the area exceeding the value 0.6 g (dark green) and that the distance to the electrodes and the current I do not have a significant effect on this response. While at low initial pH, high intensity, and a large amount of salt, the separation between the solid phase and the liquid phase are maximum.

The Pareto chart (Fig. 22) gives the initial pH and added NaCl as major factors controlling this response as well as their interaction between its two factors. The red reference line at 2.132 intersects only with the initial pH parameter, the added NaCl as well as the interactions between them as a decisive factor for this response.

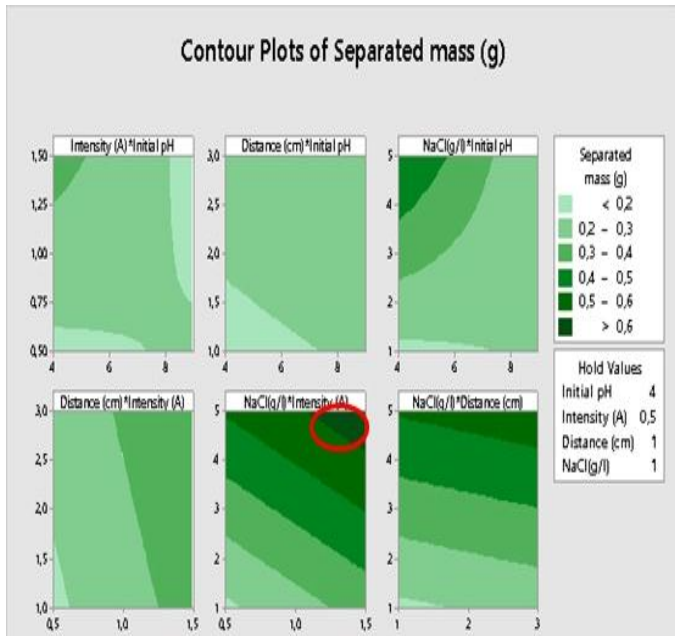


Fig. 21. Contour graphs for each two by two interactions

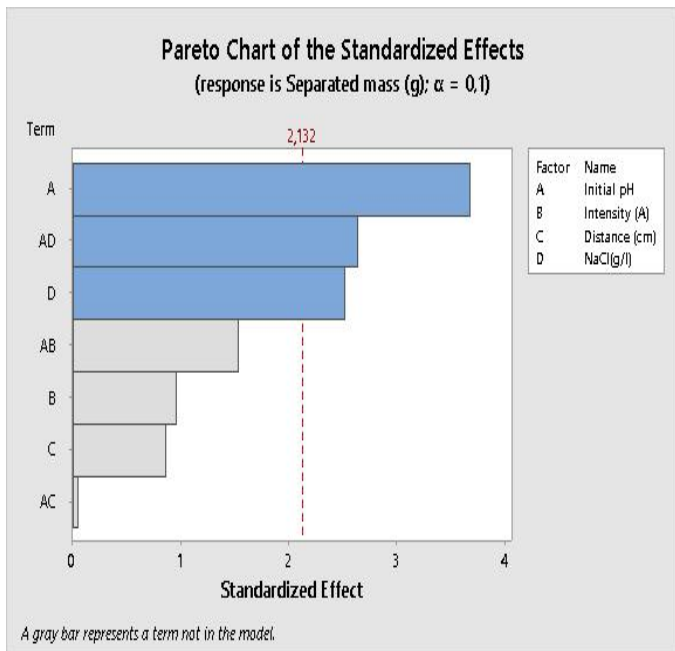


Fig. 22. Pareto chart for the separate mass response

Fig. 23a gives the effect of each of the factors on the response studied. It shows that the separated mass which cannot exceed the value 0.45 g and that the distance between the electrodes and the intensity I have no significant effect on this response, while the initial pH and the concentration of NaCl have a remarkable effect.

The diagram of the interactions for the separate mass response (fig. 23b) gives us the variation of this response according to the interactions two by two, by giving the final pH on the ordinate and the variation of the parameters on the abscissa. This varies according to the parameters is given for

the two limit values (maximum value and minimum value) for each parameter.

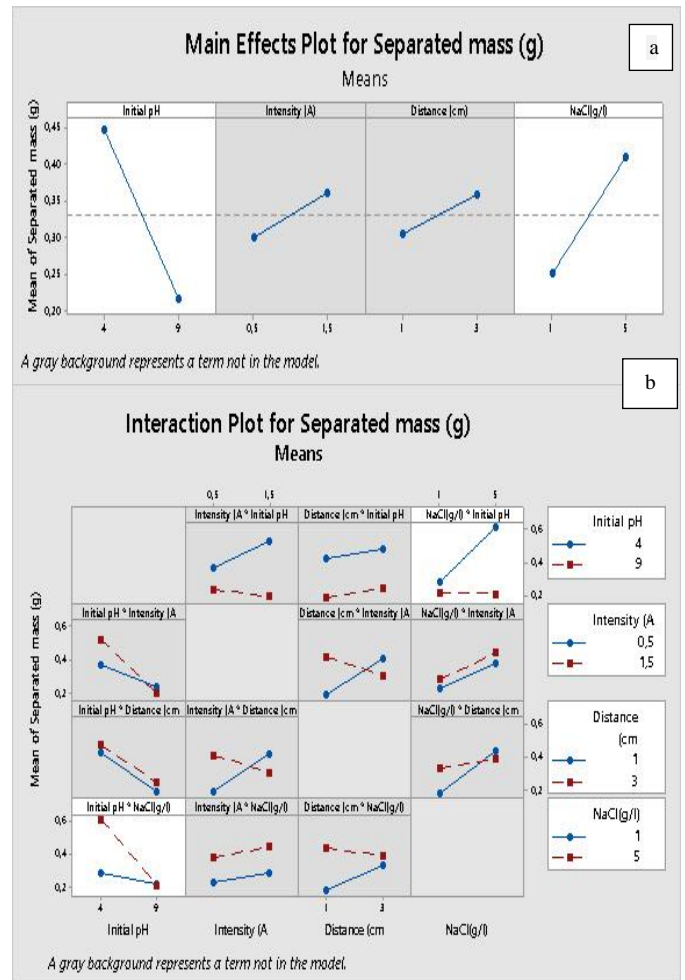


Fig. 23. Diagrams of the interactions effects for separate mass response (a and b)

The model's regression equation is given as follows in Eq.18:

$$\text{Separate mass (g)} = 0.191 + 0.0034 \text{ initial pH} + 0.1484 \text{ NaCl} - 0.01670 \text{ initial pH} * \text{NaCl} \quad R^2 = 87.05\% \quad (18)$$

3.4.6 Rate of Eliminated polyphenols

The following contours (fig. 24) shows that the current intensity (0.5A) and the initial pH 4 to 5 can eliminate a significant content of polyphenols more than 70%. It also shows the effect of the electrocoagulation process on the removal or transformation of polyphenols.

The Pareto chart (Fig. 25) shows that the interaction between initial pH and current intensity is very interesting than the factors themselves and gives the best response. The red reference line at 2.132 intersects only with the initial pH and current intensity parameter and their interaction mentioned as a decisive factor for this response.

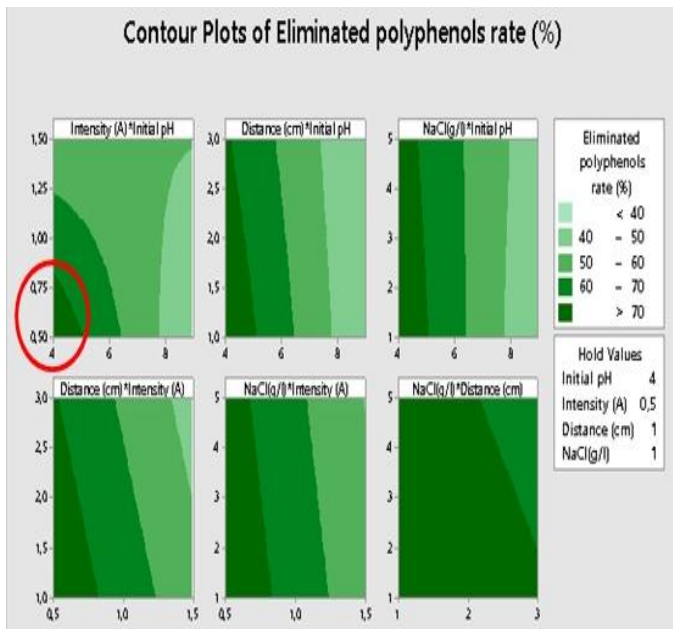


Fig. 24. Contour graphs of the rate of removed polyphenols for each two by two interactions parameters

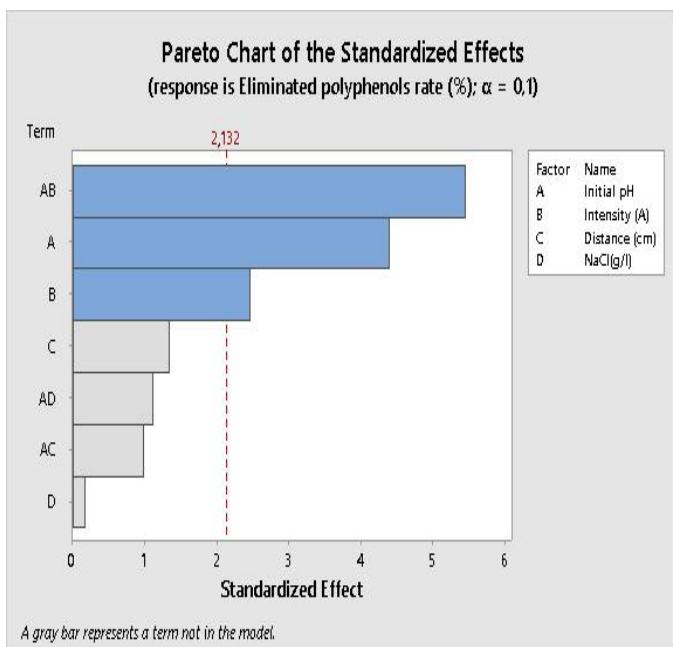


Fig. 25. Pareto chart for rate of removed polyphenols

Fig. 26a shows that this process can eliminate the maximum of removed polyphenols when its two values of the initial pH 4 and the current intensity 0.5A are minimum. The model of the regression equation is given as follows in Eq.19:

$$\text{Rate of Removed Polyphenols (\%)} = 122.94 - 9.51 \text{ initial pH} - 51.74 \text{ Intensity} + 6.78 \text{ initial pH} * \text{Intensity}$$

$$R^2 = 93.24\% \quad (19)$$

The lower is the initial pH, the higher the rate of removed polyphenols value. Therefore, it is better to work with OMW at an acidic pH. The diagram of the interactions for the final pH response (fig. 26b) gives us the variation of this response

according to the interactions two by two, by giving the rate of removed polyphenols on the ordinate and the variation of the parameters on the abscissa. This varies according to the parameters is given for the two limit values (maximum value and minimum value) for each parameter.

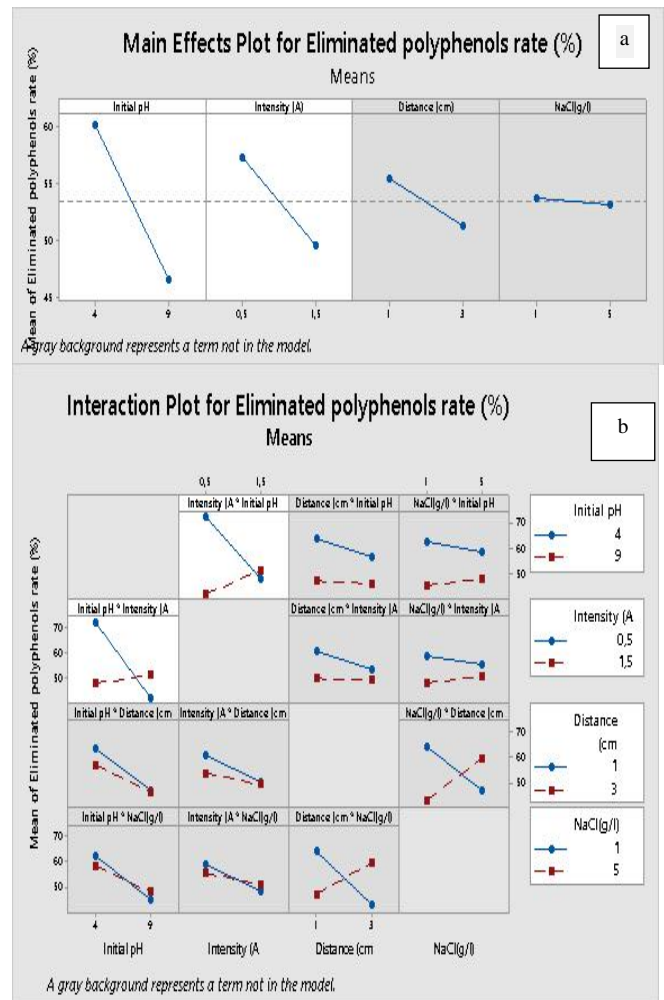


Fig. 26. Diagrams of interactions effects for rate removed polyphenols response (a and b)

Phenolic compounds include many organic substances, which possess an aromatic ring with one, or more substituted hydroxyl groups and a functional side chain. Natural phenolic compounds include simple molecules, such as phenolic acids, and highly polymerized compounds such as tannins.

The phenolic compounds of the olives are dispersed between the olive oil, the solid phase marc and wastewater from oil mills (OMW). Only 2% of the total phenolic content remains in the oily phase, 45% in the solid phase and 53%, the highest percentage in the OMW [61]. In the same order of ideas, McNamara et al reported that phenols present in olive kernel and pulp tend to be more soluble in the aqueous phase than in the oil one [62]. Phenolic compounds can be grouped into various classes according to structural characteristics and the main classes are:

- Derivatives of cinnamic acid (p-coumaric acid, caffeic acid, ferulic acid, and synaptic acid)

- Benzoic acid derivatives (p-hydroxybenzoic acid, protocatechuic, vanillic acid, veratric acid, gallic acid and syringic acid) have shown that the phenolic profiles (caffeic acid, ferulic acid, p-coumaric acid, vanillic acid), identified by HPLC, are similar for the two or three phases, but the individual amounts phenols, with the exception of vanillic acid, were higher for the system biphasic [11-63].
- Derivatives of tyrosol (hydroxytyrosol and 3,4-dihydroxyphenylacetic acid) in which we are more interested, illustrated by the fig. 27 of the HPLC chromatogram and we try to find the best way to recover, to separate, to purify and to enhance them in functional food.

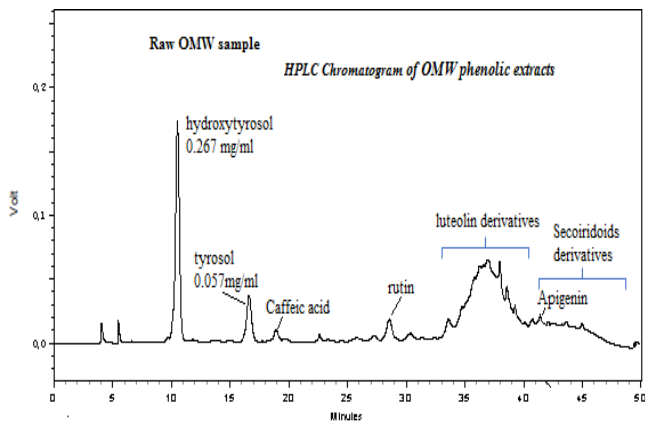


Fig. 27. HPLC Chromatogram of raw OMW

Analysis of HPLC chromatograms (fig. 27) shows that the major monomers present in the extract at ethyl acetate from raw vegetable waters is hydroxytyrosol (0.267 g/l) and tyrosol (0.057 g/l). This confirms the results mentioned by Achek et al [64] and Allouche et al. [65], who showed that an ethyl acetate extract of raw OMW is composed mainly of these two substances. These phenolic compounds give OMW antimicrobial power making it difficult to treat them by organic compounds [66]. In addition, these compounds are very toxic to aquatic and terrestrial fauna, which goes in the direction of nuisances which can be caused by the direct discharge of these effluents into the environment receiver.

Leouifoudi et al. [67] reported that tyrosol and hydroxytyrosol are the main phenolic compounds that suppress sprouting and can also lead to significant reductions in root growth. In addition, the typical brownish-color of this effluent was explained by the presence of phenol polymer, which have a lignin-like structure and constitute its resistant fractions [68].

4. Optimization of Optima

This optimum is reached by seeking the satisfaction limits for each of the optimums sought for the different responses studied.

Our objective is to find the conditions to have all the six responses at maximum optimum. In fig. 28, the values in red correspond to the optimal values of each factors, and in blue the value of each response under these optimal conditions. The

confirmed result after processing the data gives the following optimal values:

Initial pH = 4, Current Intensity = 0.5 A, D_{electrodes} = 3 cm and Added NaCl concentration = 5 g/l.

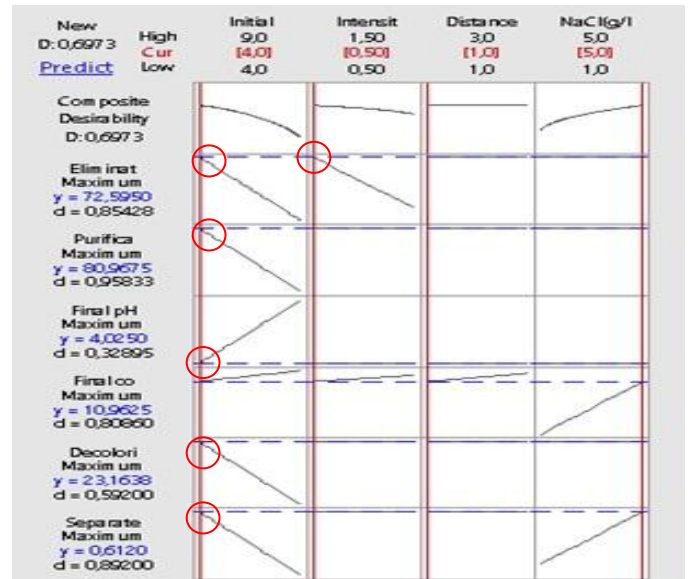


Fig. 28. Optimum optimization graph with desirability coefficient at max value

Since the sample to be optimized coincides with sample (Run 2) in Table IV and its result in Table V, we can thus compare the theoretical results given by the data processing with the practical result after electrocoagulation treatment. Table VI makes it possible to confirm the conformity of the theoretical model with the experimental values, this shows that the application of the experimental plan gives encouraging results in order to have a treatment with the minimum of experiments and a very low cost of treatment.

TABLE VI. Comparison of the validation results

Response	Theoretical	Practical
Decolorization (%)	23,16	16
final pH	4,02	4,4
Final conductivity	12,02	12,04
Purification (%)	80,9	84,42
Separate Mass (g)	0,61	0,56
Rate of removed Polyphenols (%)	72,59	67,03

We note that the effect of the distance between the electrodes is constant for all responses. A manual focus performed by the "interactive mode" of the software allows giving the desired result since our objective is to minimize the factors and optimize the electrocoagulation treatment.

To verify the removal of certain compounds by the electrocoagulation process, especially those responsible for the staining of OMW effluent, we performed an optical density reading over a whole wavelength range of 400 to 800 nm.

Fig. 29 shows a remarkable change between the absorbance of the raw sample and the sample that underwent at optimal electrocoagulation treatment.

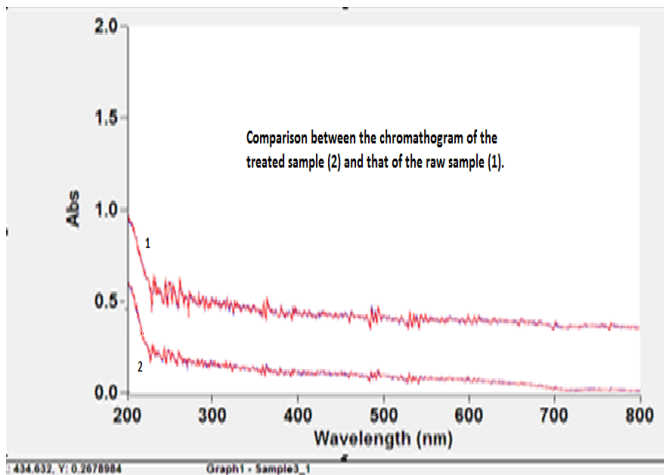


Fig. 29. Absorbance variation as a function of wavelength for the treated and the raw sample

According to the improved UV spectrophotometric method of N. Kishimoto et al. [69] for the determination of nitrate in natural waters proposed and the accuracy of the method determination was discussed in this study. Following the estimation of the proposed method, the adoption of 215 and 220 nm for the detection of nitrates and interfering substances proves that there is a very significant reduction and the variation of the relative absorbance of the interfering substances at 220 nm to 275 nm, was also very clear. This method is used for the rapid determination of nitrates in natural waters. Here are some bands of detection of chromophoric groups as following: low intensity band at 260 nm for (fine structure C_6H_6), 270-285 nm for ketone and acid cafeic, 280-300 nm for aldehyde, 280-290 nm for bond ($C = O$), 300 - 350 nm for resveratrol and chlorogenic acid, 400-500 nm for pigmented antioxidant, Beta-caroten and chlorophyll b, 650-700 nm for chlorophyll a as mentioned by Solovchenko [70]. These UV bands are totally reduced in comparison to the raw sample and electrocoagulation treated sample by approximately 75% shown in the fig. 29.

The biodegradability index (Ib) expressed by the COD/BOD₅ ratio is important as an indication of the importance of pollutants with little or no biodegradability. Indeed, a low value of the COD/BOD₅ ratio implies the presence of a large proportion of biodegradable materials and makes it possible to consider a biological treatment. Conversely, a large value of this ratio indicates that a large part of the organic matter is not biodegradable and, in this case, it is preferable to consider a physicochemical treatment which is the electrocoagulation process.

Thus in Table II, the value of the COD/BOD₅ ratio is 2.56, almost close to 3, which is the limit threshold for biodegradability. Therefore, we can conclude that our effluent has a high organic load, which gives it partial biodegradability. The examination of this report clearly underlines the biodegradable character of the OMW effluent for which the biological treatment would seem quite suitable. The COD and BOD₅ analyzes of the treated OMW show that the biodegradability becomes higher compared to the raw

untreated sample for the COD range (45.23-106.8 g/l) to (30.2-71.45 g/l) and for the BOD₅ range (17.64-41.2 g/l) to (11.82-27.91 g/l) while respecting the COD/BOD₅ ratio equal to 2.56 which is in accordance with the values mentioned by Rania et al. [71].

Finally, Fig. 30 shows clearly the result of the electrocoagulation process in the colour Change and Decolorization. The initial dark-coloured sample signifies a presence of a mixture of dyes, tannins, anthocyanins, and a significant amount of polyphenols of 1.2 µg/g OMW effluent reflecting its toxicity with suspended matter. After the electrocoagulation treatment, we obtain an as optimal sample with a transparent appearance without suspended matter and with a level of polyphenols equal to 0.003 µg/g in OMW treated effluent.

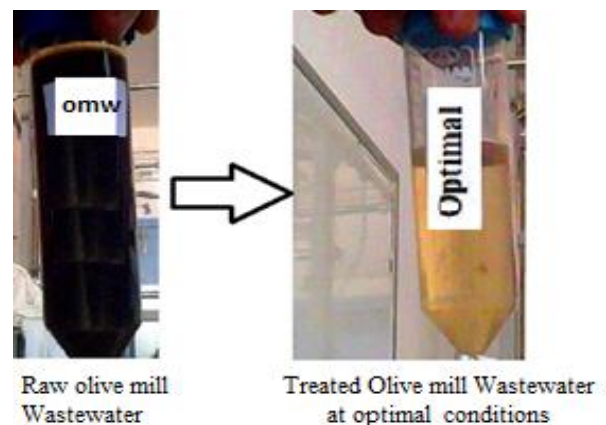


Fig. 30. Comparison of OMW samples before and after Electrocoagulation treatment

From this analysis, it is clear that OMWs have very different characteristics, together with the final quality requirements that must be taken into account when choosing the most appropriate treatment strategy.

IV. CONCLUSION

OMW effluent is the inevitable by-product in the extraction of olive oil. In addition, its chemical composition gives it toxicity that poses a huge problem for their further treatment and the cost of treating this pollution. Many studies show that polyphenols have a sought-after antioxidant value, but it considered among the sources of its toxicity. The recovery of OMW is a very interesting area in order to valorize high-value bioactive substances, reduce the toxicity of this effluent, and provide an industrial solution to circumvent this source of pollution. Among several treatments studied, we confirm that electrochemical treatment or electrocoagulation is the most effective. Manufacturers can extract the oils contained in this effluent (OMW) and then proceed with electrocoagulation treatment after delipidation to reduce its toxicity and meet the effluent discharge limits imposed by applicable legislation.

We optimized the electrochemical treatment as well as the four factors studied, namely: the current intensity (I), the distance between the electrodes, the initial pH of the plant

waters, and the salt level to be added. Working with the experimental design through the Minitab software is advised in order to minimize the number of experiments to achieve our goal in an optimized time. This experimental approach is highly recommended for its efficiency in optimizing our electrochemical treatment at a reduced cost.

With this technique, we were able to qualitatively and quantitatively characterize the level of lipids and polyphenols as well as the elements responsible for the toxicity of OMW effluent. These optimal operating levels make it possible, on the one hand, to reduce this OMW pollution by providing treated water, which can be purified biologically due to the significant elimination of polyphenols. The efficiency of the electrocoagulation process in removing all toxic substances is demonstrated by the reduction in chemical oxygen demand (COD) of approximately 80 to 85%, which will automatically result in a reduction of at least 30 % of BOD₅ value. This is illustrated by the comparison between the UV-Absorbance of the treated sample and that of the crude sample 750-760 nm wavelengths of polyphenols absorbance.

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