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Catalytic Oxidation and Dephenolisation of Olive Mill Wastewater with Hypochlorite

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Abstract: ***Removal of toxicity of organic matter of raw olive mill wastewater (OMW) of the north of Tunisia was carried out by catalytic oxidation process, using a catalytic system the $Fe(OH)_2$/1,10-phenanthroline ($Fe(OH)_2$/phen)and hypochlorite (OCl^-). The physicochemical characterization of raw olive mill wastewater (OMW) , reveal an acid pH 5.14, a high chemical oxygen demand (COD) (193.45 g O_2 L^{-1}) and total phenol content (8.99 g L^{-1}). The efficiency of our catalytic oxidation process has been assessed by reducing the (COD), total phenol content and turbidity. The results showed 98% removal of COD, 99.8% elimination of total phenol content and 100% elimination of turbidity. The effects of different operating conditions reagents concentration and temperature on the OMW oxidation efficiency were studied and evaluated. The treated effluent was subjected to a fast liming to reduce salinity (SALT) under (200 rpm for 5 min) optimal conditions (0.5 g L^{-1} of CaO), without any blackening of the treated OMW. SALT was decreased half of their initial values (from 49.3 ppt to 23 ppt).***

Keywords: Olive oil mill wastewater, catalytic oxidation process, catalytic system

1. Introduction

The major percentage of world production of olive oil isconcentrated in the Mediterranean area [1], the milling process generate about 30 million m^3 per year of liquid effluents [2]. Direct discharge of this wastewater to municipal sewage collectors is strictly prohibited as the OMW (olive oil mill wastewater) causes a serious environmental problem like severe toxicity of groundwater [3], the acute deterioration of the plants, even bacteria, and aquatic organisms. OMW modifies the ecological balance and prevents the penetration of light and oxygenation and generate a strong odor.

The variety of the olive tree, the ripening of the fruits, the climatic conditions during the harvest, these parameters affect the chemical composition of OMW [4]. Their chemical composition is the origin of their high pollution potential. They are rich in polysaccharides, sugars, polyphenols, polyalcohols, proteins, organic acids and olive oil [5], their oxidation and their polymerization are the origin of the dark color which is difficult to eliminate [6].

Many processes have proposed the treatment of OMW: either by physicochemical methods such as; flocculation, coagulation, filtration [7], or membrane processes [8], or biological treatments [9] like lagooning, or aerobic and anaerobic processes [10], also co-composting[9], even digestion [11], or electrocoagulation[12], or reverse osmosis or even ultra-filtration [13], as well electrochemical processes as ozonation [14], or wet air [15], or Fenton reaction [16], like electro-oxidation using Ti/Ta-Pt-Ir [17] or Ti/RuO_2 as electrodes [18].

Ochando-Pulido et al focus on the state-of-the-art of the advanced physicochemical treatment of OMW using various methods as ozonation, wet oxidation, photocatalysis, coagulation-flocculation, as well as electrochemical, solar-driven or hybrid processes and also by Fenton's reagent, who offers higher cost-efficiency [19]. The Fenton like treatment is still relevant. Recently, Tufaner studied the evaluation of COD (chemical oxygen demand) and color removals of raw OMW by combining an anaerobic treatment and Fenton process using Fe2+ and H2O2, the process achieved 98% of COD removal of 1/8 diluted raw OMW [20].

Flores et al. showed in his research the degradation of 4-hydroxyphenylacetic acid; a product of tyrosol oxidation using upon AO-H_2O_2 treatment with a BDD/air-diffusion cell, minimizing energy consumption, but just 67.6% of TOC was eliminated [21]. Their recent study showed the effectiveness of a sequential process involving electrocoagulation followed by electro-Fenton or photoelectro-Fenton under UVA irradiation for the treatment of raw OMW, 97.1% TOC is removed after 600 min [22].

In the same vein, Hodaifa et al. reported the effectiveness of the treatment of OMW using $FeCl_3$/H_2O_2, achieving 95.7% of COD removal, 93.6% of total phenolics and 92.5% turbidity [23].

In addition to H_2O_2, other oxidants are used like hypochlorite (OCl^-) for the treatment of OMW. So, Oxidation by hypochlorite ions is poorly described in the bibliography despite the low cost and the effectiveness of the bleaching process. G. Markou et al. have reported the results of the treatment of OMW using OCl^- derived from sodium hypochlorite and calcium hypochlorite.

The result showed that NaOCl has a greater effect on polyphenols and inorganic pollutant removal [24]. The application of $Ca(ClO)_2$ generates highly toxic byproducts; high levels of DDD, DDT, and heptachlor reported by Boukhoubza et al. [25]. The reported results have shown considerable disadvantages, revealing that most of these treatment methods are also unprofitable, or they generate toxic byproducts.

Against this background, and given the improvement of the COD treatment process, we report a new catalytic oxidation process of OMW, using OCl^- as the oxidant and $Fe(OH)_2$/1,10-phenanthroline as the catalytic system in an equimolar ratio ($Fe(OH)_2$/phen). It is an economic system characterized by its simple application and can be adapted to different volumes without specific conditions. Stored OMW is used without filtration or dilution with a combined system of oxidant and catalyst, to eliminate the organic load in contaminated vegetal water expressed in terms of COD, of total phenol, of turbidity. Liming is a post-treatment; it has been proposed to reduce the salinity.

2. Materials and methods

2.1. Olive-oil mill wastewater

OMW samples were collected from the olive press in “Sidi-Thabet” located in northern Tunisia, which has a daily processing capacity of 60 tons of olives.

No chemical additives have been used in the production of olive oil. The samples were stored at ambient temperature and pressure. They are characterized by a brown color with a strong unpleasant smell. The liquid effluents have been used directly without dilution and filtration. The physicochemical characterization values of raw OMW are summarized in Table 1.

Table 1: Physical and chemical characterization of the raw OMW

Parameters	*Contents*
pH	5.14± 0.09
COD (g L^{-1})	193.45± 2.7
Conductivity (mS cm^{-1})	11.75±1.3
SALT (Salinity) (ppt)	6.21± 0.9
Total Dissolved Solid (ppt)	5.89± 1.4
Redox potential (mV)	107.6±0.9
Suspended Solids (mg L^{-1})	13.57±1.2
Dry weight (g L^{-1})	48.87± 1.1
Ash rate (g L^{-1})	8.79± 0.7
Acidity (°D)	14.42±1.5
Sugars (mmol l^{-1})	120.37±2.9
Total phenols (g L^{-1})	8.99± 2.7
Turbidity (NTU)*	466± 1.2

* for a sample diluted 40 times

2.2. Synthesis of the catalyst

In a closed 100 mL round bottom flask, 0.352 g (0.9 mmol) of solid Mohr salt $(NH_4)_2Fe(SO_4)_2.6H_2O$ has been added to 17 mL of methanol. Under stirring the mixture is reacted with 2 mL NaOH solution (1.8 mmol, 0.075 g) for half an hour followed by the addition of 0.178 g (0.9 mmol) 1,10-phenanthroline (phen). The solution turned immediately to burgundy red. The mixture was kept stirred for 72 hours at room temperature, finally filtered and dried, giving rise to a crystalline powder (yield 67%).

2.3. Catalytic oxidation process

The commercial bleaching agent has been used directly without dilution (pH = 12.45 and 12°). The used volume of undiluted and unfiltered crude OMW has been held fixed to about 10 mL. The sample has been kept under vigorous stirring for 24 h. The concentration of hypochlorite [OCl^-] (36.8 mg mL^{-1} - 46 mg mL^{-1}) were varied according to the variation of concentration of the catalytic systems used ($Fe(OH)_2$/phen) [Fe(II)] (1.7 10^{-3}mol L^{-1} up to 0.85 10^{-3}mol L^{-1}) under various conditions. Four series of seven experiments were carried out at room temperature 293.15 K, and the two other series have been carried out at 383 K Table 2 (in a file in attachment). The characterization of all the treated samples was done at the end of the reaction without filtration.

2.4. Liming

CaO was purchased from Acros Organics technical grade. It was applied to all series of treated OMW with fixed 0.5 g L^{-1} of lime. The solutions were agitated at 200 rpm for 5 min and then allowed to flocculate at 2500 rpm for 10 min. After a period of rest, we characterize the solutions obtained.

2.5. Analytical methods

All tests were conducted according to standard methods of the EPA (Environmental Protection Agency) Manual for Industrial Waste Monitoring.

The raw OMW and the treated OMW samples were characterized by several physicochemical methods. The pH measurements were carried out with a METTLER TOLEDO pH meter, equipped with an electrode type LE40, the calibration is done with two solutions of pH 4 and 7. The COD is determined according to the potassium dichromate method standard using thermo-reactor HI 839800 HANNA as the incubator used for 2 h at 150 °C. After cooling, the amount of dissolved oxygen COD in mg O_2 L^{-1} for a diluted sample is obtained by measuring the optical density at 620 nm using the spectrophotometer MultiDirect Photometer LV6000 [26].

Total phenolic content in different samples was determined according to the Folin-Cioacalteu, the spectrophotometric method using gallic acid as a standard and the results were expressed as gallic acid equivalents [27]. Universal multi-parameter portable meter ProfiLine Multi 3320 was used for determination of conductivity expressed in mS cm^{-1}, salinity expressed and TDS expressed in ppt. Suspended solids (SS) are determined by centrifugation 20 ml of the sample at 3000 g for 15 minutes. The pellet is dried at 105 °C for 24 hours. The rate of SS is the difference between the weight of the dried sample and that of the cup expressed in g L^{-1}. The samples are evaporated at 105 °C to determine a total dry weight [28]. The acidity was determined according to the method of Dag [29]. The turbidity was measured by the portable turbidity meter the HI83749 is a portable turbidity meter.

HPLC is used to determine the concentrations of acetate and lactate, as well as residual sugars (sucrose, glucose, and fructose). The apparatus is equipped with a quaternary pump model coupled to a detector with a refractometer index (RI), the exchange columns are amines; 7.8 mm Aminex HPX-87 H (Bio-Rad), the mobile phase is sulfuric acid at 5 mmol L^{-1}

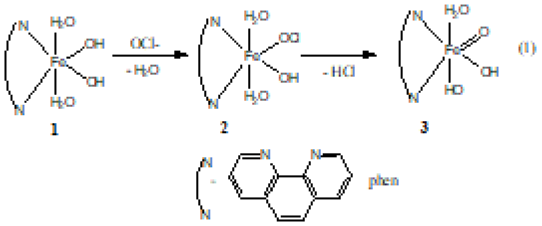
diluted with a few mL of water with a flow rate of 0.5 mL min^{-1}. The HPLC (Agilent 1200 Series, USA) was connected to a computer running the WINILAB III software (Perichrom, France). The samples are centrifuged for 5 min. The supernatants obtained are filtered with a 0.45 mL cellulose acetate Minisart syringe filter (Sartorius Stedim).

3. Results and discussion

In this research, we proposed a catalytic oxidation process for the treatment of OMW, in a single step using economical, available and stable products without filtration or dilution of OMW. we have used a combination of a mixture of the catalytic system ($Fe(OH)_2$/phen) with the commercial bleach (OCl^-). The reaction is carried out in a closed reactor at basic pH without adjustment, and ambient pressure. The main objective of this study is the determination of the most appropriate treatment process combinations, to remove toxicity of OWM. Several of Reaction parameters as the concentration of the catalytic system [Fe^{2+}] (1.7 10^{-3}mol L^{-1} up to 0.85 10^{-3}mol L^{-1}), the hypochlorite concentration [OCl^-] (36.8 mg mL^{-1} - 46 mg mL^{-1}), and reaction temperature (293 K - 383 K) are investigated Table 2, they are expressed by the removal % of DOC (Figure 1), total phenol (Figure 3), and turbidity.
Animmediate discoloration and absence of strong odors as well as a slight increase in temperature are noted from the start of the experiments, after 24 hours several samples reveal zero turbidity.

The reactions involved during the treatment of OMW are oxidative reactions proven by the presence of lactic acid and the absence of glucose as shown in the identification of sugar by HPLC of treated sample 5 (Figure6). Furthermore, no intermediate byproducts were detected in the reactor.

The catalysis system is completely soluble in the reaction medium. The reaction equilibrium is explained by oxidation according to the equation (1) hypochlorite oxidation of iron (II) in the catalytic system leads to a new iron (oxo) (dihydroxo) species. The total absence of Fe(III) during the reaction and non-formation of chlorinated compounds are an indication for oxidation in the coordination sphere of iron.No degradation of our catalytic system.



After the catalytic oxidation treatment, we have opted to add a quantity of CaO to reduce the salinity level and largely eliminate the ionic load of the treated effluent. So, 50% of the initial values of Salt, TDS, E.C. was removed by liming (Figure 5).

The raw OMW is characterized without prior treatment, without filtration or dilution, the result of the analysis showed their acidic pH 5.14 Table 1, which is in agreement with the results found by several authors, this acidity is explained by the organic acid transfer due to the contact between the washing water and the olive oil in the mixing and separation devices [31].

Our OMW rich in an organic matter [32], justified by the high values of COD 193.45 g O_2 L^{-1} and turbidity 466 NTU (for a sample diluted 40 times), these results disclose that the effluent contains ionic and mineral compounds Table 1. The values recorded in our study are in the range cited elsewhere [23]. All these parameters depend strongly on the type of olive trees, the climatic conditions, the degree of olive maturation, the cropping systems, the salting practice, the olive conservation methods and the extraction process of olive oil [33].

The proposed catalytic system makes it possible to reduce the values found in Table 1. Its apparent efficacy of eliminating the toxicity of treated OMW over raw OMW is discussed by varying the operating conditions.

On the whole, the most important factors that influence the efficiency of the degradation process in the catalytic oxidation system are the concentrations of the catalyst and oxidant, the amount of contaminants, as well as the pH and temperature of the reaction medium.

In our study, we chose to vary the temperature, the concentration of Fe(II) of the catalytic system and the concentration of [OCl^-], with a fixed amount of raw OMW (10 mL) and basic pH, the hypochlorite treatment has caused on the one hand the increase of pH that goes from 5.14 to 8.10, and induce on the other hand the increase in electrical conductivity goes from 11.75 mS cm^{-1} to 80.8 mS cm^{-1} Figure5.

In fact, the operating pH of the catalytic system must be greater than 8, basic pH affects the degradation of pollutants, and stabilize the catalytic system ($Fe(OH)_2$/phen). It has been reported that up to pH basic results in high pollutant removal efficiencies.

All experiences showed an immediate elimination of colours and strong odours of all samples of the treated OMW. Each series of experiences was carried out at different hypochlorite solution initial volume, while the other operating variables are maintained constant.

Concentrations of [Fe^{2+}] ranged from 1.7 10^{-3}mol L^{-1} up to 0.85 10^{-3}mol L^{-1} and those of [OCl^-] ranged from 36.8 mg mL^{-1} to 46 mg mL^{-1}).

Figure 1 shows the efficiency of COD removal as a function of $Fe(OH)_2$/phen and OCl^- concentrations during the catalytic oxidation process of OMW, the maximum percentage removal of COD is 98%, obtained in series four. The increased amount of OCl^- does not influence the rate of reduction of the COD, the rate of removal COD remains practically constant in the wave between [95% - 98%] for 50 mg of a catalytic system “series 4”.

Increasing the quantity of bleaching water has a positive influence on the COD removal for series two, the values change from 84% to 94%. An increase of the OCl^- the amount added to the reaction media affects the rate of COD removal positively (the value goes from 67% to 83% series one Figure 1.

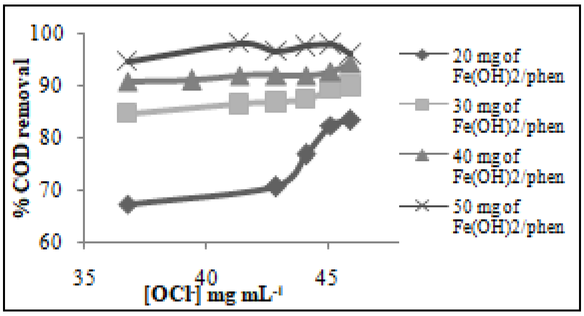


Figure 1:% COD removal values registered during OMW catalytic oxidation process (experimental conditions: basic pH, T = 293.15 K, COD initial = 198.448 g O_2 L^{-1}, OMW = 10 mL)

The elimination of the catalyst system [$Fe(OH)_2$/phen] effect makes it possible to determine the net potential of this catalytic process. For an initial concentration [OCl^-] = 36.78 mg mL^{-1} just 45.82% of COD abatement is obtained.

Therefore, the degradation rate of the organic material and the hypochlorite concentration of sodium are conditioned by the initial concentration of the catalytic system. This treatment process is applicable to the elimination of most organic matter with good energy efficiency, no trace of strong odours and brown colours in treated liquid effluents are observed. The degradation rate of the organic material is conditioned by the initial concentration of the catalytic system and the hypochlorite concentration of sodium, the removal rate of COD increases for the same quantity of bleach ([OCl^-] = 36.78 mg mL^{-1}) and for an increasing amount of catalytic system (from 20 mg to 40 mg) the value goes from 67% to 94% Figure 1.

No direct comparison can be made between the results of our researches and previous studies. Hypochlorite has been used without the catalyst.

Turbidity is the parameter that decreases when increasing the amount of OCl^-, thus 99% is removed.

Figure 2 reveals a graphic surface, it is the combination between the concentration of the catalytic system [Fe^{2+}], the oxidant [OCl^-] and the COD removal rate, the graph shows a total absence of an absolute minimum.

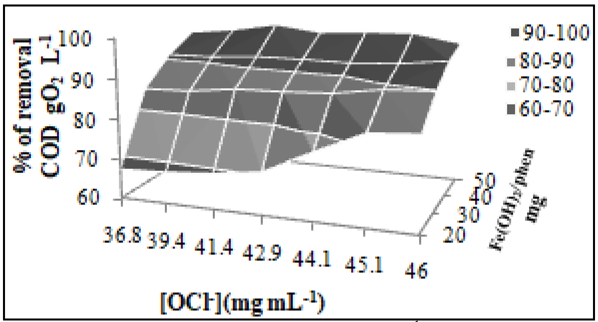


Figure 2:% of removal of COD gO_2L^{-1} as a function of amount of ($Fe(OH)_2$/phen) (mg) and [OCl^-] (mg mL^{-1}) under 293 K

In addition to the COD removal, our catalytic oxidation process has completely degraded the total phenols.

The gradual elimination of total phenols was observed for 20 mg of the catalytic system and increased value of hypochlorite, the rate goes from 13% to 89%, however, increasing of catalytic system concentration to 50 mg results in the total elimination of total phenol Figure 3.

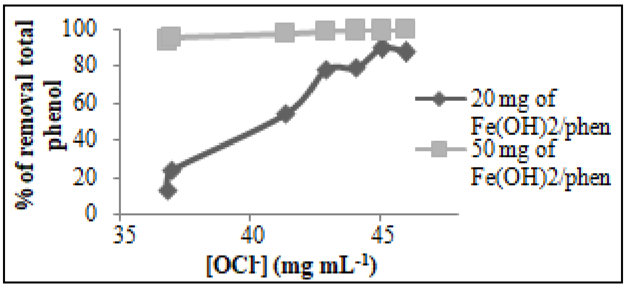


Figure 3: % of removal of total phenol as a function of [OCl^-] (mg mL^{-1})

Despite the advantage of using hypochlorite, the proposed catalytic process gives a saline medium without the effect of chlorination of organic compounds. Temperature is one of the factors that influence DOC processing, OMW Sample processing was carried out at two different temperatures, 293 K and 383 K Table 2. The results obtained are shown in Figure4. The COD removal values observed at the two temperatures are weakly different, however, the reaction is approximately eight times faster at 383 K. Removed COD values varied between 94% and 97.7% for just 30 mg of $Fe(OH)_2$/phen Figure4 analogous results have been reported by Nieto et al. using the Fenton process [26].

Temperature is an important factor to reduce not only the toxicity presented in OMW but also the reaction time from 24 h to just 3 h. In fact, for the same quantity of the catalyst (30 mg) the percentage of COD elimination rise from 84.624% at T = 293 K up to 96.847% at T = 383 K. Although the temperature promotes COD removal, it also affects the reactivity of the oxidant [34]. Indeed, whatever the quantity of OCl^- added Table 2, the elimination rate is in the range of (94% - 97.8%). To sum up, it is not necessary to provide heat to achieve an optimal rate of COD removal greater than 95%, it is sufficient to work at room temperature of the order of 293 K.

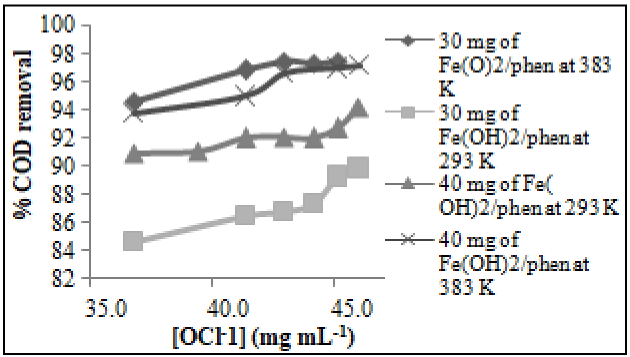


Figure 4: % of removal of COD gO_2L^{-1} as a function of amount of ($Fe(OH)_2$/phen) (mg) and [OCl^-] (mg mL^{-1}) under 293 K and 383 K

3.1. The effect of adding CaO

In our present work, we opted to add calcium oxide as post-treatment, the optimization of our results led to the conclusion that a quantity of 0.5 g L^{-1} is necessary and sufficient to reduce the salinity of our medium.

Liming was applied to treated samples after catalytic oxidation for evacuating the liquid treated in collective sanitation.

The choice of the optimal concentration is made based on two main criteria: the precipitation efficiency of ionic compounds in general and the mass of lime added without blackening.

Figure5 shows the effect of CaO expressed in amount of SALT (a decrease from 49.3 ppt to 23 ppt), a significant reduction in conductivity (E.C.) (from 80.8 mS cm^{-1} to 38.3 mS cm^{-1}), and on TDS (a decrease from 42 ppt to 19.2 ppt) is observed. Liming precipitates organic acids, the OH^- ion; ionic compounds in general.

A decrease between 52% - 57% of the TDS, SALT and conductivity levels is observed after adding the CaO in the reaction medium.

Boukhoubza et al. have reported that liming treatment used as pre- or post-treatment is a very effective, available, low-cost and high-performance depurative [25]. However, the amount of CaO should not be too high because it causes blackening.

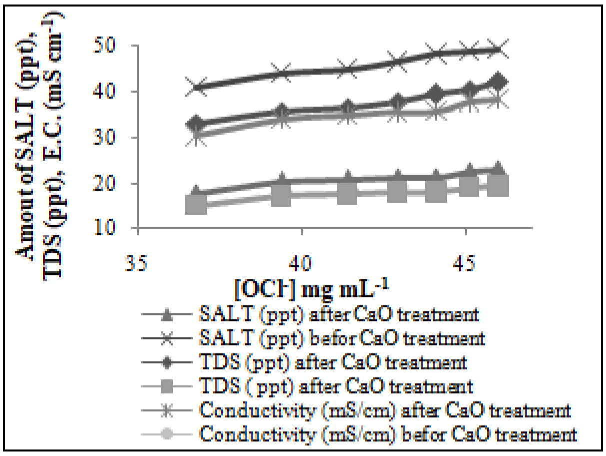


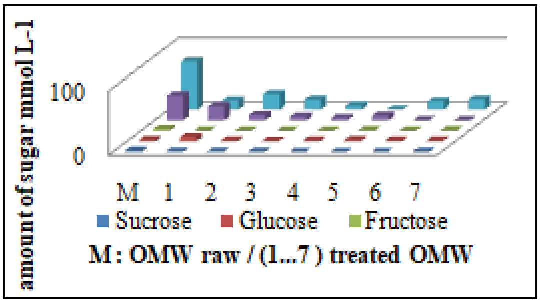
Figure 5: Effect of adding CaO to reduce SALT (ppt), TDS (ppt) and conductivity ($mScm^{-1}$) at room temperature (CaO 0.5 g L^{-1}, 20 mg of $Fe(OH)_2$/phen)

3.2. HPLC analysis

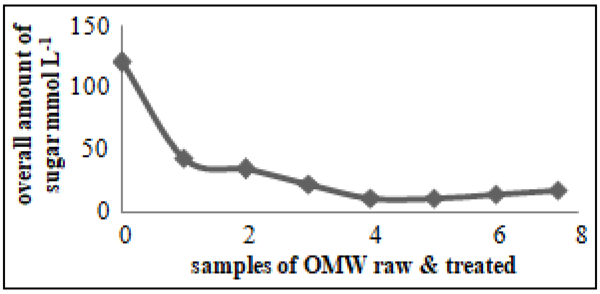
The HPLC analysis of sugar of raw OMW and of treated samples show the presence of glucose and diholosides in addition to acetate and lactate Figure 6. The amount of sugars present in the raw sample of OMW is 120 mmol L^{-1}. The maximum rate of degradation of sugars contained in the treated sample is 90.77%, whose 55.67% are lactate.

So, the more OMW is old, the more it is oxidized, the phenols turn into bisphenols. These latter are further oxidized to hydroquinone then to p-benzoquinone to give the acetic acid. So, the higher acetate concentration in the medium, the lower the amount of phenols.

Sugars and polyphenols are present in the OMW with concentrations ranging from 0.5 g L^{-1} to 25 g L^{-1} [35]. They are much more soluble in the aqueous phase than in the oil phase, which explains their high values in fresh OMW. The storage of OMW causes the degradation of sugars into organic acid.Our raw OMW is mainly rich in oses and dyolsides. Their transformation is so quick.



a) The different sugars naturally present in OMW



b) HPLC analysis Overall amount of sugar mmol/l= f(samples)

Figure 6: HPLC analysis of sugar naturally present in OMW

4. Conclusion

In this study, catalytic oxidation of OMW, with safe to handle and environmentally benign reagents at atmospheric pressure at different temperatures (293 K and 383K). The raw OMW was treated with the catalytic system $Fe(OH)_2$/Phen using the commercial OCl^-.

The process allows the elimination, in one step of color, smell and phenols. Mineralization of organic compounds did not occur. The COD removal and the decrease of phenols concentration have reached 95%, and 100% respectively with a ratio Fe2+/OMW of 0.9 g L^{-1}.

The liming was applied after the catalytic oxidation of the OMW samples as a post-treatment. More than half of the initial values of the SALT (decrease from 49.3 ppt to 23 ppt), TDS and conductivity are eliminated after adding the CaO in the reaction medium.

This study offers an effective solution to reduce the organic content and the environmental effects of OMW at a reduced price with reagents easily available. The proposed treatment process is an economic system characterized by its simplicity of application, and it is adapted to different volumes.

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