Treatment of Olive Mill Waste Water by Adsorption on Hydroxyapatite-Sodium Alginate Composite

Rabia Benaddi, Abdelillah Bouriqi, Faissal Aziz, Khalifa El harfi, and Naaila Ouazzani

***Abstract*—The olive sector and in particular that of the extraction of olive oil requires large quantities of water, therefore obtaining olive oil generates two by-products, one liquid (OMWW) and the other solid (pomace). The OMWW are the aqueous phase resulting from the crushing of olives, causing worrying environmental problems in particular that it contains large quantities of organic compounds especially phenols compounds which cause many environmental problems such as water pollution. Therefore, the treatment of OMWW is very necessary. The purpose of this work was the investigation of the efficiency of hydroxyapatite-Sodium alginate composite for the adsorption of phenolic compounds, which are contained in OMMW. It showed promising results in reducing the phenol compounds and organic matter by 60% and 64% respectively and the reduction of Hydroxytyrosol and Tyrosol by 100% and 38% respectively, which are the most predominant polyphenols in OMWW. For second cycle of adsorption-desorption, the adsorbent lost slightly its adsorption capacity, reduction rate of phenol compounds and organic matter pass from 64% and 60% to 45% and 50% respectively.**

***Index Terms*—Adsorption, alginate, desorption, hydroxyapatite, phenol compounds.**

I. Introduction

In the Mediterranean countries, the olive sector plays a very important socio-economic role, but this olive industry produces large quantities of olive mill waste water (OMWW) which is characterized by high concentration of organic compounds especially polyphenols which varies from 0.1 to 17.5 g/L [1], [2], Presence of polyphenols in OMWW makes them very toxic and causes many environmental problems [3]. Many studies have been carried out to find solutions allowing the treatment of OMWW including biological processes [4], oxidation [5], [6], electrochemistry [7], distillation [8], coagulation [9] Ozonation [10], infiltration [11] and membrane technology [12], comparison of different methods of OMWW treatment has been carried out by others authors [13]. Recently, studies have focused on the study of the adsorption of phenolic compounds using different adsorbents [14]-[19], indeed, adsorption experiments of organic compounds from OMWW using a cross-linked styrene–divinylbenzene polymer as a sorbent have been realized by Aikaterini Vavouraki, results show that the process of adsorption was rapid, 68% reduction of polyphenols was observed within the first 1 h [20]. The effectiveness of clay materials for the retention of polyphenols was stdied by Islem Chaari et al, results shows that the adsorption efficiency of polyphenols by calcined clay and raw was 84.21% and 77.61% respectively [21]. other authors have studied adsorption of polyphenols from OMWW on activated carbon prepared from peach stones, The best removal efficiency was 91% in specific experimental conditions (adsorbent mass equal to 2 g, ambient temperature and acidic medium [22]. Several studies have been carried out on the development of low-cost adsorbents to solve the problem of the high cost of adsorbents which limits their use [23]-[25] such as bioadsorbents [26], [27] or apatites [28]-[30]. The purifying power of apatites in the retention of heavy metals from wastewater is very effective [31], [32], but its use is limited for organic pollutants. In addition to the problem of their separation from the treated water due to the fact that its finely divided particles. Encapsulation of apatites within the bio-polymer beads overcomes this problem while keeping their adsorption capacity after saturation. Alginate is one of the polymers that have been the subject of numerous studies, due to its great ability to bind a wide range of metallic pollutants in aqueous solutions [33]. The aim of this work is to identify the types of polyphenols existing in the studied OMWW using the HPLC technique and study the types of polyphenols which can be eliminated or reduced using an adsorbent composed of a synthesized hydroxyapatite which is natural, very abundant and has a high specific surface (HA) and Sodium alginate (SA) which have very interesting properties especially the encapsulation of adsorbent to facilities its removing from the treated OMWW.

II. Materials and methods

A. Adsorbent Description

HA was synthesized by dissolution of natural phosphate (NP) in nitric acid [34]. A mass of 30g of NP was introduced into a 2 L reactor contains a volume of 20 mL of nitric acid solution (65%) and 500 mL of distilled water. The reaction was maintained under continuous stirring for a period of 24 hours at room temperature and at pH equal to 2. After the NP

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was completely dissolved, the mixture was vacuum filtered. The filtrate then neutralized with 200 ml of ammonia with a concentration of 25%. The maturation of the precipitate is realized during 72 hours under continuous stirring then the precipitate is filtered and washed several times with distilled water before drying at 100 °C for almost one night. The chemical composition of HA is P_2O_5 (36.84%), CaO (57.6%), SiO_2 (0.78), Al_2O_3 (1.41%) and Na_2O (2%). [35].

Hydroxyapatite-Sodium alginate beads (HA /SA) were prepared according to the protocol described by Aziz et al. [36]. Indeed, 1g of sodium alginate was dissolved in a volume of 50 mL of distilled water. Then 0,125 g of HA is added to the solution obtained by stirring for 2 hours until the production of a homogeneous dispersion. then the solution is introduced using a syringe Under magnetic stirring in a reactor containing 50 mL of CaCl2 solution (1 g / L), The coagulated beads were then washed with distilled water [35].

B. Adsorbat

The studied olive mill waste water was taken from a three-phase olive crushing unit in the region of Marrakech in Morocco and kept at a temperature less than 4 ℃ in a dark place.

C. Sorption Experiments

All the adsorption experiments were carried out in a cylindrical column 20 cm in length and 4 cm in internal diameter. Indeed, first, the column was filled with 10 g of HA/SA and a reservoir of 500 ml was filled of OMWW which was passed through the beads bed at a constant flow rate of (0.9 10^{-3} l/s). at different time intervals, solution samples were taken from the reservoir to equilibrium. To perform the OMWW desorption experiments from HA/SA, the solvent was pumped into the column with a fixed flow rate (0.9 10^{-3} l/s). at different time intervals, samples of solution were taken until complete desorption. the same protocol was adopted for the second cycle of adsorption-desorption.

Phenolic compounds of OMWW were quantified by means of the Folin–Ciocalteu colorimetric method according to Macheix et al, indeed, In the presence of polyphenols, the mixture phosphotungstic acid (H_2 $PW_{12}O_{40}$) and Folin's reagent ($H_3PW_{12}O_{40}$) is reduced to blue tungsten oxide (W_8O_{23}), the staining exhibits an absorption maximum at 760 nm. The results are expressed in equivalent gallic acid used in the standard range [37]. The phenolic compounds of the OMWW were assayed according to the colorimetric method of Folin-Ciocalteu described by Macheix et al. A high-performance liquid chromatography (HPLC) was used to identify phenolic compounds in OMWW extracts, indeed, the important characteristics of HPLC are: Column: Eurospher II 100^{-5} C18, 250 mm × 4.6 mm plus a pre-column of the same stationary phase (Knauer, Berlin, Germany). Detection: array of PDA photodiodes, Mobile phase: 5 ACN/95 water (o-phosphate pH = 2.6), flow rate: 1 mL/min at ambient temperature. many phenolic standards have been used for the identification of phenolic compounds.

To measure the chemical oxygen demand, we used a method based on digestion followed by the dichromate colorimetric method (AFNOR-T90-101) [38].

III. Results and Discussion

A. Characterization of the Adsorbent (HA/SA)

An appartus of the Tescan Vega 3 type has been adopted for carrying out the Scanning Electron Microscopy analyzes. The adsorbent has been metallized with carbon to avoid charge effects. X-ray powder diffractometer Rigaku was used to determine the structure of the adsorbent. FTIR spectrum of the studied adsorbents were obtained by Fourier transform spectrometer "Vertex 70", the pellet was obtained by crushing 0.099g of KBr with 0,001g of adsorbent. An ICP-AES spectrometer type THERMO FLASH was used to determine the main constituent elements of the adsorbents. analysis of the results obtained showed that HA/SA is composed in addition of Na and Ca of phosphate due to the insertion of hydroxyapatite in the alginate [35]. X-rays of HA/SA show that is not well crystallized, its spectrum due to the structure of the adsorbent which is semi-amorphous, some weak peaks were detected due to the structure of HA/SA, Analysis of the FTIR spectrum of the adsorbent shows the presence of bands around 614 and 1031 cm^{-1} attributed to the vibrations of the phosphate groups, absorption bands relating to ether, carboxylic groups and hydroxyl functions were also detected, and in the range of 3000–3600 cm^{-1}, stretching vibrations of the O–H bonds of alginate are detected. asymmetric and symmetric stretching vibrations of the carboxylate salt ion, were observed at 1649 and 1460 cm^{-1} respectively [39]. SEM images of the adsorbent show that the surface is porous with deformations of different sizes with a diameter of the order of a few micrometers. the entanglement of macromolecular chains following the insertion of HA/SA which can responsible of these deformations (Fig. 1).

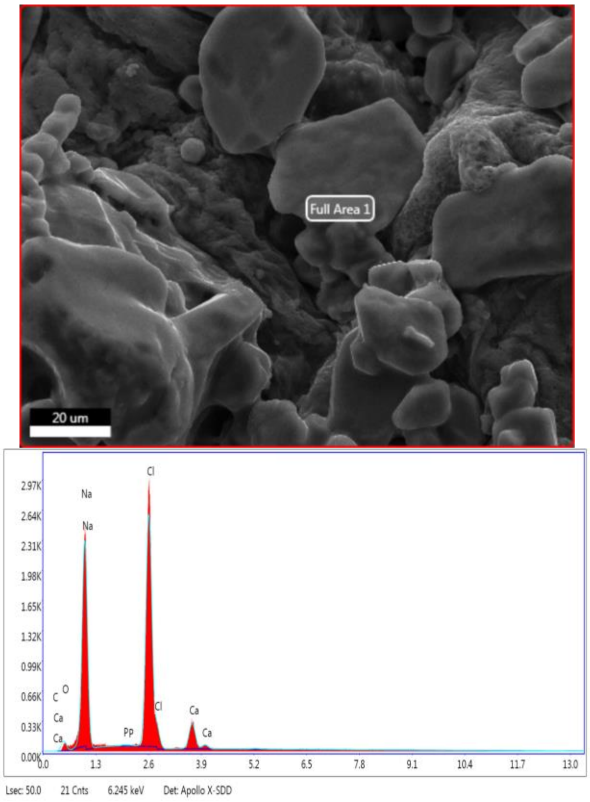

Fig. 1. SEM images coupled energy-dispersive X-ray analysis of HA/SA.

B. Characterization of OMWW

The main characteristics of OMWW were summaried in Table I, OMWW are very loaded with polyphenols (2.204 g eq gallic acid / L), This value is lower than that found by Ayoub El Ghadraoui, et al. when studying the treatment efficiency of a mixture of OMWW and a mixture of municipal wastewater [40], this difference is due to the fact that ayoub et al have used an OMWW issues from traditional units, while, we have used an OMWW issues from semi-modern units, the presence of several types of organic acids as fatty acids or phenolic acids make the pH of OMWW studied very acidic. The value of electrical conductivity of the studied olive mill waste water equal to 12.5 mS/cm, this can be linked to the ions due to the use of the salting practiced to preserve the olives until the crushing as well as the natural mineral salts of the olive [11]. The value of organic matter equals 137.5g of O2/L), this high value shows the polluting power of OMWW. The phenolic fraction after its extraction from OMWW with an ethyl acetate solvent was analyzed by HPLC chromatograph. It was found that Hydroxytyrosol and Tyrosol are the most predominant polyphenols with more than 95%, the same result was found by several authors [41]. The following polyphenols were also identified: Syringic acid, gallic acid, Catechol and Caffeic acid (Fig. 2).

TABLE I: PHYSICAL–CHEMICAL CHARACTERISTICS OF STDIED OMWW

Parameter	OMWW
T(°)	25
pH	4.56
Electrical conductivity (mS/cm)	12.5
Total polyphenols(g eq gallic acid /L)	2.204
COD(g of O_2/L)	137.5

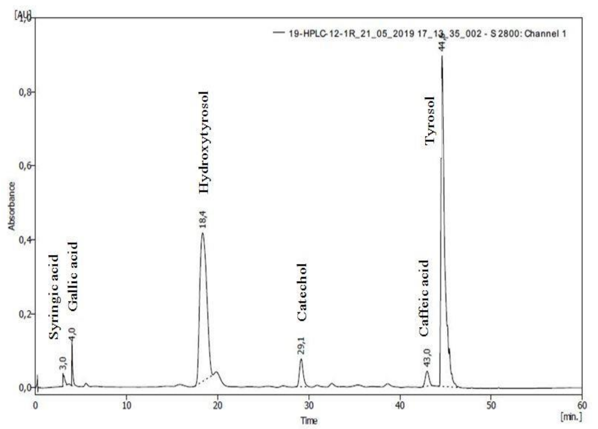

Fig. 2. HPLC chromatograph of polyphenolic fraction after its extraction from studied OMWW with ethyl acetate solvent.

C. Treatment of OMWW

The result of the treatment of the OMWW by adsorption on the composite hydroxyapatite-sodium alginate is summarized in Table II. The analysis of the result shows that the pH of the treated OMWW is increased, this is due to the retention of organic acids which are the elements responsible for the acid pH of OMWW; the same results were found by other authors during the study of OMWW treatment by infiltration/percolation on sand filter system [10]. The increase of electrical conductivity of OMWW from 12.5 to 17.8 may be due to diffusion of the salts of the adsorbent towards OMWW. Analyses of obtained results show that the treatment of OMWW by adsorption method on HA/SA reduces phenol compounds by 60%, which shows that HA/SA has a high adsorption capacity compared to others adsorbents as activated carbon or clay [42], [43] but remains lower compared to the adsorption capacity of zeolite or polymer resins[44], which shows that the encapsulation of apatites with alginates increases their efficiency, indeed, reduction rate of phenolic compounds was only 30% when we have used apatites as adsorbent to treat OMWW [45]. On another side, the adsorption capacity of adsorption's phenol compounds reaches 140 mg / g, a value lower than that found during the study of the adsorption of simple phenol on HA / SA [31], this can be explained by the fact that the phenolic compounds of OMWW occupy more sites compared to simple phenol. Results show also that the treatment of OMWW degrades COD by 64%. Analysis of chromatogram (Fig. 3) shows the disappearance of several phenolic compounds and a decrease in the others. Witch mean's adsorption of majority of phenolic compounds. To verify the types of phenolic compounds adsorbed by HA/SA. Analysis of chromatogram shows also the disappearance of Hydroxytyrosol and the reduction of Tyrosol by 38% (Fig. 3).

TABLE II: PHYSICAL–CHEMICAL CHARACTERISTICS OF STUDIED OMWW IN ITS INITIAL STATE AND AFTER TREATMENT BY ADSORPTION ON HA/SA

Parameter	Initial OMWW	Treated OMWW
T(°)	25	25
pH	4.56	4.74
Electrical conductivity (mS/cm)	12.5	17.8
Total polyphenols(g eq gallic acid /L)	2.204	0.88
COD(g of O_2/L)	137.5	50

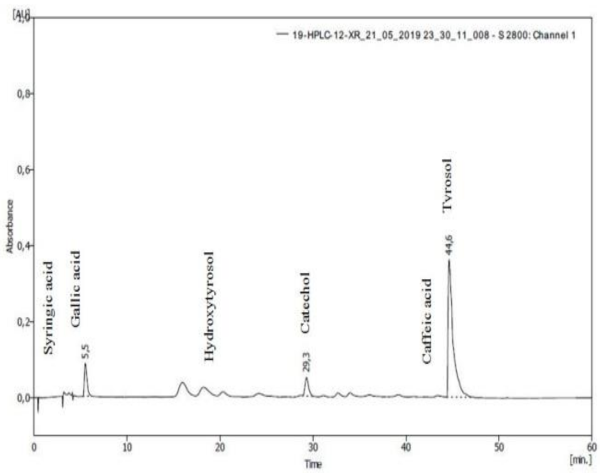

Fig. 3. HPLC chromatograph of polyphenolic fraction after its extraction from stdied OMWW with ethyl acetate solvent after treatment.

D. *Adsorption–Regeneration*

The desorbabilities of phenolic compound from HA/SA in column using water as solvent was also studied. Analysis of results (Table III) shows that 20% of the adsorbed quantity of phenolic compounds was recovered, this percentage of desorption is lower compared to that found by other authors who used other solvents [46]. This may be due to desorption only of certain phenolic compounds when we use water as solvent while the other authors have used other solvents. Indeed, analysis of the chromatogram shows the regeneration of a small amount of syringic acid, gallic acid and Tyrosol (Fig. 4).

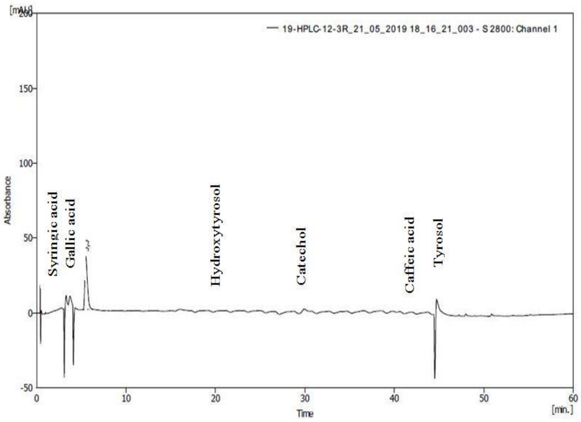

Fig. 4. HPLC chromatograph of polyphenolic fraction after its extraction from regenerated OMWW with ethyl acetate solvent OMWW with ethyl acetate solvent after second treatment.

TABLE III: PHYSICAL–CHEMICAL CHARACTERISTICS OF GENERATED OMWW

Parameter	Initial OMWW	regenerated OMWW
T(°)	25	25
pH	4.56	5.02
Electrical conductivity (mS/cm)	12.5	2.15
Total polyphenols(g eq gallic acid /L)	2.204	0.304

E. *Cycling Effect*

In order to understand the power of the adsorbent to treat OMWW several times, we performed the second adsorption-desorption cycle, the results are shown in Table IV. The results show that the adsorbent has slightly lost its adsorption capacity; indeed, reduction rate of COD and phenolic compounds has been passed from 64% and 60% to 45% and 50% respectively. This is due to the partial saturation of the adsorption sites, which means that the reversibility of the adsorption reaction is partial. Analysis of the chromatogram shows a reduction in the peaks of several phenolic compounds with a lower rate than the first cycle (Fig. 5). In fact, a reduction of hydroxytyrosol by 76% and tyrosol by 47% has been observed.

TABLE IV: PHYSICAL–CHEMICAL CHARACTERISTICS OF THE STUDIED OMWW IN ITS INITIAL STATE AND AFTER SECOND TREATMENT

Parameter	OMWW	Treated OMWW by second adsorption
T(°)	25	25
Ph	4.56	4.78
Electrical conductivity (mS/cm)	12.5	15.05
Total polyphenols (g eq gallic acid /L)	2.204	1.11
COD(g of O_2/L)	137.5	75

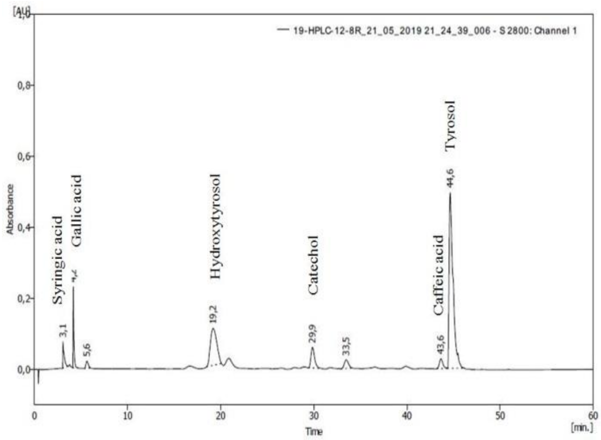

Fig. 5. HPLC chromatograph of polyphenolic fraction after its extraction from OMWW with ethyl acetate solvent after second treatment.

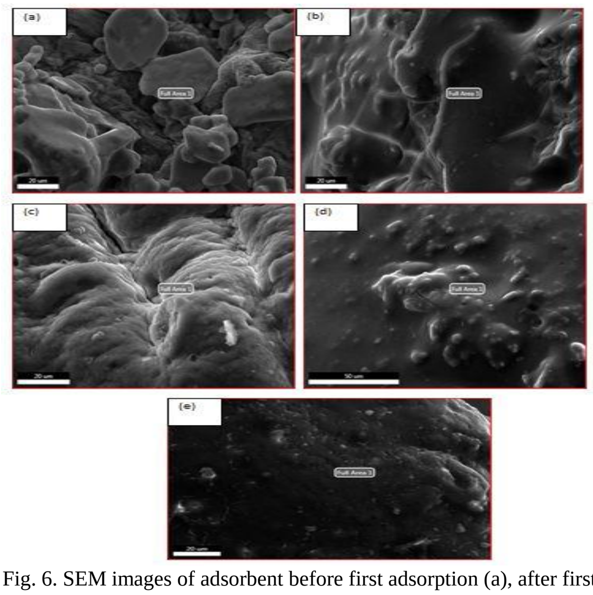

Fig. 6. SEM images of adsorbent before first adsorption (a), after first adsorption (b), after first desorption(c), after second adsorption(d) and after second desorption(e).

Analysis of SEM images illustrates the results found previously. Indeed, photo b (Fig. 6) shows the filling of the pore of the adsorbent by OMWW, part of these pores is released after desorption (photo c). This explains the decrease in the adsorption capacity during the second cycle of adsorption. The same phenomenon was observed during the second cycle of adsorption /desorption (photos d and e).

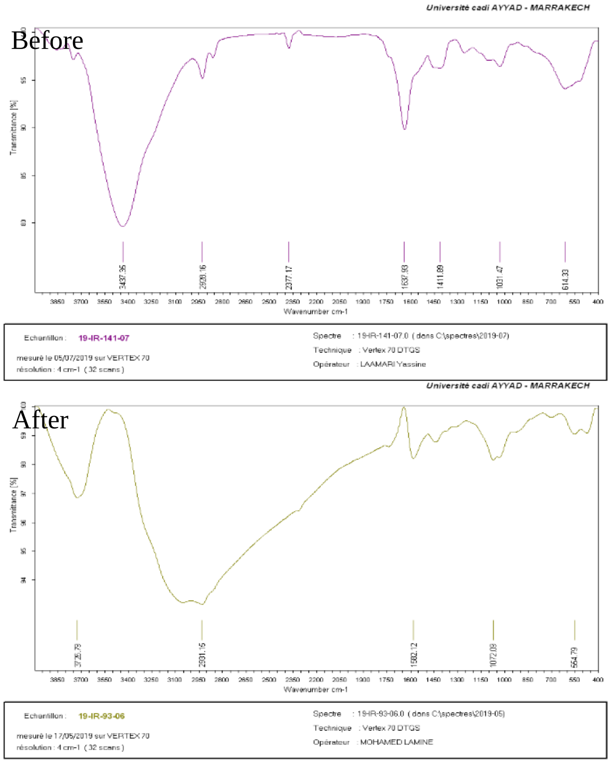

Fig. 7. Infrared spectrum of the adsorbent before and after adsorption.

Analysis of FTIR spectrum of the adsorbent before and after adsorption (Fig. 7) shows a wide band around 3000cm^{-1} which characterizes the carboxylic function of the phenolic compounds existing in OMWW.

IV. Conclusion

This study focused on the use of adsorption as a technique to degrade polyphenols in OMMW, hydroxyapatite-Sodium alginate composite is considered as an excellent adsorbent, It showed promising results in reducing the phenol compounds and organic matter by 60% and 64% respectively and the disappearance of Hydroxytyrosol and the reduction of Tyrosol by 38%, which are the most predominant polyphenols in OMWW. For second cycle of adsorption-desorption, the adsorbent lost slightly its adsorption capacity, reduction rate of phenol compounds and organic matter pass from 64% and 60% to 45% and 50% respectively. The results of the adsorption of polyphenols from OMWW using hydroxyapatite-Sodium alginate composite were very encouraging, compared with other adsorbents.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

R. Benaddi, A. Bouriqi conducted the research. F. Aziz, Kh. El harfi, and N. Ouazzani analyzed the research data, and finally, all authors contributed ideas for the paper writing and approved the final version of this manuscript.

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Authors and co-authors of two book chapters and Co-authors of 4 patents in the field of waste water treatment processes.