Removal Of Chemical Oxygen Demand (COD) From Olive Oil Mill Wastewater Using Activated Carbon

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The objective of this study is the production of an economical (inexpensive) activated carbon based on agro-food waste from the olive industry (olive pits). This activated carbon was applied in the treatment of olive oil mill wastewater (vegetation water) in order to reduce its high chemical oxygen demand (COD) and thus limit its harmful effects on the environment. The AC was prepared by the valorization of agro-food waste in the form of olive pits (calcination followed by chemical activation using phosphoric acid chosen from among other agents such as sodium hydroxide, potassium chloride, and zinc chloride, but these gave less yield.). A range of analyses was carried out for the characterization of the used adsorbent, including: iodine value, moisture content and ash content. The effect of several parameters such as contact time, amount of adsorbent and pH of the solution was studied. The best adsorption conditions are simple to achieve: ambient temperature and direct use of the olive oil mill wastewater (V = 100 mL, pH 2.05) with 3 g mass of AC adsorbent. The adsorption experiments demonstrated a significant reduction in chemical oxygen demand (COD), confirming the efficiency of the prepared activated carbon.

Keywords: Activated Carbon, COD, Olive Pits, Kinetic Adsorption, Olive Oil Mill Wastewater.

1. INTRODUCTION

The olive oil industry, in addition to its main production, which is virgin olive oil, leaves two by-products: both liquid (olive oil mill wastewater OMW: margins) and solid (pomace and leaves) [1,2]. These effluents have so far had little economic value in Algeria. Liquid waste (margins) poses serious environmental problems [3]. It is too loaded with organic matter, minerals and polyphenols. It is often discharged into sewers, stored in evaporation ponds or spread directly on the ground without any prior treatment. This results in a negative impact on the environment, leading to soil clogging, pollution of surface and ground water, and the release of nauseating odors. In addition, the presence of polyphenols, responsible for phytotoxic and antimicrobial effects, makes biological treatment ineffective [4].
Current research has shown that activated carbon derived from olive pits (and other olive waste) offers superior adsorption efficiency and lower costs compared to commercial activated carbon, thanks to the use of abundant waste from the olive industry and the absence of expensive conventional precursors [5,6].
On the other hand, olive pits and other olive-growing residues (pomace, mill solids, stones) are widely recognized as excellent, cost-effective precursors for activated carbons used to remove phenolic compounds and dyes from wastewater from olive mills and other effluents [7,8].
In addition, various processes for treating vegetable waters have been developed: physical, chemical, and even biological processes and current trends should aim

at integrating various technologies to treat vegetable waters at low cost. The different types of vegetable water treatment studied so far only solve part of the problem. Indeed, most of the proposed processes remain insufficient and incomplete, or even limited.

Activated carbon absorption is among the processes used for the successful treatment of margins. The transformation of olive pits into activated carbon is an opportunity to produce inexpensive adsorbents using local renewable resources [9].

This study aims to prepare from olive pits an activated carbon that is chemically activated using phosphoric acid. Some adsorption parameters were studied such as time contact, the used mass of AC and the initial pH of the solution.

2. EXPERIMENTAL PART

2.1. SAMPLING

The sampling of olive oil mill wastewater and olive pits was carried out in the region of Sidi Bel Abbes (West Algeria) from an oil mill extraction system by centrifugation in three phases during the olive campaign 2021-2022. The olive oil mill wastewater taken from the storage tank was homogenized and transported in 5-liter bottles. These bottles were stored away from light at 4°C for later use. This temperature is critical for preserving the characteristics of the wastewater from the olive oil mill [10-12].

2.2. DETERMINATION OF THE CHEMICAL OXYGEN DEMAND (COD)

COD was determined using potassium dichromate. The principle basis of this method is boiling oxidation (150 °C for 2 h) of the reducing materials in an acid medium (H_2SO_4) with an excess of potassium dichromate in the presence of silver sulfate as a catalyst and mercury sulfate as a complex agent of chlorides. The optical density of the sample was obtained by spectrophotometry at a wavelength of 620 nm.

2.3. SAMPLING ACTIVATED CARBON PREPARATION FROM OLIVE PITS

Firstly, the olive pits were washed with distilled water several times, dried, crushed and sieved. The dried sample was carbonized at a temperature of 700°C for 1 hour. The activation was carried out chemically using H_3PO_4 acid. This agent has been widely used for activation of carbons [13]. Next, the sample was immersed in a volume of the acid under agitation. The liquid was then separated by simple filtration and dried at 105°C for 24 h. After drying, the activated carbon was washed again with distilled water until reaching a pH of 6 in the residual water. Finally, the activated carbon was put in the oven at 110°C for 24 hours and packed in ready-to-use boxes. This is a standard protocol, widely cited in research on activated charcoal and olive-based precursors, applied to olive pits/residues and other lignocellulosic waste [14-16].

2.4. CHARACTERIZATION OF PREPARED ACTIVATED CARBON

2.4.1 Moisture content

The moisture content represents the amount of water physically not bound to the activated carbon. Moisture is a ratio expressed as a percentage; it is determined by drying the adsorbent in an oven at 105°C until its weight remains constant. It is calculated using Equation 1 [17]:

$$\mathrm{H\%} = \frac{m_0 - m_1}{m_0} \times 100 \qquad \text{(Equation 1)}$$

Where *H%* is moisture content (%) and m_0 and m_1 (g) are the mass of the AC adsorbent before and after drying, respectively.

2.4.2 Ash content

This is the inorganic, inert, amorphous and unusable part present in the material [17,18]. 1g of adsorbent was placed in a crucible. This crucible was moved to the oven and heated for one hour up to 1000°C. After cooling, the crucible was weighed. The ash content is calculated using Equation 2, as follows:

$$\mathrm{\%Ash} = \frac{p_0 - p_1}{p_0} \times 100 \qquad \text{(Equation 2)}$$

Where *%Ash* is the percentage of ash rate content (%) and P_0 and P_1 (g) are the weight of the filled crucible before and after carbonization, respectively.

2.4.3 Iodine Value

The iodine index (iodine number) is a microspore content measure of an adsorbent material. The iodine number is an indicator of the porosity of an activated carbon [18,19] [8,9].

The iodine adsorption capacity of AC material was determined according to the following procedure: 10 ml of a 0.01 N iodine solution was titrated with a 0.1 N sodium thiosulfate solution, with a few drops of a starch solution as an indicator, until the color disappeared. In the second step, 0.05 g of activated carbon was added to 15 mL of a 0.1 N iodine solution with 5 min of stirring. Then, the obtained iodine solution was filtered and titrated with 0.1 N sodium thiosulfate solution with two drops of starch solution. The iodine value (*Id*) was calculated using Equation 3, as follows:

$$\mathrm{Id} = \frac{(V_b - V_s) \cdot N \cdot 126.9 \cdot 15/10}{M} \qquad \text{(Equation 3)}$$

Where (V_b-V_S) in mL is the difference between the required volumes of sodium thiosulfate for the blank (V_b) and the sample (V_s), *N* is the normality of the sodium thiosulfate solution in (mol/L), *126.9* g/mol is the atomic mass of iodine and *M* (g) is the mass of the AC adsorbent.

2.5. THE POINT OF ZERO CHARGE (PH_{PZC})

The point of zero charge (pH_{PZC}), the pH at which the adsorbent is neutral in aqueous suspension, was determined following the procedure of Altenor et al. [20]. In this method, 50 mL of 0.01M NaCl solution was placed in closed erlenmeyer flasks at room temperature. Then, the pH of the solutions was modified to values from 2 and 12 by adding 0.1M HCl or 0.1M NaOH solutions. These pHs were mentioned as the initial pH ($pH_{initial}$). Finally, 0.1g of solid adsorbent (AC) was added to each flask and the final pH (pH_{final}) was measured after 24 h. The pH_{final} was plotted against the $pH_{initial}$ and the pH_{PZC} is the point where the curve pHfinal versus pHinitial intersects the first bisector.

2.6. ADSORPTION EXPERIMENTAL PROCEDURE

Adsorption experiments were carried out by varying the time of the solution, adsorbent mass and pH of the solution at ambient temperature by magnetic agitation. For each experiment, 100 mL of OMW was treated using the prepared activated carbon. After stirring, the solution was filtered and the filtrate was analyzed to obtain the residual chemical oxygen demand (COD). The removal yield (% Y) was calculated using the following expressions:

$$Y(\%) = \frac{COD_0 - COD_e}{COD_0} \times 100 \qquad \text{(Equation 4)}$$

Where COD_0 is the initial chemical oxygen demand (134.3 gO_2/L) and COD_e (gO_2/L) is the equilibrium chemical oxygen demand [21-23].

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF ADSORBENT

The results of the moisture content, ash content and iodine value of the prepared activated carbon are shown in Table 1. The low ash content (0.05%) implies that the activated carbon essentially consists of organic matter, therefore of the carbon element [24]. The prepared activated carbon also has a low moisture content (0.0022%), which highlights a low water content conservation. For the iodine value, the prepared activated carbon gives a high iodine value 959.33 mg/g that clearly illustrates the microporosity of an activated carbon.

Table I - Activated Carbon Properties

Characteristics	Value
Moisture content	0.05 %
Ash content	0.0022%
Iodine value	959.33 mg/g

3.2. ADSORPTION STUDIES

3.2.1 Effect of contact time

This study was carried out in order to determine the fixed quantities of the pollutant since its contact until a time t, in order to know the equilibrium time. For this, a solution for 100mL, with an initial chemical oxygen demand (134.3 gO_2/L) of OMW, was put in contact with a mass of activated carbon (1 g) at the pH of the solution (pH 4.5). The mixture obtained was immediately agitated at different contact times varying from 60 to 300 minutes.

Figure 1 shows the time effect of adsorption on activated carbon. The adsorption yields (%) of COD from olive oil mill wastewater increase exponentially with time, reaching their maximum value after 120 minutes. Beyond that comes the state of adsorption equilibrium. It thus becomes clear that activated carbon has an adsorption capacity (28.66%) of the initial COD of OMW.

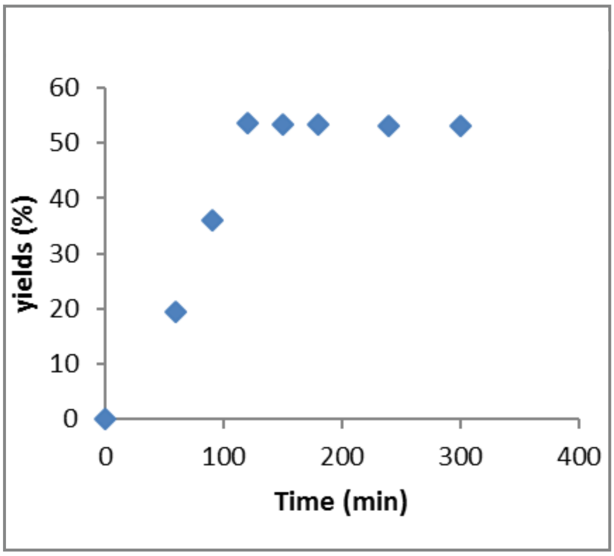

Figure 1 – Effect of time on adsorption

3.2.2 Effect of AC mass on adsorption

In this set of experiments, different masses of the AC adsorbent chosen from 0.5 to 5 g were treated with 100 mL solution of initial COD of OMW at the optimum time obtained from the effect of contact time experiments (120 minutes). Figure 2 shows the percentage of adsorption as a function of the AC adsorbent mass. In all cases, the percentage yields of this pollutant removal increases when the mass of the AC adsorbent increases until total saturation. This is due to the presence of large numbers of active sites on the surface [25]. The curve in Figure 2 shows that 3 g of carbon mass can adsorbate a maximum of COD (53.66%) from OMW. In the next step, the optimal AC mass of 3 g will be taken to study the pH effect on adsorption from OMW.

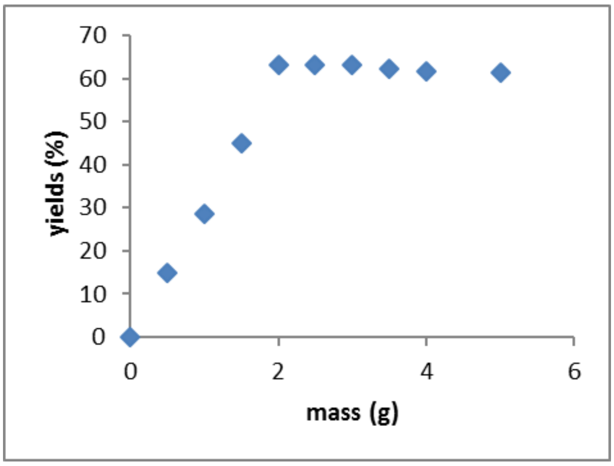

Figure 2 – AC mass effect on adsorption

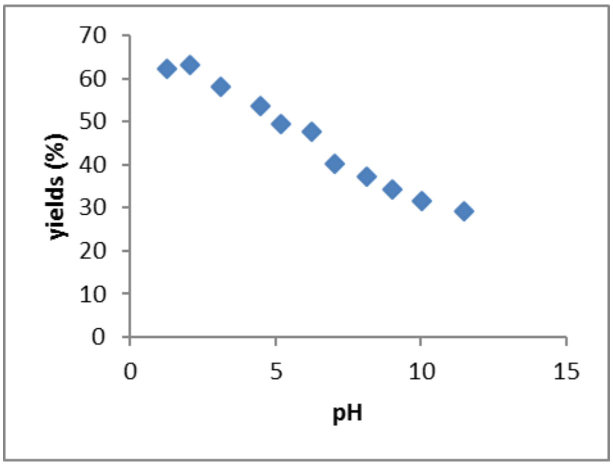

Figure 3 – Effect of pH on adsorption

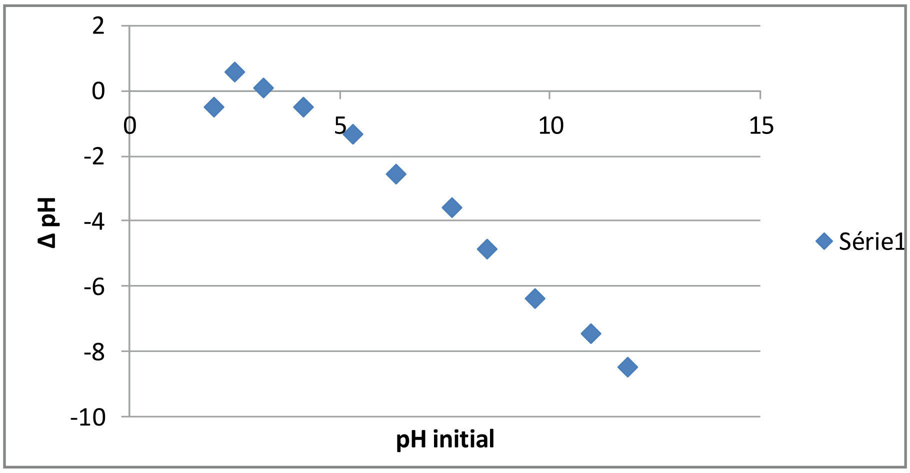

Figure 4 – The pH point of zero charge (pHpzc)

3.2.3 Effect of pH on adsorption

The pH of the solution has a very significant role in the adsorption process [26]. The pH of the OMW solution was chosen between 1.25 and 11.5 and a contact time was fixed from previous results at 120 min. The obtained results (Figure 3) show a considerable influence of the pH value on the adsorption by the activated carbon: the adsorption yields decrease with the increase of the pH values. The lower adsorption yields in an alkaline medium can be explained by an excess of OH ions in the solution, which leads to competition with this effluent on the adsorption sites of the activated carbon. Indeed, the high concentration and high mobility of OH ions would promote their adsorption relative to the pollutant [27]. The optimum pH allowing maximum adsorption of OMW on activated carbon (Y% = 63.33) is pH 2.05 under the study conditions.

3.2.4 The point of zero charge (pHpzc)

The pH_{pzc} is an important parameter based on determining the pH sensitivity range and allows for the prediction of the active surface area and adsorption capacities [28]. The pHpzc value of AC found was 3.2 (Figure 4).

This pH shows that at pH values below this value, the activated carbon surface is positively charged, which promotes attractive electrostatic interactions and improves adsorption. This result confirms the best adsorption yield (Y% = 63.33) obtained at pH 2.05 during the previous session (session 3.2.3).

4. CONCLUSIONS

The discharge of olive oil mill wastewater from olive oil-producing industries is a major problem, especially for countries in the Mediterranean basin. They contain a large organic fraction and cause several types of pollution.

In this study, activated carbon was successfully used for the elimination of the organic fraction from olive oil mill wastewater. The activated carbon was prepared from olive pits using carbonization and a chemical activation process. The material was characterized using different techniques: ash content, moisture content and iodine value. Under the operating conditions, the results of adsorption on activated carbon show that the prepared AC can adsorb close to 63.33% of

pollutant using 3 g and 100 mL volume of solution at 120 min and pH 2.05.
The obtained results indicate the possibility of valorization of olive pits in the form of activated carbon, which could have significant socio-economic impacts.

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