Integrated approach in treatment of solid olive residue and olive wastewater

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Abstract

Generally olive oil generated two forms of waste by-products: solid olive residue (SOR) and olive wastewater (OWW). In the present study a promising solution is given to treat both SOR and OWW by-products. The first process consists of converting the solid olive residue to activated carbon using pyrolysis process at 600 °C, followed by steam activation procedure at three different temperatures. The attained activated carbon was examined by different experimental techniques such as FTIR, SEM, BET and iodine number. The surface area was increased by increasing stream activation temperature (reach 1020 m² g⁻¹ BET). However, the steam activation at 700 °C was found to be ideal for environmental and economic performance. On the other hand, the activated carbon at 700 °C displayed high removal capacity of both polyphenolic compounds and COD from olive wastewater. In fact, after 2 h of treatment, 95.5% of COD and 84.2% of polyphenolic compounds were completely removed.

1. Introduction

As the worldwide consumption of olive oil increased, due to its health and medical welfares, the environmental pollution caused by olive mill wastes is also increased [1]. Olive oil production in small scale is a tradition in Mediterranean and Middle East countries. Now a days, there are three olive oil production processes: the old traditional press method, the two-phase method, and the three-phase method. All these methods produced mainly two types of waste by-products: the solid residue and the aqueous remaining named as olive-mill wastewater [2–4]. Olive oil has numerous bioactive polyphenolic compounds with antioxidant properties. Because of the hydrophilic nature of these polyphenolic compounds, most of them remain in wastewater during olive oil production. However, the generated wastewater has larger and harmful environmental effect on plants and microorganisms. It has large amounts of phenolic compounds, causing the extreme chemical oxygen demand (COD) [5]. It is a challenging task to find an economically practicable solution to handle simultaneously both solid and liquid wastes. Any safe disposal solution for the olive oil wastes must consider the fact that olive farms and mills are small and scattered in a large geographical area in most countries. Another economical problem facing the safe disposal of olive oil production waste, which is the seasonal production in nearly two months per year. Thus, a small-scale units, easily operated machines or mobile units are immediately required to surmount these obstacles. The worldwide needs for activated carbon was growing, because its important applications in water purification [6]. Activated carbon was considered as a versatile adsorbent with numerous domestic and industrial applications [7]. In general, it was used as adsorbent to remove organic materials from liquids and gases [8–10]. Thus, it is used mainly in water and air purification from pollutants [11].
The water treatment and food processing facilities consume vast amounts of activated carbon to remove unwanted organic compounds that affect taste, odour, and colour [12–14]. The main activated carbon raw materials are found in generally on coconut shells or woods [15, 16]. However, many efforts were made in countries with shortage in such raw materials, to produce activated carbon [17–20]. Moreover, solid olive residue as high carbon materials can be considered as a potential raw material to produce activated carbon materials. The production process of activated carbon follows two steps; carbonization and activation process [6]. The carbonization step aims to remove moisture and volatile components from the biomass. The activation step aims to increase the surface area and opening the pores with either chemical treatments or steam gasification [21–23]. Steam activation process was considered as environmental save and economical method [24], alongside its simplicity [25, 26]. The main advantage of steam activation is avoiding the use of chemical agent which needs to be removed by washing after activation process [27]. Furthermore, the washing step may lead to environmental contamination and the produced activated carbon needs additional drying process with more energy consumption.

The objective of current research is the development of integrated method for treatment of both solid olive residue and wastewater produced from olive oil mill. This integrated method is expected to have great environmental suitability and economic feasibility, mainly for small olive farms and mills scattered around large geographical area in Saudi Arabia. The solid olive residue will be converted to activated carbon and will be used in purification of wastewater produced from olive oil mills.

### 2. Materials and methods

#### 2.1. Materials

Solid olive residue (SOR) and olive wastewater (OWW) was obtained from oil production mill in KSA. The main physicochemical characteristics of the olive residue are summarized in table 1.

| Characteristics | %   |
|-----------------|-----|
| Moisture        | 16.2|
| Ash             | 4.5 |
| Volatiles       | 58.3|
| Fixed carbon    | 21.0|

Table 1. Solid olive residue (SOR) characteristics.

OWW chemical characteristics are summarized in table 2. OWW sample was acidic (pH = 4.01) blackish liquid with 2.13 mS cm\(^{-1}\) conductivity and very high COD (15.3 gO\(_2\)/L) level. The polyphenolic compounds content was found to be 1.03 g L\(^{-1}\).

| Characteristics         | %   |
|-------------------------|-----|
| Color                   | black |
| pH                      | 4.01 |
| Conductivity (mS/cm)    | 2.13 |
| COD (gO\(_2\)/L)        | 15.3 |
| Polyphenols contents (g/L) | 1.03 |

Table 2. Olive wastewater (OWW) characteristics.

The morphology and textural behaviour of the material was investigated using JEOL Scanning Electron Microscopy (SEM) instrument working at 100 kV. FTIR measurements were carried out using Perkin Elmer Frontier spectrometer. The thermal analysis was investigated via SETSYS Evolution-1750 SETARAM instrument. The thermal stability of the materials was characterized by thermo analytical DTA coupled with a thermo gravimetric analysis (SETSYS Evolution1750 SETARAM).
2.3. Carbonization
2 kg of solid olive residue was dried at 105 °C for 48 h in laboratory dryer. 300 g batch of the dried olive press residue was carbonization in a fixed-bed alumina tube reactor (figure 1). The alumina tube reactor was fixed in a tube furnace (CLF-T1320, CERINHITEC) that enables to control temperature up to 1000 °C. The temperature is gradually raised up to 600 °C with slow nitrogen flow with a heating rate of 10 °C min⁻¹. Nitrogen gas is continuously injected at a rate of 100 ml min⁻¹. The carbonization process was continued at this temperature for 3 h.

2.4. Steam activation
The activation of carbonized olive press residue was carried out by steam activation process. The steam generator, a stainless-steel pipe of 17.5 mm and 350 mm in diameter and length respectively, has a heating stick inserted whose temperature can be internally kept up to 250 °C. The amount of steam was controlled with the syringe pump (KDS 100, KDS scientific, USA). The porosity and the pore diameters were found to be increased after the steam activation process. On the other hand, the steam activation process was carried out in the same alumina tube reactor in 50 g batch. Slow flow of steam was introduced to the reactor, then the temperature was gradually raised to 600, 700 or 800 °C for one hour. Finally, the temperature was gradually decreased to 300 °C then steam flow was stopped and the reactor was cooled to normal temperature. We have modified the steam activation temperature from 600 to 800 °C to try to produce activated carbon with the best low cost, and effective environmental economically steam activation temperature and essentially with high surface area. However, at 600 °C the activated carbon exhibited low surface area. To increase surface area, we resorted to increase the steam activation temperature. This is because the increase of steam temperature can increased the density of micropores because steam removes carbon atoms from within the solid carbon network, resulting in the creation of new pores and opening of clogged ones.

2.5. Iodine number determination
The iodine adsorption capacity, which is called the iodine number (mgI₂/g), is directly correlated to the specific surface area and the generated active sites. The iodine number was determined by titrimetric method (ASTM D 4607-94). Briefly, the iodine number was determined by measuring the adsorbed iodine from aqueous 0.02 N iodine solution. The free iodine was determined by titration with standard Na₂S₂O₃ solution.

2.6. Sorption of polyphenols and reduction in COD
The sorption of polyphenolic compounds and reduction of COD with activated carbon were carried out in batch mode. 50 ml of OWW was established in equilibrium with 1.0 g of activated carbon for 2 h under magnetic stirring. The Polyphenols sorption and Chemical oxygen demand (COD) change was investigated at acidic conditions (pH = 3.8–4.0). After equilibrium, the activated carbon was filtered, and the free phenols and COD were calculated using this equation:

\[
\%R(COD) = \left( C_0 - C_t \right) \times 100 \div C_0
\]

where \( C_0 \) and \( C_t \) are the initial and equilibrium concentrations of COD, respectively. The chemical oxygen demand (COD) was determined according to ASTM D1252 [28]. The total phenols content in OWW was calculated using Folin–Ciocalteu method with gallic acid as standard substance [29]. Briefly, 0.5 ml of Folin–Ciocalteau solution was mixed with 5.0 ml of OWW sample or standard gallic acid solution. The mixture was mixed by shaking for 5 min, then 1.0 ml of sodium carbonate solution (15%) was added. The solution was reserved on the dark for 1 h under magnetic stirring. The absorbance was measured at 765 nm. The amount of
reduction of phenols was calculated as follows:

$$\% Rph = \frac{(C_0 - C_t)}{C_0} \times 100$$

where $C_0$ and $C_t$ are the initial and equilibrium concentrations of phenols, respectively.

### 3. Results and discussion

#### 3.1. Thermal analysis of solid olive residue

The thermal and chemical change induced in SOR raw material was investigated by thermogravimetric analysis technique. Figure 2 shows the thermogram of SOR raw material collected between 25 and 1000 °C. The TGA curve showed a minor weight loss in the interval ranging from 25 to 230 °C. The first weight loss was ascribed to residual adsorbed water molecules. In the interval from 230 °C to 350 °C, a sharp weight loss was detected and ascribed to the degradation of lignocellulose [30]. The final sharp weight loss occurred between 460 °C and 575 °C can be attributed to thermal degradation of cellulose and lignin [31]. After 575 °C, no measurable weight loss can be detected. The remaining mass was found to be around of 21.0%.

#### 3.2. Carbonization and steam activation

Figure 3 shows pictures of dried solid olive residue (SOR), carbonized SOR (carb SOR) and steam activate carbon produced at 700 °C. Table 3 displays the physical properties of carbonized solid olive residue (carb SOR) at different steam activated temperatures (AC600, AC700 and AC800). It was clearly observed that increasing the
steam activated temperatures induced an increase in both the surface area and iodine number. The carbonization of solid olive residue (carb SOR) at different steam activated temperatures (600, 700, and 800 °C) had a significant effect on the efficiency of carbonization process. The activation of carbonization was found to be the most important stage in the production process of activated carbon (AC), since this step improved porosity and specific surface area, as well as the iodine adsorption number of the product. The pores size would affect the porosity, the total surface area, and most notably, it determined the size of molecules that could diffuse into the pores of solid. Thus, development of a fitting pore structure was necessary if the activated carbon was created for a specific use [31]. The iodine number of the carbonized SOR without activation was found to be 219 mg I$_2$ g$^{-1}$. The iodine number was increased after steam activation at 600 °C to 376 mg I$_2$ g$^{-1}$. On the other hand, by increasing the steam activation temperatures from 700 to 800 °C, the iodine number also increased from 539 and 558 mg I$_2$ g$^{-1}$, respectively. As shown in figures 4(a) and (b), when the iodine number increased, the BET surface area also increased. However, the enhancement is noteworthy observed only up to 700 °C, while increasing the activation temperature to 800 °C, no significant effect is remarkable on both the surface area and iodine number. Therefore, the steam activation of 700 °C can be considered as the ideal low cost, environmental and economically effective steam activation temperature. It was also pointed out that at 800 °C activation, the sample possessed the largest adsorption capacity, clearly indicating that the porosity mostly increased under this activation condition. Comparatively, as the activation temperature was lower than 800 °C, the sample was only partially activated. However, this result was observed by other researchers [32, 33], leading to undeveloped porosity and hence lower surface area. Thus, the gradually improved reaction between steam and carbon resulted in more developed pore structures.

The steam activation process can generate carbon oxides and hydrogen compounds. However, the main physical effect of this thermal reaction is the removal of carbon atoms from carbon matrix resulting of significant
weight loss and high pore volume and diameters. Figure 5 shows the weight loss of carbonized SOR at different steam activation temperatures. The yield of activated carbon in this thermal process is related to the recuperated mass after activation. The obtained yield was 85.7%, 71.9% and 66.8% for activation temperatures 600 °C, 700 °C and 800 °C, respectively. The decrease in yield from 71.9% to 66.8% by increasing the temperature from 700 to 800 °C is another reason for selecting 700 °C as the ideal steam activation temperature.

### 3.3. ATR-FTIR spectra

The ATR-FTIR spectra of dried solid olive residue (SOR), carbonized SOR and steam activated carbon at 700 °C are given in figure 6. The FTIR spectra demonstrated the different functional groups presented in SOR and revealed the change in chemical change after carbonization and activation processes. On the other hand, the dried solid olive residue indicated a broad band at 3300–3600 cm⁻¹, which can be attributed to the adsorbed water molecules and to the stretching vibrations of O–H groups of organic biomass (such as cellulose, hemicellulose and lignin) [32]. The observed broad band was completely disappeared in the FTIR spectra of carbonized SOR and steam activated carbon. Furthermore, the two bands appeared at 2924 cm⁻¹ and 1853 cm⁻¹ were ascribed to asymmetric C–H vibrations of methylene groups presented in cellulose and lignocellulosic backbone [33]. The same phenomena was observed, these two bands are completely disappeared after carbonization and activation (carb SOR and AC700). The detected peaks at 1735 and 1688 cm⁻¹ were ascribed to asymmetric C=O and –C=O–N stretching vibration of ester amides groups, respectively. The observed peak at 1461 cm⁻¹ was assigned to the stretching vibration of –CH₃ in the carbon aliphatic backbone [34]. Furthermore, the two peaks at 1049 cm⁻¹ and 1033 cm⁻¹ were assigned to the presence of carbon-oxygen (C–O) bond in the raw SOR as well as in carbonized (carb SOR) [35].

### 3.4. Scanning electron microscopy

The microstructure of carbonized SOR and those activated at 700 °C are shown in figures 7(a) and (b), respectively. The carbonized SOR shows a small number of micropores with very thick smooth walls. Steam activation at 700 °C increased the number of small pores and thinning the pore walls (figure 7(b)). The pores and cavities aggregated to from a honeycomb-like morphology. The change in the pore structure can be attributed to the activation process and agree well with iodine number and BET measurements.

![Figure 5. Effect of steam activation temperature on the weight loss (%).](image)

**Table 3. Carbonized and activated solid olive residue (SOR) properties.**

| Materials   | BET surface area (m²/g) | Iodine numbers (mg I₂/g) |
|-------------|-------------------------|--------------------------|
| Carbo SOR   | 172                     | 219 (± 13)               |
| AC600       | 540                     | 376 (± 12)               |
| AC700       | 979                     | 539 (± 14)               |
| AC800       | 1020                    | 558 (± 15)               |
3.5. Adsorption of polyphenolic compounds and COD
A liquid sample of olive wastewater (OWW) from the same mill was filtered and kept in the dark at 4 °C for batch experimental adsorption study. Chemical oxygen demand (COD), pH, conductivity and total phenols were carried out. The initial polyphenolic compounds and COD of filtered OWW was found to be 15.3 gO₂ l⁻¹ and 1.03 g l⁻¹, respectively at pH equal to 4.01. The adsorption experiments were carried out in batch mode in triplicate. 50 ml of OWW was putted in equilibrium with 1.0 g of activated carbon for 2 h with gentle stirring. The Polyphenols sorption and Chemical oxygen demand (COD) change were investigated at acidic conditions (pH = 3.8–4.0). A promising result was noticed after equilibrium with activated carbon (AC700) for 2 h at room temperature. In fact, 95.5% of COD and 84.2% of polyphenolic compounds were completely removed from OWW.

Figure 6. ATR-FTIR spectra of SOR, carb SOR and steam activated carbon at 700 °C.

Figure 7. SEM Images of: (a) carbonized SOR at 600 °C and (b) steam activated SOR at 700 °C.
4. Conclusions

Activated carbon based solid olive residue was generated via steam activation process. The activated carbon was used for olive wastewater treatment. As the steam activation temperature increased from 600 to 800 °C, the surface area, iodine number as well as the weight loss improved. Activated carbon steam cured at 700 °C exhibited high removal capacity of both polyphenolic compounds and COD of OWW. The proposed recycling process was established in this study. On the other hand, designing a simple and small reactor for scale up the steam activation process for pilot-scale production is in progress.

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Data availability statement

No new data were created or analysed in this study.

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