



Removal of phenolic compounds from olive oil mill wastewater using kaolinite and iron oxide nanoparticles

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ABSTRACT

In this study, effective, inexpensive, sustainable, and environmentally friendly adsorbents composed of iron oxide nanoparticles immobilized on kaolinite were used to remove phenolic compounds from olive mill wastewater (OMW) in Jordan. Two phenolic compounds (tyrosol and p-hydroxybenzoic acid) were selected as models for phenols present in OMW. The best adsorbent was acid-activated kaolinite mixed with iron oxide nanoparticles with a ratio of 1:20. This mixture gave removal efficiencies up to 81.8% and 97.3% for tyrosol and p-hydroxybenzoic acid, respectively. Investigation of adsorption at different conditions showed that the best adsorption was at pH of 3, a temperature of 25°C, an adsorbent dose of 2.5 g/100 mL OMW, and the equilibrium was established after 3 h. Also, a new efficient high-performance liquid chromatography (HPLC-UV) method was developed for the determination of the target phenolic compounds in OMW. The new method showed satisfactory validation results in terms of linearity, precision, recovery, the limit of detection and limit of quantitation.

Keywords: Wastewater treatment; Adsorption; High-performance liquid chromatography; Kaolinite; Olive mill wastewater; Phenols; Nanoparticles

1. Introduction

The olive milling industry is an important pillar in Jordan's economy, as olive oil contributes to approximately 100 million JD of the national income [1]. The production of olive oil leads to the production of a large amount of wastewater known as olive mill wastewater (OMW). From about 130 olive mills distributed all over the Kingdom of Jordan, it is estimated that there is a production of 200,000 m³ of OMW annually [2]. The annual production of OMW worldwide is estimated from 10 to over 30 million m³ [3]. Those huge amounts of wastewater present a challenge in its disposal. OMW is characterized by its high loads of organic compounds which prevent the possibility of its direct use in irrigation [4].

Jordan, as a country suffering from water scarcity, needs to pay great attention to the issue of OMW treatment in order to cover some water needs, especially in the agricultural field. However, the treatment of OMW is extremely challenging due to its large volume and its high content of organic matter.

Phenolic compounds (PC) are the main cause of environmental problems associated with OMW. These compounds are found in high concentrations in OMW ranging from 0.5–25 g/L [4]. PC is hard to decompose, and they resist biological degradation [5]. Besides, they are thought to inhibit the plant growth of different vegetables [6]. Moreover, a bad odor is noticed when OMW encounters chlorinated waters due to the formation of chlorinated phenols resulted from the interaction between PC and chlorine [7]. Among the PC that could be found in OMW are tyrosol and p-hydroxybenzoic acid. These two compounds were proved to be toxic for different plant seeds as well as many organisms [8].

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Adsorption is a common method that has been successfully used to remove phenolic compounds from wastewater. However, commercially available adsorbents are relatively expensive, and they require costly regeneration technologies [9]. Therefore, the search for economically better alternatives is under continuous development.

Kaolinite is an abundant clay mineral in the Jordanian environment, readily available in large quantities and at a low cost. Kaolinite has been proven to be an effective adsorbent for removing organic pollutants from wastewater through the interaction of its hydroxyl group with the polar groups in the pollutants [10].

On the other hand, iron oxide nanoparticles showed excellent adsorption property due to their capability of electrostatic interaction, high surface area, porosity structure as well as strong magnetic properties which foster the magnetic recovery step [11].

Incorporating clay and iron oxide nanoparticle together could give an adsorbent with distinctive features of high surface area, high chemical, and mechanical stability, and strong magnetic response [12].

Attempts to remove the phenolic compound from OMW have been studied by several groups using different methods [9,13]. However, most studies have focused on removing the total phenolic content without paying attention to removing each compound individually [4,14,15]. Moreover, no study, to our knowledge, has included the use of kaolinite or iron oxide nanoparticles in the treatment of OMW.

In this study, adsorbents based on kaolinite and iron oxide nanoparticles were prepared and used to remove two PC (tyrosol and p-hydroxybenzoic acid) from OMW from an olive mill in Jordan. We chose these two compounds because tyrosol is one of the most abundant compounds in the OMW [16]. p-Hydroxybenzoic acid is also always detected in the effluent of olive mills. This compound is characterized by its high toxicity and high resistance to biological degradation [17]. The adsorbents were prepared using different proportions of kaolinite and iron oxide nanoparticles, and then its effectiveness in removing PC was tested. We also studied the various factors that affect the efficiency of removal to find the optimal conditions that achieve the best removal. Moreover, a new high-performance liquid chromatography (HPLC-UV) method was developed and validated for the determination of the target PC in OMW.

2. Material and methods

2.1. Materials

Kaolinite supplied by Natural Resources Authority in Jordan from Al Disis area. The chemical composition was studied previously by Awwad et al. [18] and it was found to contain: SiO₂, 59.18%; Al₂O₃, 26.22%; Fe₂O₃, 1.52%; TiO₂, 1.42%; CaO, 0.11%; Na₂O 0.11%; K₂O 1.12%; P₂O₅ 0.11%; Limit of linearity 10.21% (wt.%). Cation exchange capacity is about 3.83 cmol (+)/Kg [19]. Iron oxide nanoparticles (Sigma-Aldrich, 99% (Manufacturer Location is Germany)), (particle size < 50 nm). Standards of tyrosol (98%), p-hydroxybenzoic acid (99%), and 3-methoxyacetophenone as internal standard (I.S.) were purchased from Sigma-Aldrich (Manufacturer Location is Germany). All the solvents used in this study were HPLC grade;

acetonitrile (Fisher) HPLC grade 99.9% UK; methanol Sigma-Aldrich HPLC grade ≥99.8% (Manufacturer Location is Germany); hexane Tedia HPLC grade 99% (Manufacturer Location is USA); ethyl acetate Sigma-Aldrich HPLC grade 99.8% (Manufacturer Location is Germany).

2.2. Sampling

The samples were collected from Al-Manaseer olive mill which is located in south Amman in Jordan. Sampling was done during October and November 2018. The selected olive mill applies a 3-phase centrifugation process to produce the olive oil. Samples were collected from the effluent of the olive mill; each sample was 20 L in volume. The collected samples were opaque and dark brown-red in color and turbid. We stored the samples at 4°C in a sealed plastic container.

2.3. HPLC-UV chromatographic conditions for quantitative analysis of phenolic compounds

HPLC method was developed and optimized for the determination of PC in OMW. Chromatographic analysis was carried using a Shimadzu HPLC system equipped with a UV-Visible detector. PC were separated on a C18 column (4.6 mm × 250 mm, 5 μm) which was controlled at 30°C using a temperature-controlled column compartment. The mobile phase consisted of distilled water, 2.5% acetic acid (solvent A), and (acetonitrile/methanol) 1.2:1 v/v% (solvent B). The system was run with the following gradient elution program: 0.1–1 min, 95% A; 0.1–26 min, 70% A; 26–40 min, 65% A. The flow rate was 0.5 mL/min, and the injection volume was 20.00 μL for UV detection at 280 and 340 nm.

Calculation of the amount of each compound was done using the multi-point calibration method in which the response applied for the analyte was its relative peak area (RPA); (RPA = area of the peak of analyte/area of the peak of I.S.).

2.4. Extraction of phenolic compounds

Extraction of PC from OMW has been accomplished following Alfarawati et al. [20] method with slight modifications. A 20.0 mL of OMW sample was mixed with 30.00 mL hexane and centrifuged for 5 min at 2,000 rpm, then the hexane layer was decanted and the OMW was moved to a separatory funnel and extracted with 30.00 mL hexane to remove the lipid layer. After that, the OMW was acidified with concentrated HCl solution to pH = 2 to ensure that the PC are in their protonated form. The OMW was then extracted 4 times with 30.00 mL ethyl acetate. Finally, the ethyl acetate extract was collected and left to dry in the fume hood. The extract was reconstituted in 20.00 mL of a mixture of A and B mobile phase and 20 μL was injected into the HPLC system.

2.5. Validation of HPLC-UV method for determination of PC in OMW

The method was validated following the Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater under EPA's Alternate Test Procedure Program [21].

The validation process was performed for the developed HPLC-UV method. The following parameters of quality were studied: linearity, precision, recovery, detection limit LOD, and the limit of quantitation LOQ.

Standard mixture solutions with concentrations of (10, 20, 30, 40 and 50 mg/L) of the target PC (TY and HB) and 50 mg/L 3-methoxyacetophenone (I.S.) were used to establish the calibration curve for each targeted phenolic compound.

The instrument's LOD and LOQ were obtained by injecting a clean blank solution containing IS into the HPLC seven times, then the values were calculated according to Eqs. (1) and (2):

$$\text{LOD} = \frac{3S_b}{m} \quad (1)$$

$$\text{LOQ} = \frac{10S_b}{m} \quad (2)$$

where S_b : standard deviation of blank; m : the slope of each target analyte.

Three samples, each 20.0 mL of OMW were spiked with the standard mixture of phenolic compounds to give the concentrations 50, 75, and 100 mg/L. These samples were extracted, cleaned up, and analyzed according to the procedure method described in section 2.4. The percentage recoveries were calculated using Eq. (3). The recovery tests have been done in triplicate at different times and the average was calculated.

$$\text{Recovery\%} = \frac{\left(\frac{\text{spiked sample concentration} - \text{non spiked sample concentration}}{\text{spiked concentration}} \right) \times 100}{1} \quad (3)$$

The precision of the instrument was measured through the injection of each standard solution (35, 75, and 120 mg/L) three times.

2.6. Activation of kaolinite

Kaolinite was activated with acid by placing 10 g of kaolinite in 100 mL of 0.25 M solution of HCl for 24 h in an orbital shaker at 150 rpm and 25°C. The activated kaolinite was washed with distilled water until the litmus test showed it is not acidic anymore and then it was dried in the oven for 24 h at 120°C and it was labeled acid-activated kaolinite (AC kaolinite). For base activation, the same procedure was followed, replacing the acid with 0.25 M NaOH, and it was labeled base activated kaolinite (BA kaolinite). This activation followed the procedure of Kumar et al. [22] with slight modification.

2.7. Preparation of adsorbent removal efficiency of phenolic compounds for different adsorbents

Nine adsorbents were tested for their efficiency in removing PC from OMW, namely: iron oxide nanoparticles; kaolinite; AC kaolinite; BA kaolinite; a mixture of AC kaolinite and iron oxide nanoparticles with 10:1 ratio; a mixture of AC kaolinite and iron oxide nanoparticles with 20:1 ratio; iron oxide nanoparticles sintered in AC kaolinite with 5:1

ratio; iron oxide nanoparticles sintered in AC kaolinite with 10:1 ratio; iron oxide nanoparticles sintered in AC kaolinite with 20:1 ratio.

2.8. Preparation of nanoparticles sintered in acid activated kaolinite

Sintering is a process in which powdered solid particles are compacted under appropriate conditions heat and pressure [23]. For sintering of iron oxide nanoparticles on AC kaolinite, we followed the method used by Ulucan et al. [24], with some modifications. We started by milling the AC kaolinite and mixing it with the iron oxide nanoparticles in different ratios; 5:1, 10:1, and 20:1. Then, a drop of distilled water was added, and the mixture was pressed into a uniform disk. After that, the disk was sintered in a muffle furnace at 500°C for 1 h. Later, it was characterized using a Fourier-transform infrared (FTIR) spectrometer (Bruker VERTEX 70v, Manufacturer Location is Germany).

2.8.1. Determining the removal efficiency of PC from OMW

To study the removal efficiency of the different adsorbents, 20.0 mL of OMW was filtered. Then, it was mixed with 0.5 g of each adsorbent at pH 3 and a temperature 25°C. The adsorption allowed to take place for 24 h under agitation using an orbital shaker (Kuhner, Switzerland) at 150 rpm. After that, the adsorbent was removed by filtration (or by a magnet in case of sintered adsorbents), the aqueous sample was extracted as described in section 2.4 and left to dryness. The dry extract was dissolved in 150.0 mL of the mobile phase containing I.S. and passed through a 25 µm syringe filter. Finally, 20 µL was injected into HPLC to determine the concentration of the PC.

2.8.2. Effect of different factors on the removal efficiency of PC from OMW

After selecting the optimum adsorbent, we investigated the effect of different parameters on the adsorption efficiency of PC. First, we studied the effect of adsorbent dose by mixing variable masses of the adsorbent (from 0.3 g to 0.9 g) with 20.0 mL of OMW sample at pH = 3 and temperature 25°C for 24 h. Secondly, the effect of the initial pH of the OMW on the removal efficiency of phenolic compounds was studied at four pH values: 3, 5, 7, and 9. The initial dose of the adsorbent was kept 0.5 g in 20 mL of OMW for all the measurements and the temperature was 25°C for 24 h. The pH was adjusted using 0.1 M of HCl or NaOH. Thirdly, the effect of temperature on the removal efficiency was studied by treating 20.0 mL of OMW at pH = 3 with 0.5 g of the adsorbent at five temperatures (20°C, 22.5°C, 25°C, 30°C, and 40°C), for 24 h. Finally, the effect of contact time was studied by mixing a 20.0 mL of OMW at pH 3 with an 0.5 g of the adsorbent and it was agitated at 25°C, 3.0 mL increments of the sample were taken at different times 1, 2, 3, 4, 6, 8, 10, 16, and 24 h. After the adsorption took place in all the experiments, the adsorbent was filtered, phenolic compounds were extracted from the filtrate as described in section 2.3.2 and left to dry, then dissolved in 20 mL mobile phase containing the I.S. and analyzed by HPLC.

3. Results and discussion

3.1. Validation of HPLC-UV method for determination of PC in OMW

3.1.1. Calibration, linearity, LOD and LOQ

Table 1 shows the equation of the calibration curve obtained for each compound and the regression coefficients (R^2), that confirm the linearity of the selected range. Table 1 also shows the LOD and LOQ of each PC with their retention times and peak numbers.

3.1.2. Precision and recovery

The developed method showed good precision as indicated by the values of the relative standard deviation RSD% (as shown in Table 2) which lies within the acceptable range for trace analyses related to HPLC/UV-Visible instrument (RSD% \leq 15%) according to González and Herrador [25].

The mean recovery of each PC at three concentration levels are presented in Table 2. It can be noticed that all values fall within the permissible range for trace analyses which are 70%–120% [25]. The recoveries obtained in this study are comparable to those obtained from previous studies as indicated in Table 2 89.5% [16], 95% [26].

3.2. Characterization of OMW

OMW samples were prepared three times and each extract was injected into the HPLC system to determine the concentration of each PC. Fig. 1 shows a sample chromatogram for the PC in the effluent OMW from Al-Manaseer olive mill. Table 3 shows the mean level of the tested PC in OMW samples in addition to other characteristics of this wastewater. By comparing the tested PC concentrations

with the concentrations obtained in the previous studies [9,28], we notice a difference in the values due to the difference in the water characteristics of the samples of those studies in terms of chemical oxygen demand (COD) of the samples and the variation in the phenolic content among olive species.

3.3. Removal efficiency

3.3.1. Removal efficiency of phenolic compounds using different adsorbents

The removal efficiency is calculated using Eq. (4):

$$\text{Removal efficiency \%} = \frac{C_i - C_f}{C_i} \times 100 \quad (4)$$

where C_i is the initial concentration of the PC in the raw wastewater and C_f is the final concentration of the PC after treatment [29]. Results of the removal efficiency of tyrosol and p-hydroxybenzoic acid after treatment with different types of adsorbents are shown in Table 4.

The results showed that the best adsorbent for the removal of phenolic compounds is acid-activated kaolinite mixed with iron oxide nanoparticles in a 20:1 ratio. Our results indicated an increase in the removal efficiency with the increase AC kaolinite content in the adsorbent. Because the acid activation process makes kaolinite more hydrophilic, due to the increase in the number of hydroxyl groups, which leads to an increase in the number of hydrogen bonds [30]. This, in turn, indicates that PC form stronger hydrogen bonds with AC kaolinite, and thus better removal is achieved.

This is confirmed by inspecting Fig. 2 which shows the FTIR spectra for the adsorbents used in this study. The broad peak at $3,387 \text{ cm}^{-1}$ assigned to hydrogen bonding in AC

Table 1
Phenolic compound name and structure, retention time (t_R), calibration curve equations, R^2 , LOD, and LOQ

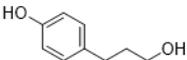
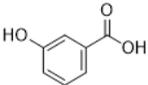
Phenolic compound name	t_R min	Calibration equation	R^2	LOQ mg/L	LOD mg/L
Tyrosol 	6.13	$y = 0.0476x - 0.0186$	0.996	4.92	1.50
p-Hydroxybenzoic acid 	8.21	$y = 0.0928x - 0.182$	0.988	11.3	3.95

Table 2
Mean recovery, relative standard deviation RSD% and relative error for PC in OMW

Compound	Tyrosol	p-Hydroxybenzoic acid
Mean recovery \pm S.D.	78.1 \pm 3.50	108.4 \pm 10.3
Instrument precision RSD%	1.59	1.77
Relative error	18.8	-8.43
Recoveries from previous studies	93.8% from olive oil using HPLC [27]	95% from soil and plant using Gas Chromatography with flame Ionization Detector [26]

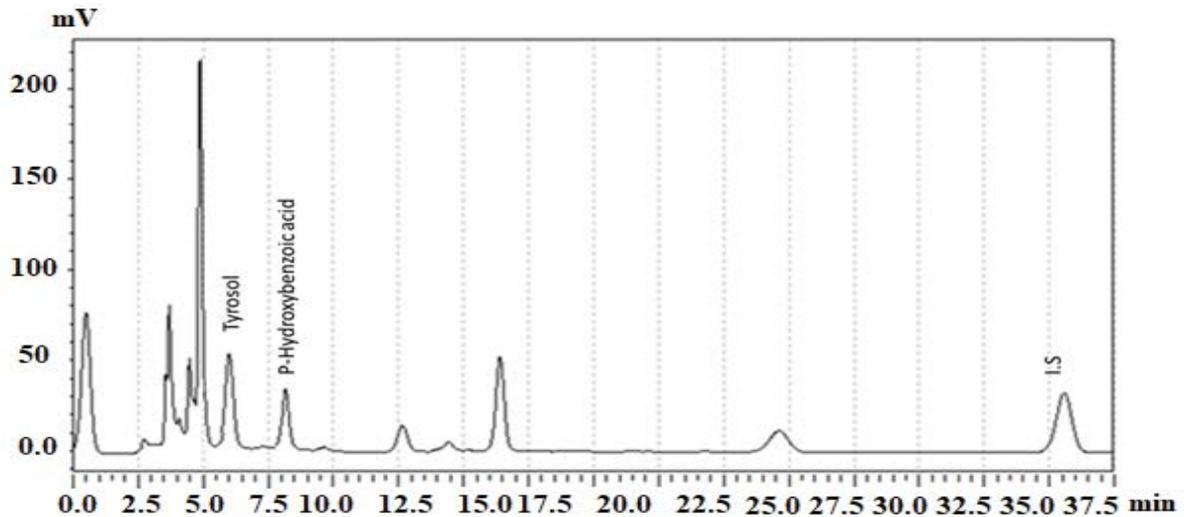


Fig. 1. HPLC chromatogram for phenolic compounds in OMW.

Table 3
Characteristics of OMW taken from Al-Manaseer olive mill in Jordan

Property	Amount
Concentration of tyrosol, mg/L	98.2 ± 0.5
Concentration of p-hydroxybenzoic acid, mg/L	45.8 ± 2.12
Chemical oxygen demand, mg/L	68,000
pH	5.2
Total dissolved solids, mg/L	31,570
Total suspended solids, mg/L	2,025

kaolinite was stronger compared to the same peak in both raw kaolinite and BA kaolinite which indicates the presence of more hydrogen bonds.

Incorporating iron oxide nanoparticles in the adsorbent (entries 5 and 6 Table 4) was found to enhance the removal efficiency since it provides a larger surface area for adsorption as well as the opportunity for electrostatic interaction with PC [31]. However, it was noticed that an increase in the percentage of iron oxide led to a decrease in the removal efficiency (entry 6 in Table 4) due to the possibility of aggregation of nanoparticles [32]. This, in turn, reduces the sites that kaolinite can be distributed on uniformly [33,34].

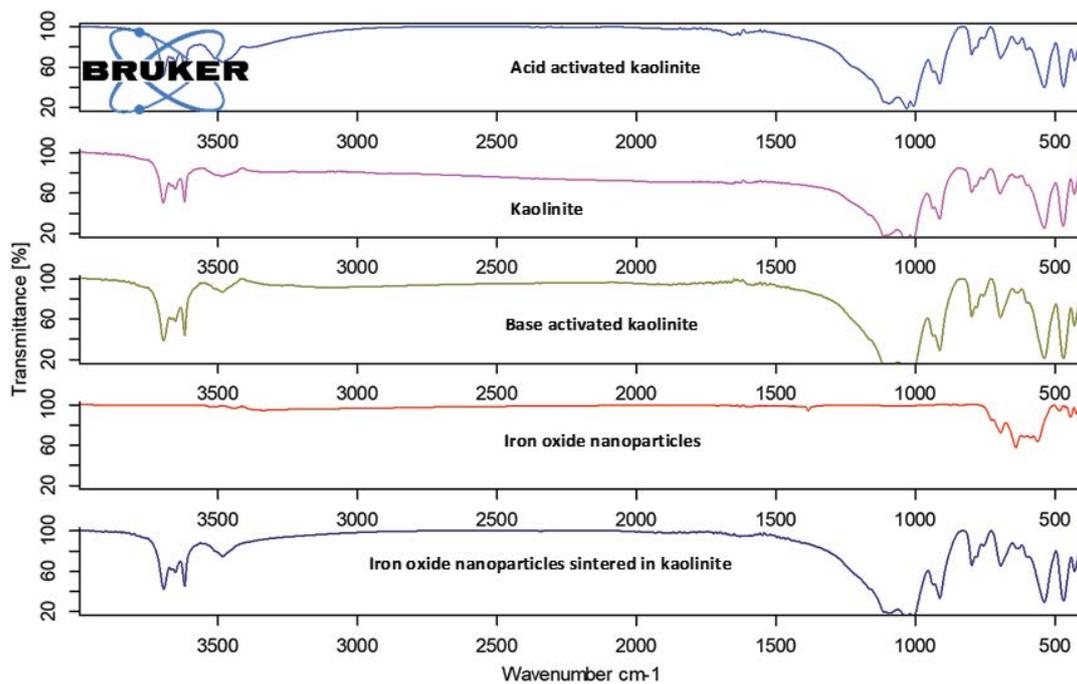


Fig. 2. FTIR spectra for the different adsorbents used in this study.

Table 4
Removal efficiencies for tyrosol and p-hydroxybenzoic acid using different types of adsorbents

Adsorbent number	Adsorbent	Tyrosol	p-Hydroxybenzoic acid
1	Iron oxide nanoparticles	5.24%	10.9%
2	Kaolinite	40.3%	85.9%
3	AC kaolinite	54.1%	91.7%
4	BA kaolinite	47.6%	60.3%
5	AC kaolinite with nanoparticles in 10:1 ratio	60.2%	89.1%
6	AC kaolinite with nanoparticles in 20:1 ratio	67.0%	95.2%
7	Nanoparticles sintered in AC kaolinite in 20:1 ratio	61.4%	77.3%
8	Nanoparticles sintered in AC kaolinite in 10:1 ratio	52.3%	63.8%
9	Nanoparticles sintered in AC kaolinite in 5:1 ratio	41.5%	48.1%

Adsorbent dosage: 0.5 g; pH = 3; Temperature = 25°C

AC kaolinite: acid activated kaolinite

BA kaolinite: base activated kaolinite

It was observed that immobilization of iron oxide nanoparticles on AC kaolinite using the sintering process led to a decrease in the removal efficiency of PC (entries 7–10 in Table 4) compared to the mixture containing the same proportion of substances unsintered. This can be explained by the fact that the sintering reduces the available surface area as well as hinders the access of PC to the inner kaolinite layers [24]. Although sintering reduces removal efficiency, it provides an advantage that does not present in the unsintered adsorbent, which is the ease of recovery. Where the adsorbent can be recovered with a magnet and reused after a simple regeneration process. This eliminates the filtration step, which usually takes a longer time.

From the FTIR spectra in Fig. 2, it can be noticed that there is no significant difference in the spectra of the adsorbent containing sintered and unsintered iron oxide nanoparticles. This indicates that no substantial interaction occurred between the nanoparticles and kaolinite as a result of the sintering process.

From the above discussion, we conclude that despite the acceptable efficiency of the adsorbent containing the sintered nanoparticles and the advantage of easy recovery it provides, its effectiveness in removal is still less than that of the unsintered adsorbent. Hence, the sintering process needs to be modified to achieve better effectiveness. Therefore, we decided to study the factors that affect adsorption using the unsintered adsorbent, a mixture of AC kaolinite and iron oxide nanoparticles, with a ratio of 20:1, in order to find out the optimum conditions that lead to the best removal of PC.

3.3.2. Removal efficiency of PC using different doses of the adsorbent

Different weights of adsorbent (all containing AC kaolinite and iron oxide nanoparticles in a ratio of 20:1) were used to study the effect of the dose of the adsorbent on the efficiency.

According to what we can observe from Table 5, the best adsorbent dose was 0.5 g per 20 mL of OMW. It is also noted that the efficiency increased with increasing dose until we reached a concentration of 0.5 g and then decreased. This is

Table 5
Removal efficiencies of tyrosol and p-hydroxybenzoic acid after the treatment with different adsorbent doses (the adsorbent is a mixture of ac kaolinite and iron oxide nanoparticles with of a ratio of 20:1)

Adsorbent dose in g per 20 mL of OMW	Tyrosol	p-Hydroxybenzoic acid
0.30	55.1%	70.3%
0.40	43.8%	81.3%
0.50	66.9%	94.8%
0.60	64.0%	82.6%
0.70	62.2%	77.0%
0.90	57.5%	64.7%

because an increase in the adsorbent dose means, in principle, the availability of more binding sites within the PC. However, at doses greater than 0.5 g, the lower efficiency could be explained as a consequence of the aggregation of the adsorbent particles due to their intermolecular bonds with themselves through the available active sites [35]. The same trend was observed by Achak et al. [9], who noticed that increasing the adsorbent dose to more than 30 g/L leads to a decreased efficiency.

3.3.3. Effect of the pH

One of the most important factors affecting adsorption is pH. As it affects the nature of the materials, whether they are adsorbed or adsorbed, and thus affects the mechanism by which the adsorption process takes place [36].

After examining the removal efficacy at different pH values, it was found that pH 3 gave the best removal as observed from Fig. 3. The increase in efficiency at a low pH can be attributed to the fact that at lower pH, O–H groups of kaolinite are in their acidic form [37] making them more capable of forming hydrogen bonds with PC, which in turn, boosts the efficiency of removal. On the other hand, PC are also in their protonated form at lower pH levels, which enhances their chances of forming hydrogen bonds with kaolinite and iron oxide nanoparticles [10].

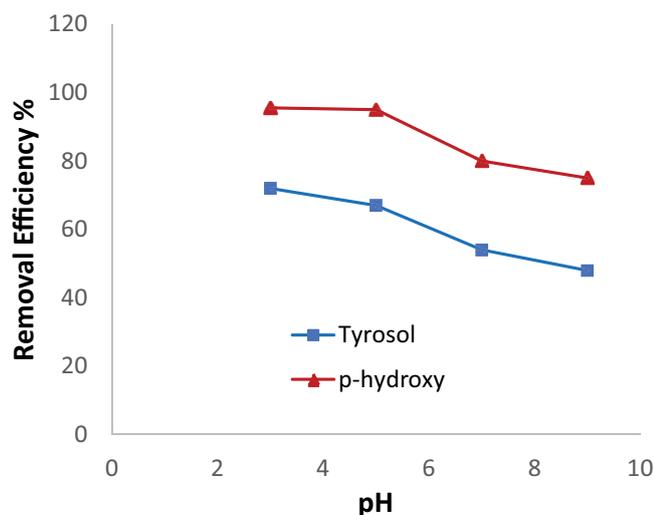


Fig. 3. Removal efficiency of tyrosol and p-hydroxybenzoic acid from OMW at different pH values.

The effect of pH can be also explained by considering the point of zero charge (pzc) which is the pH at which the net total particle charge of adsorbent equals to zero [38]. PZC is of particular importance when explaining adsorption phenomena [39]. The points of zero charge for kaolinite (2.7–3.2) [40]. This means that the hydroxyl groups on surface of kaolinite become ionized at $\text{pH} > 3.2$. On the other hand, the pK_a values for tyrosol and p-hydroxybenzoic acid are 10.2 and 4.3, respectively. This implies that at pH values less than 4, both compounds are in their protonated unionized form. This in turn promotes the formation of hydrogen bonds between the unionized hydroxyl groups on the surface of kaolinite adsorbent, so the removal efficiency is best at $\text{pH} = 3$.

However, from Table 3, we can notice that the pH of OMW is 5.2 which causes a slight decrease in the removal efficiency due to the ionization of hydroxyl groups on kaolinite surface along with the ionization of p-hydroxy benzoic acid. Hence, the hydrogen bonding efficiency decreases, and the removal efficiency is also reduced. Therefore, the pH of the raw OMW must be adjusted to achieve the optimum removal efficiency.

There are no previous studies that investigated the effect of pH on the adsorption of PC using kaolinite or any of the other clay minerals. However, some studies have tested the effect of pH on PC removal but using other adsorbents other than kaolinite. Most of these studies have found that absorption increases with increasing pH [9,13].

3.3.4. Effect of temperature

The principal mechanism by which PC are removed from OMW is adsorption, which is an equilibrium process that is expected to be affected by temperature. Since temperature can alter the solubility of adsorbates in addition to its effect on the adsorption equilibrium constant [41].

Table 6 illustrates the findings of our investigation into the influence of temperature on eliminating PC from OMW in the range of 20° to 40° . It can be seen that the

Table 6

Removal efficiencies for tyrosol and p-hydroxybenzoic acid after treatment at different temperatures

Temperature $^\circ\text{C}$	Tyrosol removal efficiency	p-Hydroxybenzoic acid removal efficiency
20.0	68.4%	90.0%
22.0	70.6%	92.3%
25.0	72.1%	95.5%
30.0	62.8%	87.2%
40.00	57.2%	76.4%

best removal occurred at a temperature of 25° . This is comparable to the findings of Alkaram et al. [10] and Dolaksiz et al. [42]. Also, it can be observed that raising the temperature from 20° to 25° led to an increase in the adsorption. But, when the temperature increased further, the same trend did not continue, and we notice a significant decline in the effectiveness of removal. The increase in efficiency with increasing the temperature from 20° to 25° can be attributed to several reasons. Among them, the higher packing density of PC within the pores of adsorbent at the higher temperatures [43]. The explanation could also be the occurrence of irreversible chemisorption and/or polymerization of adsorbed molecules, as suggested by Garcia-Araya et al. [41]. Alternatively, the decrease in adsorption that occurs in the range of 25° to 40° can be explained by the fact that an increase in temperature leads to a weakening of the forces of attraction between the surface of the adsorbent and the PC, and that the compounds tend to leave the surface of the adsorbent and return to the solution, thus reducing the absorption [44].

3.3.5. Effect of contact time

Removal efficiencies of tyrosol and p-hydroxybenzoic acid after treatment for different periods of time are shown in Fig. 4. The figure shows that equilibrium was reached after 3 h, and this is consistent with what was obtained by the study of Achak et al. [9]. After 3 h, the efficiency began to decrease, forming a plateau. This could be explained by taking into consideration that initially a large number of vacant binding sites are available for adsorption, which causes the adsorption rate to increase rapidly, after 3 h most vacant sites on the outer layer of the adsorbent are saturated and it becomes more difficult for the PC to bond to the outer layer due to the repulsive forces with other molecules, which means that the molecules have to penetrate deeper to get adsorbed, which explains the decrease in the adsorption rate after 3 h.

3.3.6. Effect of nature of phenolic compounds

Another important factor affecting removal efficiency is the nature of the adsorbate. In our current study, the compounds we studied are tyrosol and p-hydroxybenzoic acid. Where we noticed that, in general, the adsorption was greater in the case of p-hydroxybenzoic acid. To explain this, we must refer to the structures and chemical

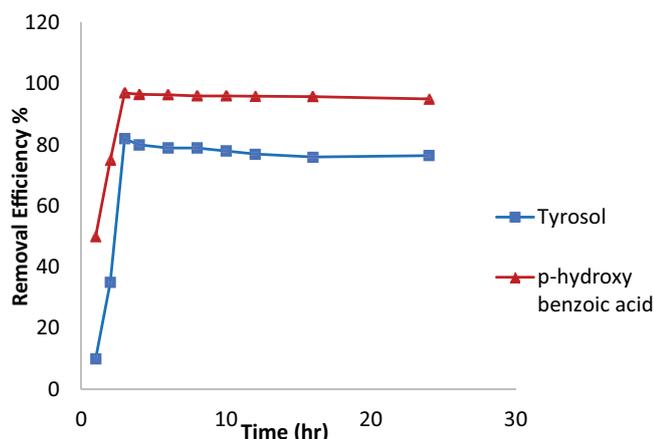


Fig. 4. Effect of contact time on the removal of phenolic compounds from OMW.

properties of these compounds shown in Table 1. We can notice that the p-hydroxybenzoic acid contains a carboxyl group, which can form stronger hydrogen bonds [45], either with kaolinite or iron oxide [46]. Consequently, the adsorption is better for p-hydroxybenzoic acid and its removal efficiency from OMW is higher.

3.3.7. Comparison of the results of this study with previous studies

In this study, we obtain a maximum removal efficiency of 81.8% for tyrosol and 97.3% for hydroxybenzoic acid. These values are better than those of Al-Malah et al. [7] who reported a maximum removal efficiency of total phenols from OMW of 81% using bentonite as adsorbent. Our results also demonstrated better removal efficiency for tyrosol compared to the work of Flores et al. [47] who achieved maximum removal from the water of 74.1% by employing carbonaceous materials and electrochemical advanced oxidation processes. Our work, however, gave lower removal efficiencies than Achak et al. [9] who achieved a tyrosol removal of 100% from OMW using banana peels as an adsorbent. Also, comparing our results with the study conducted by Oladipo [48,49], we find that he achieved better tyrosol removal efficiency which reached 86% by applying $\text{CuCr}_2\text{O}_4/\text{CaFe-LDO}$ photocatalyst in the dark and the performance reached 99% by applying the catalyst in sunlight. It is worth noting none of the previous studies involved the specific removal of p-hydroxy benzoic acid.

4. Conclusion

In this study, an efficient and simple HPLC-UV method has been developed for the extraction and quantification of two phenolic compounds namely (tyrosol and p-hydroxybenzoic acid) in OMW. This is the first time that a method has been proposed for the simultaneous determination of these two compounds using HPLC in an extremely complex OMW matrix. The new method is proved satisfactory in terms of validation results. It has been applied to analyze OMW taken from an olive mill in Jordan. We have

prepared adsorbents based on kaolinite and iron oxide nanoparticles in different proportions and tested their effectiveness in removing PC from OMW. The best adsorbent was AC kaolinite mixed with iron oxide nanoparticles in the ratio of 20:1. According to our knowledge, this is the first time that these two materials (kaolinite and iron oxide nanoparticles) are used in OMW treatment. This inexpensive, easy-to-prepare, the environmentally friendly adsorbent is found out to be highly effective in removing PC from OMW and could replace other costly adsorbents. The study has expanded to examine the effect of various factors on the efficiency of PC removal from OMW. Several factors have been found to influence the removal efficiency such as the adsorbent dose, pH, temperature, contact time, and the nature of the phenolic compound. The highest accomplished removal efficiencies were 81.8% and 97.3% for tyrosol and p-hydroxybenzoic acid, respectively, at 25°C, pH = 3, 3 h contact time, and an adsorbent dose of 2.5 g/100 mL. We intend to improve the efficiency by applying further modifications to the adsorbent. We're also excited to investigate the method of readily recovering the adsorbent, as well as the prospect of its regeneration and reuse.

Declarations

Authors' contributions

All authors whose names appear on this submission had made substantial contributions to the work.

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Compliance with ethical standards

Conflict of interest/competing interests

The authors have no conflicts of interest to declare that are relevant to the content of this article.

Disclaimer

The authors declare that all the data in this work are original and not reused from other sources.

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