

Olive mill wastewater treatment using a simple zeolite-based low-cost method



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ABSTRACT

Olive mill wastewater (OMW), a liquid by-product of the olive oil industry, represents a severe environmental problem owing to its high pollution load. In this study, successive columns containing different types of natural materials were investigated for their OMW treatment efficiency. Passing OMW through three columns of gravel, fine sand, and a mixture of acidified cotton and zeolite (weight:weight ratio of cotton:clinoptilolite of 2:1), followed by treatment with activated charcoal (AC) and lime, was the best treatment in terms of the quality of water obtained. This treatment decreased concentrations of NO_3^- , B, K, P, and total fat in OMW by mean percentages of 78.0, 92.4, 66.6, 48.3, and 93.3%, respectively. Furthermore, it decreased OMW turbidity and electric conductivity (EC) by 96.8 and 48.4%, respectively. Most contaminants were removed from the OMW in the cotton/clinoptilolite column owing to the high sorption affinity of clinoptilolite on its active sites. The AC was efficient for organic particle removal; meanwhile, lime was used to raise the pH of the treated OMW (TOMW) from 2.9 to 5.1. This simple method enables us to obtain environmentally friendly TOMW that can be safely used for irrigation.

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1. Introduction

Environmental pollution by toxins has accelerated dramatically in recent years due to increasing industrialization (Tiwari et al., 2008). Mankind's demand for resources and raw material treatments has intensified the ecological and economic contradictions in the industrial sector (Sen and Chakrabati, 2009). Widespread industrial development in urban areas has radically reduced land areas for waste disposal. Disposal of untreated industrial and domestic wastes into the environment affects the quality of the soil and groundwater and makes this soil and groundwater undesirable for use (Quazilbash et al., 2006). Water produced by industry generally contains potential hazardous wastes, such as heavy metals and toxic organic compounds, and carries these hazardous wastes into our environment (Azumi and Bichi, 2010). In this context, the waters produced by the olive oil industry usually contain hazardous materials that cause severe environmental problems (Mekki et al., 2007).

1.1. Olive mill wastewater production

Olive processing has been important in Mediterranean countries for centuries. Moreover, the growing interest in the consumption of olive oil as an essential of the Mediterranean diet has increased the importance of the olive oil sector in recent decades. Recently, the Kingdom of Saudi Arabia (KSA) started heavy olive oil production in the northern part of the Tabuk and Al-Jouf regions. According to the International Olive Oil Council (IOOC), worldwide production of olive oil was approximately 3,024,000 t during 2009/2010, and the European Union (EU) produced 74% of this total (Cara et al., 2012). Olive oil production involves producing considerable amounts of liquid effluent, which is referred to as olive mill wastewater (OMW). The OMW amounts to 0.5–3.25 m³ per 1000 kg of olives, depending on the process used (Paraskeva and Diamadopoulos, 2006; Kapellakis et al., 2012). Furthermore, Mekki et al. (2013) recorded that the annual production of OMW in Mediterranean countries reached 30 million m³ in the years 2005/2006. In the KSA alone, the annual olive oil production has been reported to be 80,000 t; consequently, the calculated OMW production could be around 160,000 m³.

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1.2. Olive mill wastewater characteristics

Typically, OMW is composed of the water from the tissue of the fruit, the water used for the various stages of oil production, olive pulp, mucilage, pectin, and oil, among other things, suspended in a relatively stable emulsion. Moreover, it contains toxic organic compounds and inorganic compounds (Mekki et al., 2009, 2013). In general, OMW is characterized by an intensive violet–dark brown up to black color, strong specific olive oil smell, high degree of organic pollution (chemical oxygen demand (COD) of 40–220 g/L and biochemical oxygen demand (BOD) of 35–110 g/L), pH of 3–6, 25–45 g/L of organic compounds in total, high electrical conductivity (EC), high content of polyphenols (0.5–2.4 g/L), reduced sugars ($\leq 60\%$ of the dry weight), and high solid matter content. Potassium is the predominant inorganic material (~ 4 g/L) in OMW (Niaounakis and Halvadakis, 2006). Typically, OMW is an acidic effluent with a high nutrient content that can be used to fertilize soil; however, it is very rich in toxic phenolic compounds (Aggelis et al., 2003). Additionally, the C/N ratio of OMW is unfavorable for biodegradation processes (Mekki et al., 2006a, 2013). Using OMW in irrigation without treatment increases soil salinity, which results from the presence of the main ionic species (K^+ , Na^+ , and HCO_3^-) of the OMW (Zenjari and Nejmeddine, 2001). In recent years, there has been increased attention directed toward finding the best methods to treat OMW and toward recycling both the organic matter (OM) and nutritive elements in the crop production system. Some OMW characteristics are favorable for agriculture, because this effluent is rich in water, OM, N, P, K, and Ca; however, other characteristics are unfavorable for agriculture, including the presence of phenolic compounds (Lesage-Meessen et al., 2001; Komilis et al., 2005; Mekki et al., 2006b).

1.3. Olive mill wastewater treatment

Subsequently, Kapellakis et al. (2012) reported the widespread use of evaporation ponds to manage OMW, which can be attributed to the low cost of this method. However, evaporation ponds are associated with odor development, leaking of OMW to surface waterways or groundwater, and relatively high area requirements in regions with low evaporation rates. Many different treatment methods of OMW have been proposed previously, including aerobic treatment, anaerobic digestion, and composting (Sayadi and Ellouz, 1995; Ehaliotis et al., 1999; Kissi et al., 2001; Marques, 2001). However, an environmentally safe and cost-effective solution to OMW treatment has not yet been found (Zagklis et al., 2013). Most studies devoted to building efficient treatment technologies for OMW are not economically feasible owing to the short olive oil season, typically biennial olive harvest cycle, and the small isolated area of olive mills (Zenjari and Nejmeddine, 2001).

The main objectives of this study were as follows: to evaluate the physicochemical characteristics of the KSA's olive mill wastewater; to investigate a suitable and feasible method for olive wastewater treatment that will decrease toxic compound concentrations; and to assess the suitability of treated water for irrigation purposes.

2. Materials and methods

2.1. Collection and preservation of olive mill wastewater

Five hundred liters of fresh OMW was collected during the 4th quarter of 2013 from the National Agricultural Development Company (NADEC) Al-Jouf Project, which is located in the Al-Jouf region about 1250 km north east of Riyadh City, KSA. At this site, olive oil is produced by the centrifugal method. The OMW samples

were collected in plastic containers (20 L) and transported immediately to a laboratory at King Saud University and stored at approximately 8 °C.

2.2. Analytical methods

OMW chemical analyses were carried out to assess the quality of water according to procedures described by Matiti (2004), and then different types of water treatments were examined. Water reaction (pH) was determined using a pH meter (pH meter, CG 817). Total soluble salts were measured by using an EC meter in units of $dS\ m^{-1}$ at 25 °C (Test kit Model 1500_20 Cole and Parmer). Bicarbonate (HCO_3^-) concentration was determined by titration with sulfuric acid (H_2SO_4), while Cl concentration was determined by titration with silver nitrate ($AgNO_3$) (Matiti, 2004). Sulfate (SO_4^{2-}) concentration was determined by the turbidity method (Tabatabai, 1996), and the nitrate (NO_3^-) concentration was determined by the phenoldisulfonic acid method (APHA, 1998). Soluble Na and K concentrations were determined using a flame photometer (Corning 400). Phosphate concentration was determined using the method described by Matiti (2004). Boron was determined using the azomethine-H method (Keren, 1996). Concentrations of Ca, Mg, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn were determined using inductively coupled plasma (ICP) spectrometry (Perkin Elmer Model 4300DV). UOMW was digested by nitric acid (HNO_3) (Matiti, 2004) and then injected into the ICP. TOMW was injected directly into the ICP after acidification by nitric acid and without digestion.

2.3. Treatments of olive mill wastewater

2.3.1. Treatment of olive mill wastewater by the sedimentation and flotation method (S and F)

Sedimentation and flotation (S and F) is a solid–liquid separation technique using gravity settling to remove suspended solids having densities higher or lower, respectively, than water (Kapellakis et al., 2012). The removal of suspended solids from wastewater by gravity separation is one of the most widely used unit operations in wastewater treatment (Al-Farraj et al., 2013). In this study, physical separation was carried out using glass cylinders with diameter of 20 cm and length of 24 cm. After 6 h of gravity separation, two kinds of suspended solid were observed: a floating part (containing total fat content of 9.39%) and a precipitated part (containing total fat content of 1.64%).

2.3.2. Treatment of olive mill wastewater using successive steps

After OMW physical separation, the water was extracted using a siphon method and then passed through six different designed treatment methods, with each treatment consisting of 3–4 successive columns containing different natural materials (Table 1).

The columns used in this experiment were made of transparent polyvinyl chloride (PVC) and had an internal diameter of 10 cm and a length of 40 cm. The columns were sealed from the bottom using two pieces of gauze fabric firmly held by strings and tape. The columns were packed with the material to 25 cm height. The bulk densities of the sand columns were $1500\ kg\ m^{-3}$. The packing process was conducted in 10 cm increments to avoid segregation of particles. The columns were mounted vertically on a wooden holder inside the laboratory and kept at a controlled temperature of 22 ± 2 °C. Each treatment system was replicated three times. Cumulative TOMW versus time were collected for analysis. The contact times between the OMW and substrates were 1 min for gravel, 10 min for fine sand, and 0.5 min for the cotton:clinoptilolite column. The grass and unactivated charcoal columns recorded contact times of just a few seconds. Five physicochemical parameters were

Table 1

Materials (gravel, coarse and fine sand, grass, cotton, zeolite, and activated and unactivated charcoal) used to fill the treatment columns.

Treatment no.	Successive column materials			
	Column 1	Column 2	Column 3	Column 4
1	Gravel	Coarse sand	Fine sand	Unactivated charcoal
2	Gravel	Fine sand	Acidified grass (<i>Bermudagrass (Cynodon dactylon L.)</i> cv. Tifway 419) using diluted (1:10) HCl	–
3	Gravel	Fine sand	Acidified cotton (<i>Gossypium herbaceum L.</i>) using diluted (1:10) HCl	–
4	Gravel	Fine sand	Mixture of acidified grass (<i>Cynodon dactylon L.</i>) using diluted (1:10) HCl and cotton (<i>Gossypium herbaceum L.</i>) [1 (g) grass:1 (g) cotton]	–
5	Gravel	Fine sand	Mixture of acidified cotton (<i>Gossypium herbaceum L.</i>) using diluted (1:10) acetic acid and zeolite (clinoptilolite) [2 (g) cotton:1 (g) clinoptilolite]	–
6	Gravel	Fine sand	Mixture of acidified cotton (<i>Gossypium herbaceum L.</i>) using diluted (1:10) acetic acid and zeolite (clinoptilolite) [2 (g) cotton:1 (g) clinoptilolite]	Activated charcoal, and then lime application

used to evaluate the treatment efficiency for each method: EC, pH, potassium (K), turbidity, and color.

2.3.3. Gravel and sand characterization

The gravel diameters used in the present study were in the range 3.0–5.0 mm and the gravel consisted of combinations of sedimentary rocks, i.e., limestone, dolomite, and sandstone. The fine sand characterization used in OMW treatment is summarized in Table 2.

2.3.4. Zeolite (clinoptilolite) and activated charcoal (AC) characterization

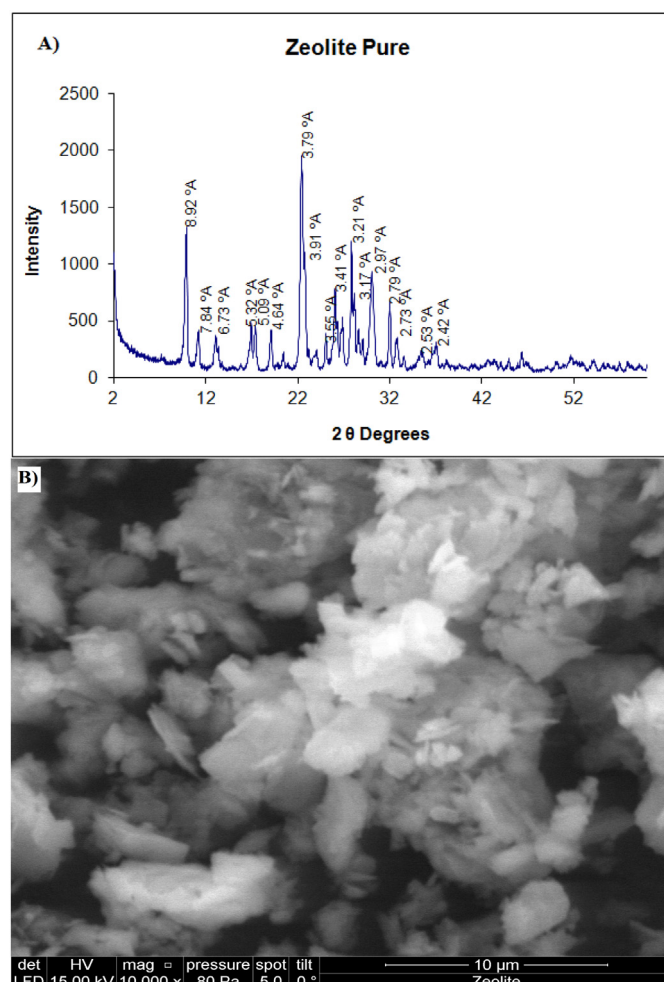
Zeolites are crystalline aluminosilicates with open framework structures. The fundamental building blocks of these structures are infinitely extended three-dimensional networks of silicon dioxide (SiO_4) and sodium aluminate (AlO_4) tetrahedrally linked to each other through oxygen atoms. Zeolites may be generally represented by the formula $\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where M is a cation of valence, n, that compensates the negative charge of the framework, $x \geq 2$ (depending on the type of zeolite), and y can vary from 0 to 10. These framework structures consist of interconnected channels and cages that are occupied by the M cations and water molecules. A very important property of the zeolite clinoptilolite is the ability to exchange the cations, M, located at specific sites in the channel/

cage systems for various cations from solution (Kosanovic et al., 1997; Basaldella and Tara, 1995). In this study, clinoptilolite was purchased from the Mineralogical Society of America (MSA) and was characterized by high cation exchange capability ($\text{CEC} = 2.16 \text{ meq g}^{-1}$), high void volume (34%), channel dimensions of $3.9 \times 5.4 \text{ \AA}$, and high relative thermal stability. The representative unit cell formula of the clinoptilolite was $(\text{Na}_3\text{K}_3)(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$ (Fig. 1).

Table 2

Physiochemical properties of sand used in the study.

Parameter	Value
Particle-size distribution (%)	
Sand (2000–20 μm)	85.5
Silt (20–2 μm)	10.0
Clay (<2 μm)	4.5
Textural class	Loamy sand
Saturation water content ($\text{m}^3 \text{ m}^{-3}$)	0.389
Bulk density (Mg m^{-3})	1.5
Organic matter content (%)	0.01
Calcium carbonate content (%)	35.72
pH	7.9
EC (1:1, sand:water extract) (dS m^{-1})	0.9
Soluble cations (1:1 extract), (meq L^{-1}):	
Ca^{2+}	3.6
Mg^{2+}	2.1
Na^+	2.3
K^+	0.4
Soluble anions (1:1 extract) (meq L^{-1}):	
CO_3^{2-}	–
HCO_3^-	1.6
Cl^-	2.5
SO_4^{2-}	3.9

**Fig. 1.** A) XRD and B) SEM results for clinoptilolite.

The high applicability of Activated charcoal (AC) is related to its high porosity, rapid adsorption, and thermal stability (Hesas et al., 2013). The AC used in this study was purchased from Loba Chemie (India) and was acidic. The AC was characterized and then washed with distilled water before use. The characterization of AC before washing is summarized in Table 3. The AC used in the study had a weight:volume ratio for AC:OMW of 1:20. However, the lime ratio (i.e., OMW:lime) was 4:1 (volume:weight). The shaking period was 15 min for both AC and lime. The ratios and agitation time adopted in this study were selected based on the results of batch adsorption experiments and kinetic studies, respectively.

3. Results and discussion

3.1. Untreated olive mill wastewater (UOMW) characteristics

The KSA's UOMW is characterized by an intensive green–dark brown to black color and strong specific olive oil smell. These observations agree with those of Niaounakis and Halvadakis (2006). The chemical composition of the KSA's OMW is complex owing to the water from the milled olives (vegetation water) and the soft tissues from the olive fruit. The chemical characteristics of the studied UOMW were as follows: pH of 3.8, COD of 46.0 g L⁻¹, total fat content of 7.4% by weight, total phenol content of 4.5 g L⁻¹, NO₃⁻ content of 200 mg L⁻¹, B content of 9.8 mg L⁻¹, K content of 89.9 mg L⁻¹, HCO₃⁻ content of 60 meq L⁻¹, phosphate (PO₄) content of 31.8 mg L⁻¹, turbidity of 86.3 NTU, OM content of 0.65%, and EC of 6.4 dS m⁻¹. No heavy metal (Fe, Cd, Co, Zn, Mn, Ni, Pb, or Cu) contamination was detected in the studied UOMW, similar to results found by D'annibale et al. (2006) and Mekki et al. (2013). In the studied OMW, K was the predominant inorganic material (3.5 g/L); consequently, it was considered the main cause of increasing OMW salinity, similar to results found by Niaounakis and Halvadakis (2006) and Mekki et al. (2006a, 2013).

3.2. The treatment effect on olive mill wastewater using different successive steps

Table 4 summarizes the TOMW characterization using each treatment method. Treatments 5 and 6 were the best treatments in terms of salinity, K, turbidity, and color removal. On the other hand, treatment 1 was the best treatment for neutralization of OMW acidity. Treatment 5 decreased the OMW EC by 70.3% (from 6.4 to 1.9 dS m⁻¹), decreased K by 83.8% (from 89.9 to 14.6 meq L⁻¹), decreased turbidity by 50.9% (from 86.3 to 42.4 NTU), and changed the color from black to slightly yellow. Although treatment 5 was efficient in improving OMW physiochemical characteristics, it was inefficient in neutralization of OMW acidity. Using treatment 5, pH decreased from 3.8 to 2.8 (Table 4). On the other hand, the use of AC and lime in treatment 6 was efficient in lightening TOMW color and increasing pH (Hesas et al., 2013; Daifullah et al., 2003; Maree and Du Plessis, 1994). The TOMW color changed to colorless (instead of yellow) and pH increased to 5.1 (Table 4, Figs. 2 and 3). The results indicate that treatment 6 is efficient in decreasing EC, K, and turbidity by 48.4, 66.6, and 96.8%, respectively. Most contaminants

Table 3
Activated charcoal characterization.

Parameter (1:1 extract)	Value
pH	7.5
TSS (%)	1.0
Chloride (%)	0.2
Sulfate (%)	0.2
Nitrate and heavy metals (mg L ⁻¹)	Traces

Table 4
Effects of different treatment type on olive mill wastewater physiochemical parameters.

No.	Treatment method	Mean physicochemical parameters after treatment (n = 3)				
		EC (dS m ⁻¹)	K ⁺ (meq L ⁻¹)	pH	Turbidity (NTU)	Color
–	No treatment	6.4	89.9	3.8	86.3	Black
1	Gravel, coarse then fine sand, un-activated charcoal	7.2	93.1	6.2	70.0	Black
2	Gravel, fine sand, acidified grass	6.8	89.5	4.9	65.0	Reddish brown
3	Gravel, fine sand, acidified cotton	6.7	90.0	4.0	62.9	Reddish brown
4	Gravel, fine sand, mixture of acidified grass and cotton	6.4	91.9	4.1	64.3	Reddish brown
5	Gravel, fine sand, mixture of acidified cotton and zeolite	1.9	14.6	2.8	42.4	Slightly yellow
6	Gravel, fine sand, mixture of acidified cotton and zeolite, activated charcoal and lime application	3.3	30.0	5.1	2.8	Colorless

were removed from OMW using treatments 5 and 6 on the clinoptilolite column owing to the high sorption affinity of clinoptilolite on its specific sites in the channel/cage systems (Kosanovic et al., 1997; Basaldella and Tara, 1995). AC was efficient in colloidal and soluble organic particle removal; moreover, the lime was able to raise TOMW pH from 2.8 to 5.1. This simple method enables us not only to obtain environmentally friendly TOMW, but also to use this treated water for irrigation with some restrictions imposed to salinity, according to the Ayers and Westcott (1985) guidelines. Table 4 demonstrates that the other successive columns of gravel, coarse and/or fine sand, and then unactivated charcoal, acidified grass (Bermudagrass (*Cynodon dactylon* L.) cv. Tifway 419), acidified cotton (*Gossypium herbaceum* L.), or a mixture of acidified cotton and zeolite (treatments 1, 2, 3, 4, respectively) were inefficient in OMW treatment.

3.3. The treatment of olive mill wastewater by natural zeolite (clinoptilolite)

Clinoptilolite is a selective scavenger of various metal cations that can be removed from liquid effluents through the process of ion exchange. Clinoptilolite is an excellent ion exchanger, and useful for the removal and recovery of cations from OMW (Lu et al., 2011). This study found that the filtering abilities of clinoptilolite mean that it offers a versatile and environmentally friendly option to capture most contaminants in OMW. The results indicate that passing OMW through three successive columns containing gravel, fine sand, and a mixture of acidified cotton using diluted (1:10) acetic acid and clinoptilolite (with a weight:weight ratio of cotton:clinoptilolite of 2:1), and then treating the OMW with AC and lime, is an efficient treatment method for OMW and decreases concentrations of NO₃⁻, B, K, P, turbidity, total fat, and EC by 78.0, 92.4, 66.6, 48.3, 96.8, 93.3, and 48.4%, respectively (Table 5). Most contaminants were removed from OMW in the third column, the clinoptilolite column (Figs. 4 and 5), owing to the high sorption affinity of clinoptilolite on its specific sites in the channel/cage systems. The AC was efficient for colloidal and soluble organic particle removal, and the lime performed well by raising TOMW pH from 2.8 to 5.1.

This study confirmed that the most common cation in UOMW is K, which potentially increases water salinity (Niaounakis and

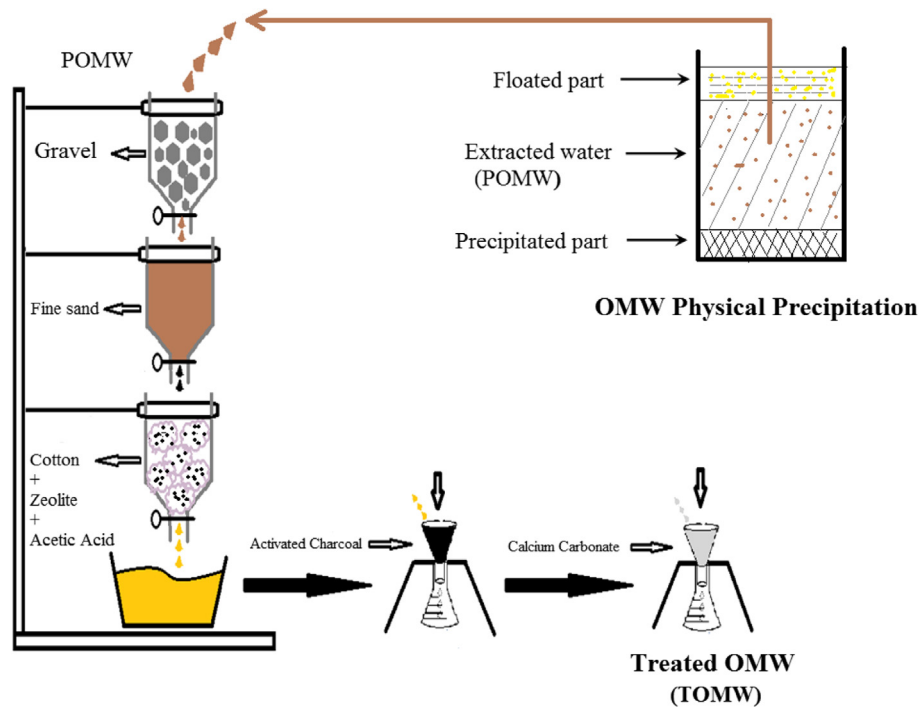


Fig. 2. Diagram illustrating the components of the olive mill wastewater treatment model.

Halvadakis, 2006; Lu et al., 2011). Experimental results indicated that treating OMW using a clinoptilolite column (Table 1, and Figs. 2 and 5) was efficient in K removal and, consequently, decreasing the OMW salinity. Using clinoptilolite for desalination is considered a valid desalination method only for OMW, since K⁺ is not a predominant cation for other wastewater, brackish groundwater, and seawater. When used as a filtration media, clinoptilolite helps remove even large amounts of K⁺ from water through the cation exchange process, where the K chemically bonds to the clinoptilolite molecules. In this study, 66.6% of K was removed by passing OMW through the clinoptilolite column, similar to the findings of Lu et al. (2011). The removal of ammonia by natural zeolitic materials has been widely investigated in recent decades. However, K removal from saline water by clinoptilolite has not been widely considered by scientists, because K does not exist in high concentrations in natural water and is not classified as a toxic element

(Hedström, 2001; Northcott et al., 2010; Wang and Peng, 2010). Farkas et al. (2005), Weatherley and Miladinovic (2004), and Jorgensen and Libor (1976) indicated that clinoptilolite is the most effective natural zeolite for ammonia (NH₃⁺) and K⁺ removal owing to its high selectivity for ammonium (NH₄⁺) and K⁺ in the presence of competing cations such as Na⁺, Ca²⁺, and Mg²⁺. Farkas et al. (2005) sorted the alkaline and earth-alkaline cations according to the order of affinity for clinoptilolite as follows: K⁺ > NH₄⁺ > Ca²⁺ > Na⁺ > Mg²⁺. The actual K⁺ adsorption capacity

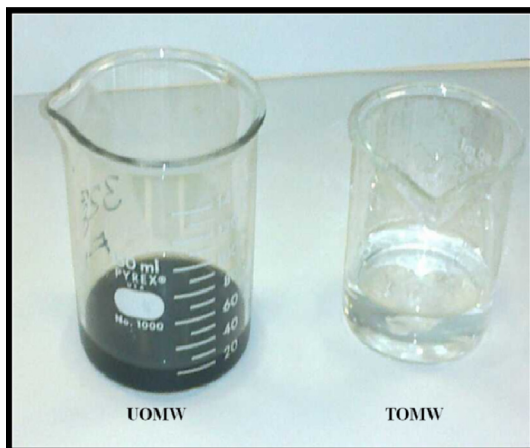


Fig. 3. Illustration of the effect of treatment on olive mill wastewater color (treatment no. 6).

Table 5

Average Physicochemical characteristics of untreated and treated olive mill wastewater (±SD).

	UOMW (n = 5)	TOMW (n = 5)
Water content (% v/v)	70	100
pH	3.8 ± 0.2	5.1 ± 0.5
EC (dS/m) (at 25 °C)	6.4 ± 0.4	3.3 ± 0.5
Ca ²⁺ (meq L ⁻¹)	0.6 ± 0.1	11.2 ± 0.4
Mg ²⁺ (meq L ⁻¹)	0.5 ± 0.1	10.7 ± 0.2
Na ⁺ (meq L ⁻¹)	6.8 ± 0.08	12.8 ± 0.3
K ⁺ (meq L ⁻¹)	89.9 ± 0.08	30 ± 0.1
NO ₃ ⁻ (mg L ⁻¹)	200 ± 2.0	44 ± 1.4
HCO ₃ ⁻ (meq L ⁻¹)	60 ± 0.09	40 ± 0.1
Cl ⁻ (meq L ⁻¹)	8 ± 0.2	20 ± 1.0
SO ₄ ²⁻ (meq L ⁻¹)	2.5 ± 0.2	0.21 ± 0.1
B (mg L ⁻¹)	9.80 ± 0.1	0.74 ± 0.1
PO ₄ (mg L ⁻¹)	31.8 ± 1.4	16.5 ± 0.8
TDS (mg L ⁻¹)	4096	2112
OM (%)	0.65 ± 0.2	0.00
Turbidity (NTU)	86.3 ± 0.4	2.8 ± 0.2
Total fat (% wt/wt)	7.4 ± 0.08	0.5 ± 0.08
Fe (mg L ⁻¹)	0.89 ± 0.2	0.22 ± 0.1
Cd (mg L ⁻¹)	N.D. ^a	N.D.
Co (mg L ⁻¹)	N.D.	N.D.
Zn (mg L ⁻¹)	N.D.	2.5 ± 0.01
Mn (mg L ⁻¹)	N.D.	0.1 ± 0.01
Ni (mg L ⁻¹)	N.D.	N.D.
Pb (mg L ⁻¹)	N.D.	N.D.
Cu (mg L ⁻¹)	N.D.	0.33 ± 0.08

^a Not detected.

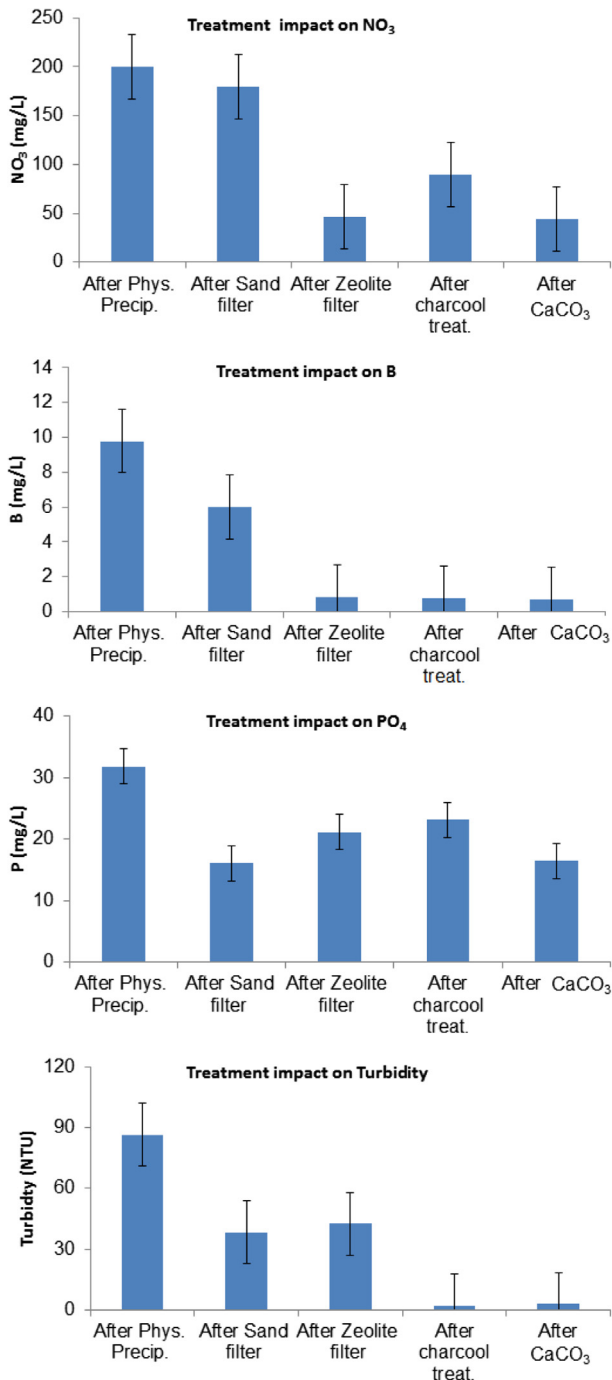


Fig. 4. Impact of different treatment steps on olive mill wastewater physicochemical parameters: nitrate, boron, phosphorus, turbidity (\pm SD).

and efficiency of the removal process depends upon the type of zeolite used, contact time, initial concentration of K, temperature, the amount of zeolite loading, particle size, and the presence of competitive ions (Northcott et al., 2010).

Lu et al. (2011) concluded that the coexistence of NH₃ would not affect the K adsorption by clinoptilolite, that the maximum adsorption of clinoptilolite to K₂O was 48.92 mg g⁻¹, and that the main factors influencing K adsorption were concentration, time, and temperature.

In this study, the acidic conditions of the clinoptilolite column were obtained by using diluted acetic acid (1:10), and these

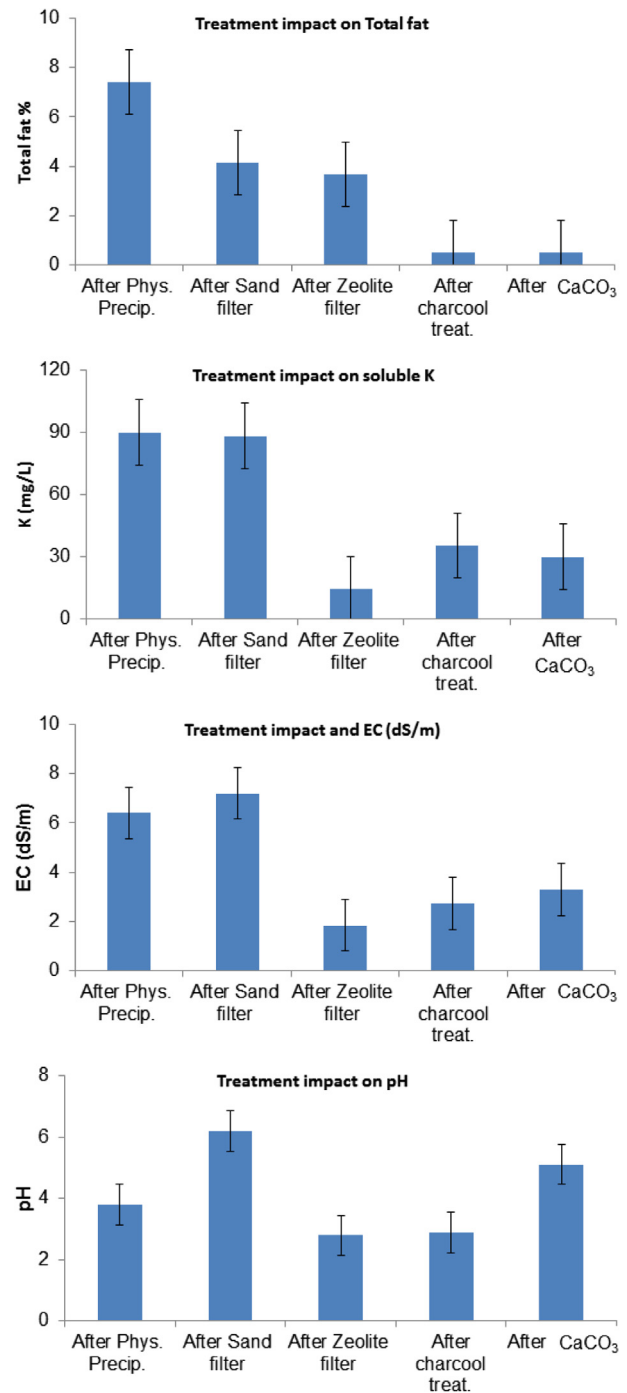


Fig. 5. Impact of different treatment steps on olive mill wastewater physicochemical parameters: total fat, potassium, electrical conductivity, pH (\pm SD).

conditions were prepared to facilitate phenol sorption into clinoptilolite. In this context, Schmidt and Swiderska-Dabrowska (2013) found that the largest rate of phenol removal by zeolite was observed at pH values in the range 2–4, with the highest phenol removal rate observed at a pH of ~2. Furthermore, phenol adsorption decreases with increasing pH in the range 5–12. This is due to phenol solubility increasing at higher pH values. Moreover, Saravanakumar and Kumar (2013) observed that the uptake of phenol by sodium zeolite was almost constant in the pH range 3–6. On the other hand, adsorption decreased with increasing pH in the range 7.0–9.0. Asgari et al. (2013) found that the optimum pH for

adsorption of phenol using zeolite was at 3. Ponizovsky and Tsadilasc (2003) also noted that the use of clinoptilolite under acidic conditions was efficient in phenol removal in accordance with recommended values in the United States Environmental Protection Agency regulations (USEPA, 2002). The acidity of TOMW is favorable for arid KSA soils owing to compensation by the predominance of carbonate (CO_2^{-3}) and alkalinity in this soil type (Sierra et al., 2001).

4. Conclusions

Great amounts of OMW are produced in Saudi Arabia, where this waste causes negative environmental impacts. The KSA's UOMW is characterized by an intensive green–dark brown to black color and strong specific olive oil smell. UOMW's chemical characteristics include low pH and high total fat content, total phenols, NO_3^- , B, K, CHO_3^- , P, turbidity, OM%, and EC. In contrast, no heavy metal contamination was recorded in the KSA's UOMW. Potassium was found to be the predominant inorganic material (3.5 g L^{-1}); consequently, it is considered to be the main cause of UOMW salinity.

Several methods have been proposed for OMW treatment; however, very little research has been performed regarding the treatment of OMW using natural products. In this study, a simple low-cost method is proposed for treating the OMW produced in Saudi Arabia. Different treatments methods were investigated. The treatment of OMW using three successive columns of gravel, fine sand, and a mixture of acidified cotton using diluted acetic acid (1:10) and clinoptilolite (weight:weight ratio of cotton:clinoptilolite of 2:1), followed by treatment of the OMW with AC and lime, was found to be the most efficient treatment in terms of decreasing the concentration of NO_3^- , B, K, P, turbidity, total fat, and EC. Most contaminants were removed from OMW in the third column, the clinoptilolite column, owing to the high sorption affinity of clinoptilolite on its specific sites in the channel/cage systems. The AC was efficient in removing colloidal and soluble organic particle and the lime increased TOMW pH up to 5.1. This study confirms that K, which potentially increases water salinity, is the most common cation in UOMW, and the results show that the removal of K from UOMW by clinoptilolite decreased the salinity of OMW (desalination).

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