Abu-Dalo et al. BMC Chemistry (2024) 18:234
https://doi.org/10.1186/s13065-024-01348-3

BMC Chemistry

RESEARCH

Open Access

Olive mill wastewater treatment using vertical flow constructed wetlands (VFCWs)

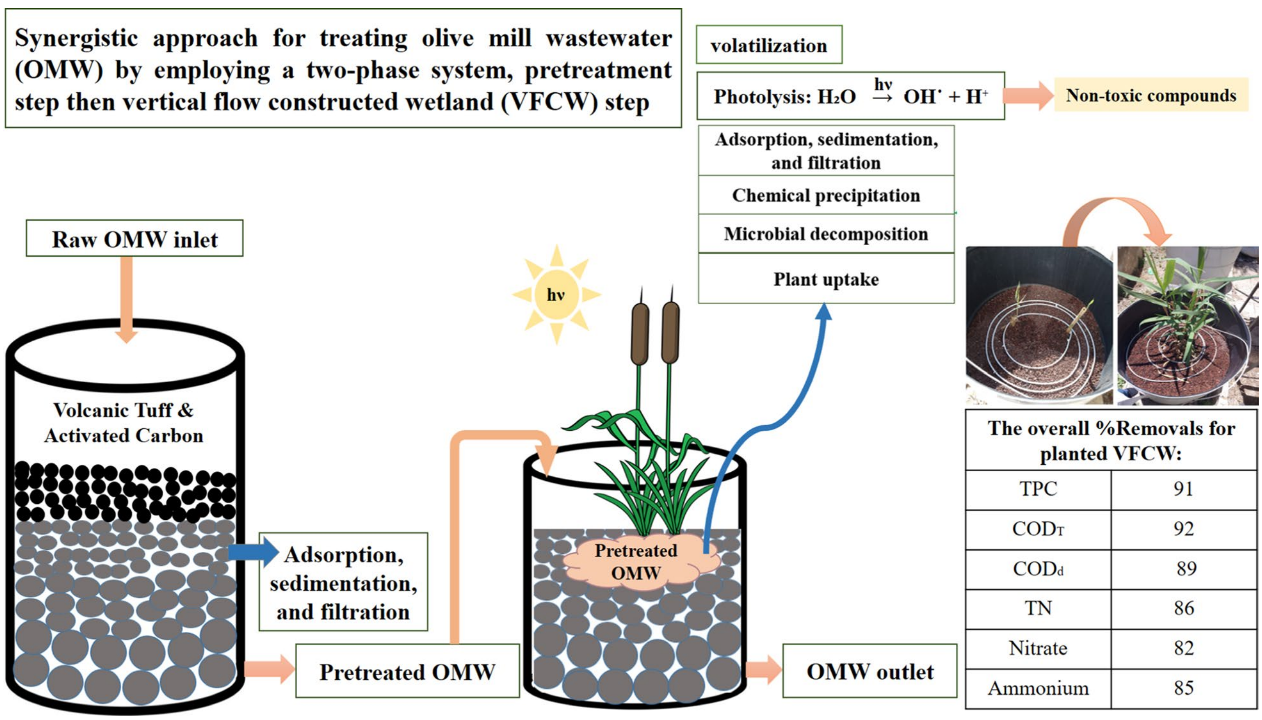
Muna Abu-Dalo[1*], Duaa Abu-Dalo[2,3], Maha Halalsheh[4] and Abeer Al Bawab[2,5,6*]

Abstract
The study explores a synergistic two-phase system to treat olive mill wastewater (OMW), comprising a multilayer adsorbent filter (pretreatment) and a vertical flow constructed wetland (VFCW). The pretreatment phase includes layers of commercial granular activated carbon (CGAC) and volcanic tuff (VT), while the VFCW phase consists of planted tank with *Phragmites australis reeds* and unplanted tanks. Initially, municipal wastewater is introduced into the VFCW to establish the required microbial community. Then, pre-treated OMW is passed through the VFCW. The removal rates of various pollutants were assessed. The planted VFCW showed superior removal efficiencies, averaging 97.82% for total chemical oxygen demand (COD_T), 92.78% for dissolved oxygen demand (COD_d), 99.61% for total phenolic compounds (TPC), 98.94% for total nitrogen (TN), 96.96% for ammonium, and 95.83% for nitrate. In contrast, the unplanted VFCW displayed lower removal efficiencies, averaging 91.47% for COD_T, 77.82% for COD_d, 98.53% for TPC, 97.51% for TN, 92.04% for ammonium, and 90.82% for nitrate. These findings highlight the significant potential of VFCWs, which offer an integrated approach to OMW treatment by incorporating physical, chemical, and biological mechanisms within a single treatment system.

Keywords Olive mill wastewater (OMW), Vertical flow constructed wetland (VFCW), Phenols, Total chemical oxygen demand, Dissolved chemical oxygen demand, Biological oxygen demand, *Phragmites australis reeds*

*Correspondence:
Muna Abu-Dalo
maabudalo@just.edu.jo
Abeer Al Bawab
drabeer@ju.edu.jo
Full list of author information is available at the end of the article

Graphical Abstract



Introduction

Olive mill wastewater (OMW) is an organic wastewater that results as a by-product of olive oil production [1]. It is a dark red to black acidic liquid with a pH of 4–5. It is considered one of the most polluting effluents since it contains high levels of organic compounds, total phenolic compounds (TPC), biological oxygen demand (BOD), chemical oxygen demand (COD), microorganisms, and toxic compounds [1].

TPCs are a group of phenolic compounds that exist in OMW such as phenols, phenolic acids, flavonoids, phenolic alcohols, secoiridoids, and secoiridoids derivatives. Phenolic acids include cinnamic, ferulic, coumaric, caffeic, gallic, etc. and phenolic alcohols include hydroxytyrosol and tyrosol [2]. They classify as hazardous compounds since they are difficult to biodegrade and can persist in the environment for extended periods, posing risks to humans, animals, plants, or any organism, including aquatic life. Moreover, they exhibit high reactivity with water or other compounds, leading to harmful byproducts such as alkylphenols, chlorinated phenols, nitrophenols, etc. [3].

In Jordan, most mills are automated and use the three-phase method in oil production since it is relatively the lowest in cost. However, a large amount of wastewater is thereby produced [4]. The Ministry of Environment has designated three dumpsites: Al-Ekaider in the north, Al-Humra in the middle, and Al-Lajjun in the south. Unfortunately, none of these sites have lined evaporation ponds, making them not equipped to manage OMW risks to the environment [5]. Consequently, addressing the pollution issue associated with OMW and implementing water recovery and reuse measures becomes imperative. Moreover, it is essential to consider the cost-effective management of OMW, including the utilization of low-cost technologies for operation and maintenance, alongside other management alternatives including OMW land application, OMW valorization, and capitalizing on decentralized disposal sites [4].

The treatment of OMW has emerged as a significant economic and environmental issue. Various methods have been explored to recover bioactive chemicals and phenolic compounds for several applications such as fertilizer production [6], nutritional uses [7], pharmaceutical applications [8], bio-products [2], and cosmetic formulations [9]. However, in regions facing water scarcity issues, treating OMW holds the potential for reusing the treated water in agricultural activities [10]. In Jordan, various approaches are tested for treating OMW, encompassing physical, chemical, biological, physiochemical, and biophysical technologies for treatment gain advantages and promising treatment, however, in the scale-up the costs still a limiting factor so currently OMW disposed into the dumpsite, evaporation ponds, or agricultural lands without any treatment [11–21].

Constructed wetlands (CWs) are natural treatment systems for wastewater, integrating physical, chemical, and biological processes into one system, utilizing planted shallow water bodies [22]. They were developed over the past many decades and offer a natural treatment method low-cost construction, improvement of the quality of wastewater by decreasing the concentration of contaminants, and an easy operation and maintenance approach [23]. However, there are two frequent treatment challenges in CWs; insufficient oxygen delivery and inadequate hydraulic flow [24]. CWs were initially used in municipal wastewater treatment then they were applied for the treatment of other types of wastewater such as landfill leachate, sludge, industrial wastewater, pharmaceutical wastewater, etc. [25]. According to the biological degradability ratio (BOD_5/COD), which measures the possibility of treatment of different types of wastewater by constructed wetlands, if this ratio is more than 0.5 the wastewater can be treated directly by CWs but a pretreatment step is essential for OMW treatment by CWs due to the low biological degradability ratio, which equals to 0.07- 0.19, primarily attributed to the high phenols content. This step is implemented to reduce the total phenolic compounds (TPC) and total suspended solids (TSS), thus increasing the biological degradability ratio, preventing clogging, and reducing pollutant concentrations to create a suitable environment for microorganism development [26, 27].

Pretreatment for OMW has been investigated using various technologies including physical treatment such as dilution [28] and adsorption [29], as well as biological treatments such as full-scale trickling filter [30]. Many studies have examined different operational conditions for the treatment of OMW using CWs. For instance, Mandi et al. utilized a sand filter in the pretreatment step along with dilution at 50% by domestic wastewater. Then they used a basin of *macrophytes plants* filled with gravel and soil planted with a mixture of aquatic plants [31]. In another study, Yalcuk et al. constructed a vertical subsurface flow wetland pilot scale using gravel, zeolite, and sand as bed media, with plantings of *Typha latifolia* and *Cyperus alternatifolius*. They introduced OMW, initially diluted with tap water to the wetland. Basins W1 and W2 were planted with *Typha latifolia* and *Cyperus alternatifolius*, respectively and W3 was left unplanted [32].

Herouvim et al. tested a pilot-scale vertical flow CW planted with *Phragmites australis reeds* and filled with various porous media (i.e., cobble, gravel, and sand). OMW was pretreated using a trickling filter and a recirculation tank [33]. Then two free water surface CW (FWSCW) were evaluated by Kapellakis et al. filled with coarse gravel as a substrate and planted with *Phragmites australis reeds*. The percentage removal of COD, TSS, and TPC reached 90%, 98%, and 87%, respectively [34]. A free water surface CW (FWSCW) with a large surface area planted with *Phragmites australis reeds* was used for OMW treatment, a trickling filter was used as a pretreatment step to reduce COD by 51% and TPC by 46%. The removal efficiency for FWSCW was 94% for COD and 95% for TPC [35].

Vertical Flow CWs (VFCWs) were used in many studies. One study employed a trickling filter as a pretreatment step. The VFCWs were planted with *Phragmites australis reeds* [30]. In another study, a sand filter was used for pretreatment and the VFCW was planted with a mixture of aquatic plants The authors concluded that the presence of aquatic plants was more efficient in removing nutrients and organic load [28]. El Ghadraoui et al. (2020) evaluated the efficiency of VFCW filled with sand, pozzolan, and gravel layers planted with *Phragmites australis reeds*, obtaining similar results for the removal of TPC, COD, and TSS. They achieved this by pretreating OMW through dilution with municipal wastewater [36] or urban wastewater [37].

This study, considered one of the few in Jordan to explore the dual-stage approach of CWs for OMW treatment, focused on developing VFCWs to address OMW treatment mechanisms through using different bed media, pretreatment procedure, type of plants, organic loading rates, and the surface area of the tank compared to previous studies. Initially, OMW underwent a pretreatment step aimed at reducing pollutants, including TPC, utilizing a tank filled with various adsorbent layers. Subsequently, the VFCWs were exposed to municipal wastewater to establish a biological treatment system. Once this first step was completed, the pretreated OMW was introduced into the VFCWs as the second phase of the process.

Experimental

Analytical methods

COD analysis was performed using the procedure in standard methods for the examination of water and wastewater [38], TPCs were measured via the Folin-Ciocalteu method using gallic acid as calibration standard [39], and BOD Measurement System BD600 (Lovibond, Greenwich, London, UK) was used to measure BOD for municipal wastewater in the first stage of CWs. According to the instruction manual (Spectrophotometer-Lovibond, 2017, Fisher Scientific, Oslo, Norway) the TN, nitrate, and ammonium were measured using method numbers 280, 265, and 60, respectively.

Characterization of OMW

The wastewater from various olive mills located in different regions of Jordan (including Jarash Mountains mill and Zayy automated mill) was collected and stored in a large tank for a month. Table 1 presents the characteristics of OMW before and after settling for a month, with a pH range of 4.10 to 4.80.

OMW pretreatment

Two adsorbents were selected for the pretreatment step, volcanic tuff (VT) with an adsorption capacity of 1.62 mg/g, collected from Al-Mafraq in Jordan, and commercial granular activated carbon-ULTRA type (CGAC) with an adsorption capacity of 3.31 mg/g, purchased from Chemviron carbon, USA. OMW was underwent two treatment stages. The first stage involved pretreatment, which utilized a large tank with a surface area of 0.95 m^2 filled with different layers of adsorbents and particle sizes. Specifically, the bottom layer, 18.00 cm in height was filled with 40–50 mm VT, the second layer, 23.00 cm in height, was filled with 10–40 mm VT, and the upper layer, 24.00 cm in height, was filled with a mixture of VT and CGAC (30% CGAC and 70% VT by weight) with an average particle size of 5–10 mm. The mean hydraulic retention time (HRT) of OMW in the pretreatment step was 38.26 d for the first month and then 70.64 d for the later months. The effluent from the first stage was then divided into two portions to feed the two second-stage reactors as shown in Fig. 1.

Table 1 The characteristics of OMW before and after settling at a pH range of 4.10 to 4.80

OMW characteristics	Raw OMW (ppm)	Feed OMW (ppm)
COD	58,452.00	55,333.00
TPC	176.00	176.00
TSS	5.44×10^4	0.48×10^4

VFCWs experiment

The vertical flow constructed wetlands were constructed within the University of Jordan (UJ) campus in Amman; adjacent to the Hamdi Mango Center for Scientific Research, as shown in Fig. 1 and Fig. 2. The study on CWs consists of two stages. In the first stage, the wetland tanks were continuously fed for over four months, from October 27, 2022, to March 2, 2023, with municipal wastewater collected from Wadi Shoaib wastewater treatment plant at As-Salt City having an average organic loading rate (OLR) of 30.32 g BOD/d.m^2 and average flow rate for municipal wastewater of 25.04 L/d to cultivate a bacterial

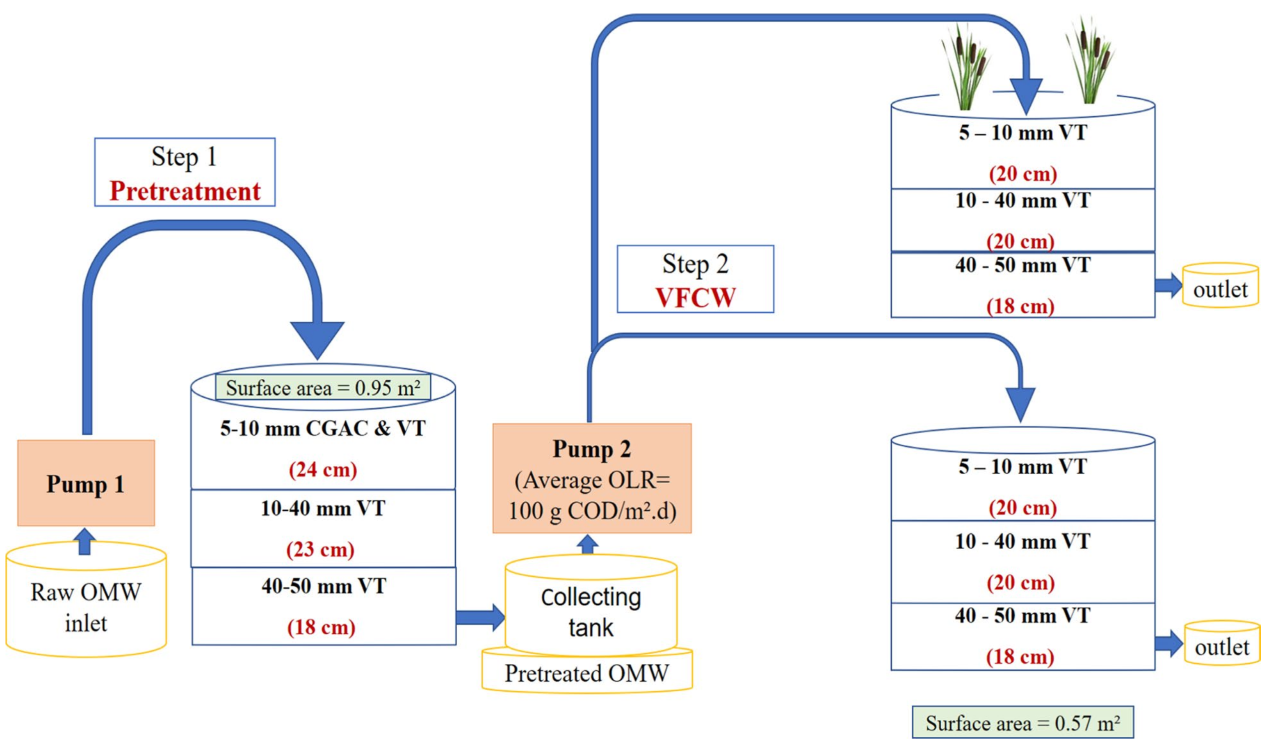


Fig. 1 The schematic system of the pretreatment step and VFCWs (unplanted and planted)

Fig. 2 The real constructed system

population in the wetlands, thereby enhancing biological processes. The mean hydraulic retention time (HRT) of municipal wastewater was 13.20 d. The BOD_5, total COD (COD_T), dissolved COD (COD_d), and nitrate content were analyzed for both the inlet and outlet. Inlet means values for BOD_5, COD_T, COD_d, and nitrate for planted and unplanted CW were 667.90 ppm, 848.33 ppm, 288.87 ppm, and 4.05 ppm, respectively. The removal of COD_d and nitrate served as indicators for the development of the bacterial community

In the second stage, the OMW underwent two treatment steps, the first step involved pretreatment, while the second stage consisted of wetlands of two identical tanks, each with a surface area of 0.57 m^2, both filled solely with VT. The bottom layer of each tank was 18.00 cm in height and consisted of particles sized 40–50 mm, the second layer was 20.00 cm high with particles sized 10–40 mm, and the upper layer was 20.00 cm high with particles sized 5–10 mm. Both VT and CGAC were used without any modification or sieving, the required particle sizes were purchased and used directly. One of the tanks was planted with *Phragmites australis reeds* (4 plants/m^2) sourced from Jerash stream (Fig. 3) and directly planted on October 20, 2022, while the other tank remained unplanted. The OLR of COD through the CWs was gradually increased to 100 gCOD/d.m^2. Initially, the mean OLR was 49.33 gCOD/d.m^2 (a flow rate of 4.80 L/d) for the first month, then it increased to 59.30 gCOD/d.m^2 (a flow rate of 2.31 L/d) for two weeks, further rise to 70.30 gCOD/d.m^2 (a flow rate of 2.80 L/d), and finally reached 100.57 gCOD/d.m^2 (a flow rate of 4.01 L/) by July 19, 2023. The mean HRT of OMW in the first month was 25.05 d then it was changeable according to the OLR values then in the steady state the Mean HRT was 17.34 d. This step-wise increase in OLR was attributed to the acclimation of the microorganisms to new environmental

Fig. 3 Jerash stream, the *Australian reeds plants*, were directly planted on October 20, 2022

parameters as their activity is variable depending on factors such as temperature, pH, salinity, nutrient concentration, pollutants concentration, etc. [40].

The flow was controlled using two peristaltic pumps (masterflex, USA) one for the pretreatment step and the other with two heads for the VFCW tanks. The flow rate was verified beforehand by measuring the volume of flow per unit time for each pump. The TPC, total COD, dissolved COD, total nitrogen (TN), ammonium (NH_4-N), and nitrate (NO_3-N) were weekly analyzed for the inlet and outlet. The temperature during the CWs experiment varied from 10 °C up to 28 °C, encompassing winter, spring, and summer.

Results and discussion

The first operational period for the VFCW (Municipal Wastewater)

This stage extended from October 27, 2022, to March 2, 2023; BOD_5, nitrate, COD_T, and COD_d analyses were conducted. Dissolved COD_d and nitrate analysis were used as indicators for development of bacterial communities. Figure 4 presents the percentage removal of BOD_5, nitrate, COD_T, and COD_d in the first stage for planted VFCW and unplanted VFCW. Figure 5 depicts the treated municipal wastewater samples in planted and unplanted CWs. It is evident that the presence of the reed plant improves and decolorizes municipal wastewater effluents, Alwared et al. demonstrated that the presence of reed is effective as a biosorbent for dyes uptake and decolorization of wastewater influents [41]. *Al-Balawenah used Australian reeds* in Jordan and found that the reeds provide sites for bacterial film adhesion, help with wastewater ingredient filtration and adsorption, introduce oxygen into the water column, and inhibit the growth of most algae by limiting sunlight penetration [42].

Figure 6 presents the growth of reeds during the first stage. Initially, the CWs were fed with municipal wastewater during which the reeds were 10.00 cm in height. The continuous feeding of municipal wastewater significantly enhanced the growth of reed plants. By the end of this stage, the reeds had grown to more than 1 m in height, and their green leaves had developed strongly, indicating a preliminary success of this step.

The COD_d and nitrate analysis confirm that the bacterial population effectively began growing on December 8, 2022. However, municipal wastewater continued to pass through CWs until March 2, 2023, to ensure that the biological mechanisms were in progress. Nitrogen removal processes in constructed wetlands are complex and involve various mechanisms, including assimilation by plants and microorganisms, adsorption by the substrate, sedimentation of organic nitrogen, ammonia volatilization, ammonification, nitrification, and denitrification. While traditional denitrification was once considered the primary pathway for nitrogen removal, alternative processes may also occur, such as anaerobic ammonium oxidation, where ammonium is directly converted to nitrogen gas (N_2) under anaerobic conditions at underlying zones at which the oxygen penetration cannot exist [43]. The nitrification–denitrification reactions are highly effective and can occur under aerobic conditions through two oxidation steps including the transformation of ammonium-N to nitrite-N and then the transformation of nitrite-N to nitrate–N and then the reduction of nitrate to N_2 or N_2O by denitrifying bacteria under anoxic conditions [24]. Another indication of bacterial growth is the high removal of BOD_5 and COD_d which confirms the presence of different biodegradation mechanisms. For example, the removal of BOD_5 occurs through bacterial oxidation of organic matter to produce CO_2 gas, which in turn, plays

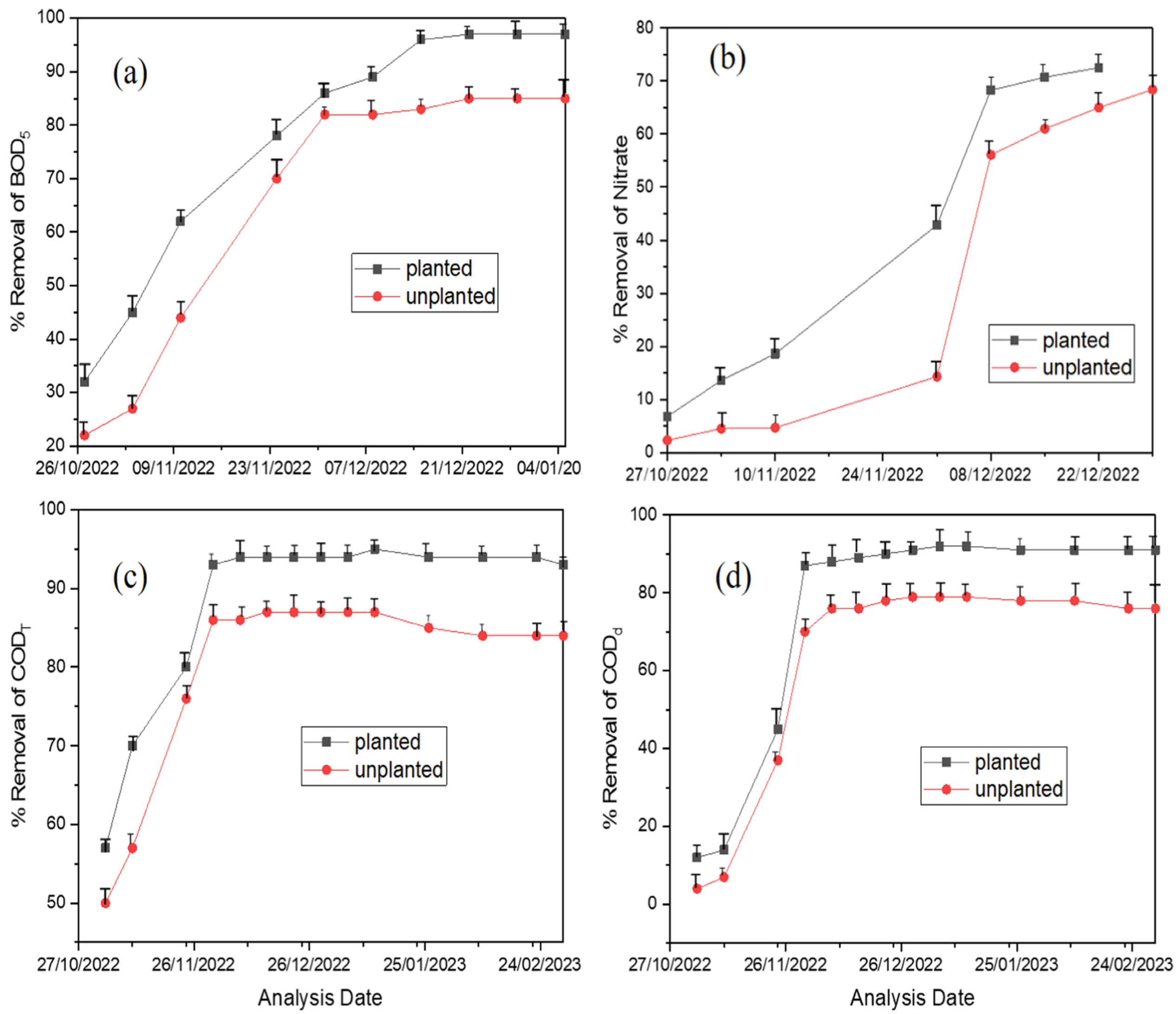


Fig. 4 The % removal of (**a**) BOD_5, (**b**) nitrate, (**c**) COD_T, and (**d**) COD_d of the first stage for planted VFCW and unplanted VFCW

a role in microbial photosynthesis to produce biomass [44].

The mean percentage removals of BOD_5, COD_T, COD_d, and nitrate were 93.70%, 93.90%, 90.31%, and more than 73.24% for planted CW and 83.72%, 85.80%, 77.51%, and more than 68.12% for unplanted CW, respectively. Several studies in the literature have been conducted to treat wastewater using the CWs approach with different systems and OLRs. Lower OLRs than those in this research were used. For instance, Nivala et al. tested two full-scale vertical flow (VF) constructed wetlands and demonstrated removal efficiencies in COD and BOD_5 of 95% and 97%, respectively, which were higher than those achieved in this research, this disparity may be attributed to the use of lower OLRs. In their study, they investigated two full-scale vertical flow (VF) constructed wetlands: one was a recirculating VFCW, which is considered a modification step, and the other was a single-pass two-stage VFCW. They concluded that the modification step didn't significantly alter the removal of BOD_5 and COD_T; however, the TN removal was enhanced but still limited to 45% [45]. Abunaser and Abdelhay developed four VFCW, and the removal efficiencies for BOD_5, COD, and TSS were 90%, 90%, and 92%, respectively, lower than those achieved in this research. However, the effluent concentrations of TP, TN, nitrate, Mg^{2+}, Ca^{2+}, SO_4^{2-}, turbidity, and heavy metals were consistent with the Jordanian standards [46]. A significant enhancement was achieved using VFCW and recirculating the effluent back into a recirculation tank containing treated wastewater

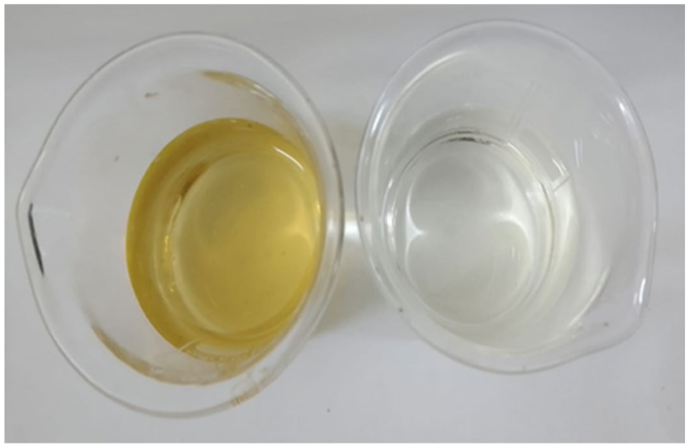


Fig. 5 Treated municipal wastewater samples in planted and unplanted VFCWs on February 23, 2023

Fig. 6 *Phragmites australis reeds* growth during the first stage of the CWs experiment starting on October 27, 2022, until March 2, 2023

to enhance the nitrification process. The efficiency of the nitrification process reached 83% after a contact time of 48 h., and the removals of TSS, COD, BOD_5, TN, and NH_4-N were 96.1%, 95.5%, 93.7%, 51.9%, and 98.2%, respectively, using hydraulic loading rate (HLR) of 108 L/m^2.d [47]. These removal rates are higher than those obtained in this research, possibly due to using a recirculation tank that enhances the nitrification process.

Different studies have been conducted in CWs for wastewater treatment, but they achieved lower removal efficiencies than those in this research. Silveira et al. achieved COD_d and nitrate removal efficiencies of 50% and 85%, respectively, through the analysis of the ability of VFCW using two-pilot scale systems planted with *Phragmites australis* over 16 months [48]. Ajibade, and Adewumi, explored the potential of three aquatic macrophytes (plants) for the treatment of municipal wastewater: *Phragmites australis reeds*, *Water Hyacinth*, and *Cyanea*. They found removal efficiencies for BOD_5, COD_T, and nitrate of 62%, 48%, and 87% for *reeds*, 74%, 69%, and 93% for *Water Hyacinth*, and 59%, 53%, and 90% for *Cyanea*, respectively [49]. Jácome et al. reported that the average removals of COD and BOD_5 reached 69% ± 21 and 76% ± 17, respectively, by using a septic tank, followed by a horizontal subsurface flow constructed wetland (HSSF CW) filled with gravel and planted with *reeds* as a secondary step in the treatment of domestic wastewater [50].

The second stage (VFCWs Experiment)

The pretreatment step

The pretreatment step commenced from February 9, 2023, to July 12, 2023. TPCs, COD_T, COD_d, TN, ammonium, and nitrate analyses were conducted for both the influent and the effluent.

Figure 7 presents the removal efficiencies of COD_T, TPC, TN, ammonium, and nitrate for the pretreatment step. The results reveal excellent TPC removal, with influent OMW concentrations ranging from 186 to 178 ppm and effluent not exceeding 5 ppm. COD_T shows high removal rates of up to 95% from February 9, 2023, until March 22, 2023, indicating effective adsorption, filtration, and sedimentation processes. However, the removal decreases to 5.37% after 7 weeks of feeding, likely due to the adsorbents' surfaces becoming covered, thereby reducing available adsorption sites. It is important to note that COD_d will not be completely removed in the pretreatment step, as its removal requires biological and chemical mechanisms, such as advanced oxidation processes (AOPs), rather than physical mechanisms [51, 52]. The influent COD_T mean value was 37.65 g/L, with the effluent ranging from 0.85 to 15.23 g COD/L and a mean value of 6.31 g/L. This finding is consistent with the results of a study by Herouvim et al. (2011), which involved 12 pilot-scale VFCWs utilizing a trickling filter as a pretreatment approach, yielding a mean COD effluent concentration of 14.120 g/L [33].

TN, primarily originating from nitrogen-containing organic compounds [53], is predominantly removed in the pretreatment step through physical mechanisms. Nitrate is initially removed up to 91.40% of this step (from February 9, 2023, to March 15, 2023), after which the removal efficiency decreases to 61.31%. Similarly, ammonium removal starts at 85.08% and decreases to 66.37%. The high removal of TN compared to nitrate and ammonium is due to the superior physical mechanisms such as adsorption and sedimentation in the pretreatment step which were able to remove TN more likely than nitrate and ammonium which are in turn required biological mechanisms [53, 54]. Achak et al. utilized sand filters and dilution for the pretreatment of OMW, reporting average TN and ammonium removal efficiencies of 60.4% and 74.4%, respectively [28]. These values indicate lower mean removals in TN and almost equivalent removals in ammonium compared to this study, which is attributed to the use of activated carbon, believed to possess high sorption properties in this study. The excellent TPC removals are conducive to feeding low TPC concentrations into VFCWs, as phenols are highly toxic for microorganisms due to their antimicrobial agents [55, 56]. It is worth noting that the pretreatment step is essential for supporting microorganisms in the VFCWs and the improvement observed in this step is attributed to the use of CGAC ULTRA-type activated carbon, which exhibits high sorption properties.

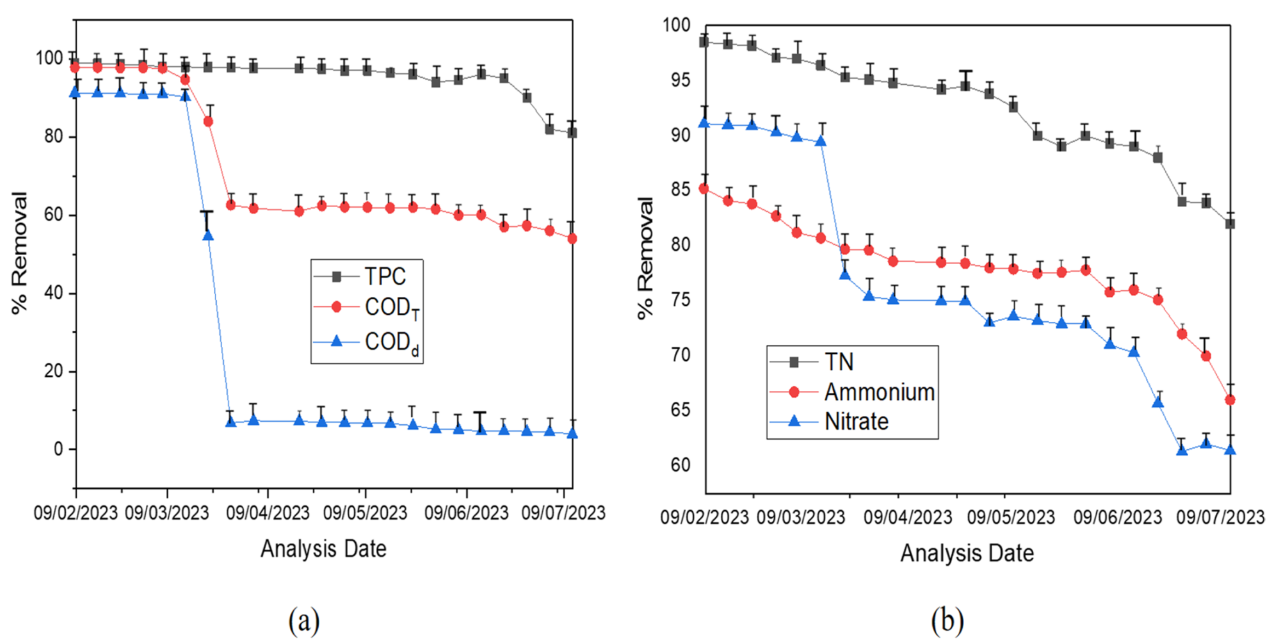


Fig. 7 The removals of (**a**) TPC, COD_T, and COD_d, (**b**): TN, ammonium, and nitrate for the pretreatment step from February 9, 2023, to July 12, 2023

Figure 8 illustrates the color change in OMW during the pretreatment step. Initially, the OMW effluents were colorless in the first month, but they gradually turned yellow in the subsequent months. The literature suggests several reasons for the formation of yellow-colored wastewater effluents, including slight increases in TPC or variations in oxygen concentrations within the volcanic tuff (VT) and CGAC, leading to oxidation–reduction chemical reactions. Consequently, new chromophores such as elemental chlorine-free (ECF) compounds are formed [57, 58].

The VFCWs step

Figure 9. displays the COD_T, COD_d, TPC, TN, ammonium, and nitrate results for planted and unplanted VFCWs. Initially, COD_T and COD_d (Fig. 9, a and Fig. 9, b) removals were low but increased over time, reaching optimal removal rates of 95% and 83% for COD_T, and 95% and 80% for $COD_{d,}$ in planted and unplanted CWs, respectively. TPC removal (Fig. 9, c) reached up to 95% and 72% for planted and unplanted CWs, respectively. Regarding nitrogen removals, TN (Fig. 9, d) and ammonium (NH_4-N) (Fig. 9, e) initially showed no removals, but their efficiency increased over time, reaching 89% and 70% for TN, and 88%, and 66% for ammonium in planted and unplanted CWs, respectively. This lack of initial removal is believed to be due to low dissolved oxygen concentrations within CWs, hindering the oxidation of TN and ammonium. Ammonium removal is highly dependent on oxygen availability [59], while nitrate reduction relies on the availability of carbon sites, enhancing denitrification reactions and potential uptake by plants [28]. Nitrate removals (Fig. 9, f) were very high during the period from March 2, 2023, to April 19, 2023, with effluent concentrations below 1 ppm, falling below the spectrophotometer's detection limit. However, from May 10, 2023, to June 7, 2023, nitrate removals decreased, likely due to increased ammonium concentrations promoting nitrification reactions and yielding higher nitrate concentrations [60]. Planted CWs demonstrated higher treatment efficiency than unplanted ones, indicating that reeds play a significant role in nitrogen and COD removal, a conclusion consistent with existing literature [30, 61, 62]. According to the results in the pretreatment step and CW step, the suggested mechanisms of pollutant removal at the pretreatment step are mainly adsorption according to the use of previously tested adsorbents (volcanic tuff and activated carbon) in CW, in addition to the adsorption, biological and chemical mechanisms are included due to the comparison between the inlet and outlet concentrations of TPC, COD_T, COD_d, nitrate, ammonium, and TN.

Table 2 presents the mean values of the characteristics of OMW at the pretreatment step, the VFCW step, the percentage removals for each stage, and the maximum allowable limits according to Jordanian standards compared to this research [63]. The pretreatment step enhanced the removal of TPC and TN mainly through the adsorption mechanism but exhibited high operation costs due to the use of CGAC. The removal efficiencies

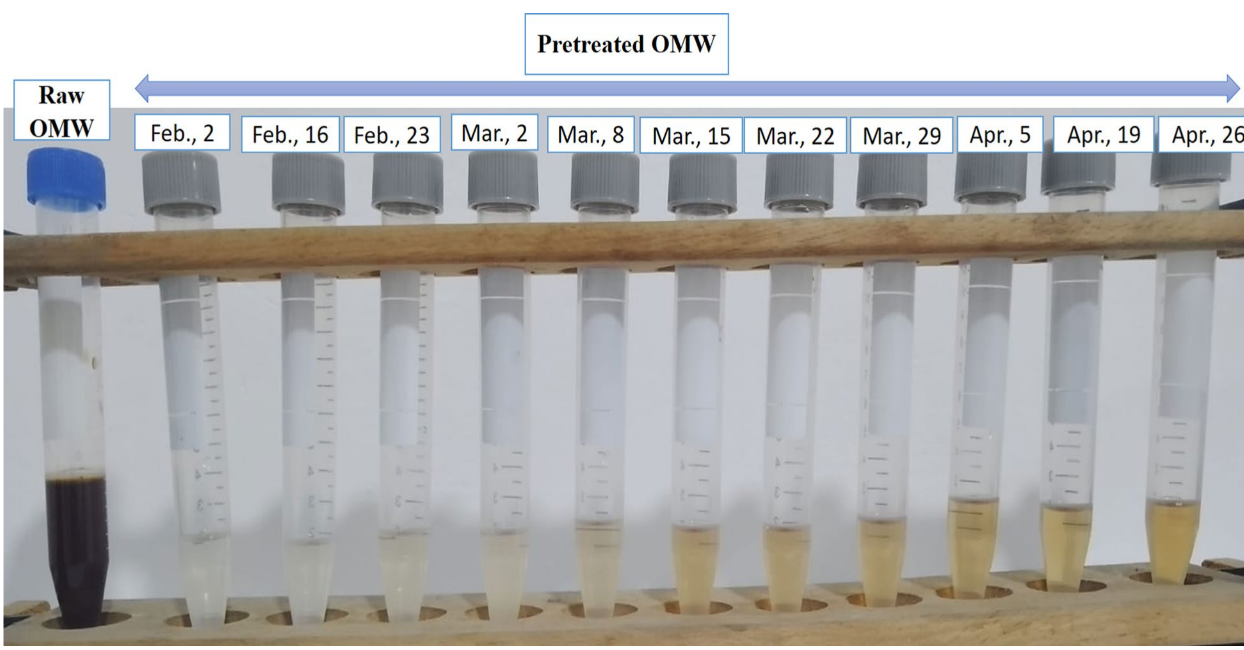


Fig. 8 The color change for OMW in the pretreatment step from February 2, 2023, to April 26, 2023

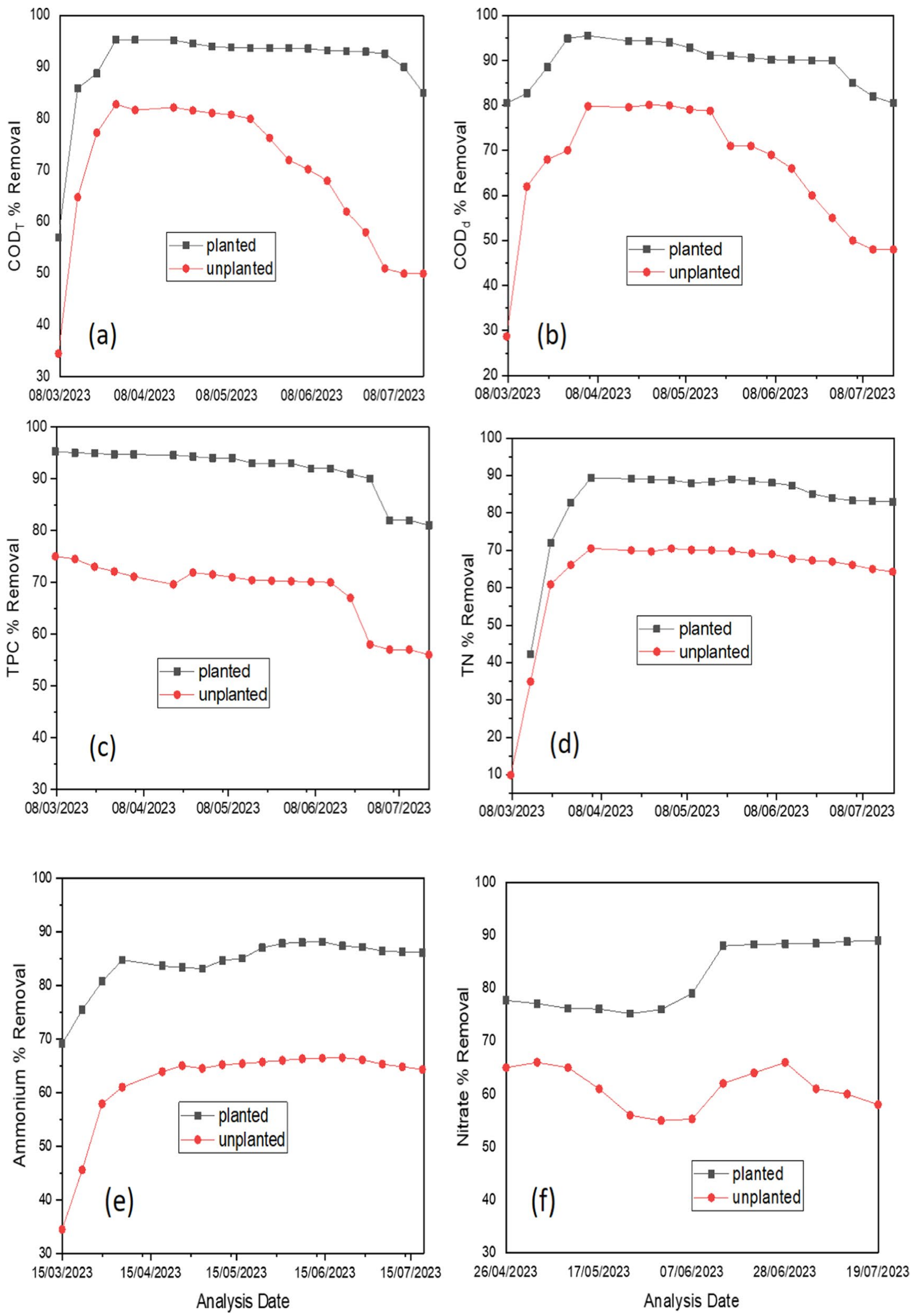


Fig. 9 The removals for planted and unplanted VFCW; **a** COD$_T$, **b** COD$_d$, **c** TPC, **d** TN, **e** ammonium, and **f** nitrate. The analysis started from May 8, 2023, until July 19, 2023. (SD = 0.13 – 1.48)

Table 2 The maximum allowable limits according to the Jordanian standards compared to this research and the mean values of the characteristics of OMW for the pretreatment step and VFCWs step (SD = 0.05 – 0.83)

	Pretreatment			VFCWs							
Characteristics	**OMW inlet**	**OMW outlet**	**%**	**Un-planted outlet**	**%**	**Overall % removal**	**planted outlet**	**%**	**Overall % removal**	**Max. allowable conc. for sewage-discharged wastewater**	**Max. allowable conc. of reclaimed water for Wadi discharge**
pH	4.83	6.81	–	7.08	–	–	6.99	–	–	5.5–9.5	6–9
COD_T (g/L)	37.61	10.82	71.32	3.20	70.41	91.51	0.81	92.50	97.80	1500	150
COD_d (g/L)	10.82	7.40	31.50	2.44	67.61	77.83	0.78	89.51	92.82	–	–
TPC (ppm)	182.58	8.51	95.31	2.73	68.22	98.69	0.74	91.33	99.61	5	< 0.002
TN (ppm)	610.60	46.78	92.36	15.10	67.70	97.54	6.70	85.74	98.92	100	70
Ammonium (ppm)	2.86	0.63	78.04	0.23	63.52	92.34	0.09	85.72	96.91	120	5
Nitrate (ppm)	102.52	24.32	76.33	9.45	61.10	90.81	4.31	82.30	95.78	–	80

in this study can be compared with the Achak et al. research [28]. They employed similar OLR and utilized planted CWs with a mix of aquatic plants including *Phragmites australis reeds*, *Typha latifolia*, and *Arundo donax*. Their study reported overall removal efficiencies as 99.05% for COD_T, 62.48% for TN, 90.43% for ammonium, and 77.25% for nitrate. Comparatively, the results in this research are similar in terms of COD_T and ammonium removal, but higher in TN and nitrate removal. This discrepancy can be attributed to the use of CGAC in the pretreatment step, which exhibits a high removal efficiency of TN. Despite the high removal percentage of TPC, its concentration in the effluent exceeded the allowable limits for discharge into water bodies as per Jordanian standards. This suggests the need for additional post-treatment approaches or the reuse of OMW effluent in other industries that adhere to allowable standards. Potential strategies to enhance the treatment process include increasing the percentage of ULTRA carbon in the pretreatment step.

The proposed mechanisms for OMW treatment using VFCWs in this research (Fig 10) can be included due to the comparison between the inlet and outlet concentrations of TPC, COD_T, COD_d, nitrate, ammonium, and TN, the pretreatment step are mainly physical mechanisms such as adsorption and sedimentation. In CW, biological and chemical mechanisms are included in addition to physical mechanisms such as microbial degradation, plant uptake, pyrolysis, etc. In general, according to the literature, CW constitutes a complex mixture of wastewater, plants, substrate, and a variety of microorganisms, where each component plays a distinct role in pollutant removal through various chemical, physical, and biological mechanisms, including adsorption, sedimentation, filtration, precipitation, degradation, microbial reactions [24, 64, 65]. During the initial operational period, utilizing municipal wastewater, which contains numerous electron donors, enhances biological mechanisms such as the development of aerobic and anaerobic organisms, promoting microbial decomposition processes like denitrification, aerobic nitrification, and soluble COD biodegradation [51, 66–68]. In the subsequent stage, the pretreatment step primarily involves physical mechanisms. The VT and CAGC serve as support for the plants, offering numerous sites for chemical and biological interactions, effectively storing pollutants through adsorption, sedimentation, and filtration. These mechanisms facilitate the removal of solids, suspended COD/

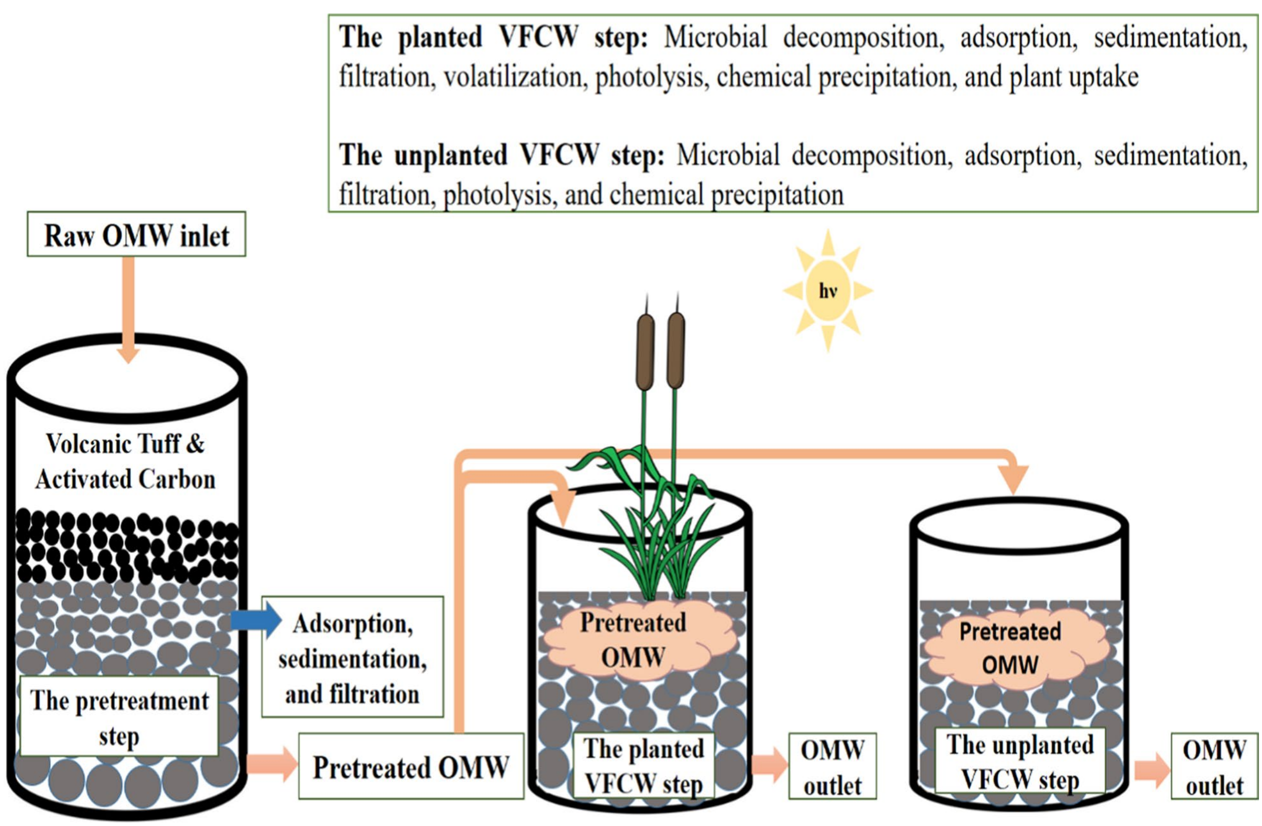


Fig. 10 The proposed synergistic mechanisms for the OMW treatment using VFCWs in this research

BOD, heavy metals, synthetic organics, pathogens, and nutrients [24, 69]. The utilization of CGAC provides significant advantages, particularly in enhancing the adsorption of TPC, TN, COD_d, and other suspended pollutants. CGAC is regarded as an ideal adsorptive material due to its potential for regeneration, large surface area, ease of handling, and provision of high contact time between wastewater and carbon [19, 70].

In the VFCW step, apart from physical and biological mechanisms, the role of plants significantly influences removal mechanisms. Nitrogen, organic matter, phosphorous, and heavy metals can be removed through various mechanisms occurring at different parts of the plants. These mechanisms include different aerobic degradation processes, facilitated by the leakage of O_2 from plant roots into the rhizosphere (oxygen diffusion), the photolysis process occurring within plant tissues (phytodegradation), which generates radicals that serve as an energy source for microbial activity, subsequently aiding in the decomposition of organic matter, and the growth of microorganisms around the roots, where the roots act as a suitable surface, slowing down the hydraulic flow and providing carbon for denitrification processes [24, 69, 71, 72]. Other treatment mechanisms can be involved in CWs including photolysis, volatilization, and chemical precipitation [24, 69].

Recommendations

Cost analysis was not the purpose of this research but it is important to study the cost in the future to enhance the performance of CW using cost-effective materials in the scaling-up experiments. Cost analysis will be done after the optimization experiment.

Conclusions

Constructed wetlands (CWs) have gained significant attention recently as a promising alternative technology for wastewater treatment. In this study, a vertical flow constructed wetland (VFCW) was specifically designed to utilize integrated mechanisms for treating olive mill wastewater (OMW) and improving the removal of both organic and inorganic substances present in OMW. The research demonstrated that a pretreatment step before the CWs effectively reduced the concentration of harmful TPC, thereby enhancing the efficiency of CWs.

Moreover, the planted VFCW showed promising treatment efficiencies, outperforming the unplanted counterpart. This underscores the importance of vegetation in OMW treatment via CWs. However, selecting suitable plant species for constructed wetlands requires thorough assessment through large-scale experiments, considering the challenges associated with long-term plant development and species competition dynamics in constructed wetland environments. In summary, CWs provide an integrated approach to OMW treatment, incorporating physical, chemical, and biological mechanisms within a single treatment system. While the study demonstrated promising removal efficiency, further research is needed to optimize TPC removal and meet Jordanian standards for wastewater reuse or discharge.

Abbreviations

BOD	Biological oxygen demand
CGAC	Commercial granular activated carbon
COD_d	Dissolved chemical oxygen demand
COD_T	Total chemical oxygen demand
OLR	Organic loading rate
OMW	Olive mill wastewater
TN	Total nitrogen
TPC	Total phenolic compounds
TSS	Total suspended solids
VFCWs	Vertical flow constructed wetlands
VT	Volcanic tuff

Acknowledgements

We acknowledge the use of ChatGPT for assistance in proofreading.

Author contributions

"Conceptualization, M.H., A.B.A., and M.A.; methodology, M.H., D.A, and M.A.; validation, M.H., D.A., A. B.A., and M.A; formal analysis, D.A., A.A.B., M.A., and M.H.; investigation, D.A.; resources, A.A.B., M.A., and D.A.; data curation, D.A.; writing—original draft preparation, D.A.; writing—review and editing, D.A., M.H., M.A. and A.A.B.; visualization, D.A; supervision, A.A.B., and M.A.; project administration, A.A.B., and M.A.; funding acquisition, A.A.B., M.A. All authors have read and agreed to the published version of the manuscript."

Funding

This research was funded by the Middle East Desalination Research Center (MEDRC) (project No. 18-PJ-01) and the Deanship of Academic Research (DAR) (project No. 1942). /The University of Jordan", Amman, Jordan.

Availability of data and materials

The data that support the findings of this study are available on request from the corresponding authors.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

Author details

[1]Chemistry Department, Faculty of Science and Arts, Jordan University of Science & Technology, Irbid, Jordan. [2]Chemistry Department, School of Science, The University of Jordan, Amman, Jordan. [3]Basic Pharmaceutical Science Department, Faculty of Pharmacy, Middle East University, Amman, Jordan. [4]Water Energy and Environment Center, The University of Jordan, Amman, Jordan. [5]Hamdi Mango Center for Scientific Research, The University of Jordan, Amman, Jordan. [6]Nanotechnology Center, The University of Jordan, Amman, Jordan.

Received: 25 June 2024 Accepted: 13 November 2024
Published online: 21 November 2024

References

1. Zahi MR, Zam W, El Hattab M. State of knowledge on chemical, biological and nutritional properties of olive mill wastewater. Food Chem. 2022;381: 132238.
2. Rahmanian N, Jafari SM, Galanakis CM. Recovery and removal of phenolic compounds from olive mill wastewater. J Am Oil Chem Soc. 2014;91:1–18.
3. Mohamad Said KA, Ismail AF, Abdul Karim Z, Abdullah MS, Hafeez A. A review of technologies for the phenolic compounds recovery and phenol removal from wastewater. Process Saf Environ Prot. 2021;151:257–89.
4. Halalsheh M, Kassab G, Shatanawi K. Impact of legislation on olive mill wastewater management: Jordan as a case study. Water Policy. 2021;23:343–57.
5. S Ayoub. Management of olive by-products in Jordan. 2017.
6. Galanakis CM. Recovery of high added-value components from food wastes: Conventional, emerging technologies and commercialized applications. Trends Food Sci Technol. 2012;26:68–87.
7. Zhou J, Gullón B, Wang M, Gullón P, Lorenzo JM, Barba FJ. The application of supercritical fluids technology to recover healthy valuable compounds from marine and agricultural food processing by-products: a review. Processes. 2021;9:357.
8. Jimenez-Lopez C, Fraga-Corral M, Carpena M, García-Oliveira P, Echave J, Pereira AG, et al. Agriculture waste valorisation as a source of antioxidant phenolic compounds within a circular and sustainable bioeconomy. Food Funct. 2020;11:4853–77.
9. Gil-Martín E, Forbes-Hernández T, Romero A, Cianciosi D, Giampieri F, Battino M. Influence of the extraction method on the recovery of bioactive phenolic compounds from food industry by-products. Food Chem. 2022;378: 131918.
10. Federici F, Fava F, Kalogerakis N, Mantzavinos D. Valorisation of agro-industrial by-products, effluents and waste: concept, opportunities and the case of olive mill wastewaters. J Chem Technol Biotechnol Int Res Process Environ Clean Technol. 2009;84:895–900.
11. Abu-Dalo M, Abdelnabi J, Bawab AA. Preparation of activated carbon derived from jordanian olive cake and functionalized with Cu/Cu2O/CuO for adsorption of phenolic compounds from olive mill wastewater. Materials. 2021;14:6636.
12. Abu-Dalo M, Abdelnabi J, Al-Rawashdeh NAF, Albiss B, Al BA. Coupling coagulation-flocculation to volcanic tuff-magnetite nanoparticles adsorption for olive mill wastewater treatment. Environ Nanotechnol Monit Manag. 2022;17: 100626.
13. Abu-Dalo MA, Al-Atoom MA, Aljarrah MT, Albiss BA. Preparation and characterization of polymer membranes impregnated with carbon nanotubes for olive mill wastewater. Polymers. 2022;14:457.
14. Al Bawab A, Ghannam N, Abu-Mallouh S, Bozeya A, Abu-Zurayk RA, Al-Ajlouni YA, et al. Olive mill wastewater treatment in Jordan. IOP Conf Ser Mater Sci Eng. 2018. https://doi.org/10.1088/1757-899X/305/1/012002.
15. Al Bawab A, Abu-Dalo M, Khalaf A, Abu-Dalo D. Olive mill wastewater (OMW) treatment using photocatalyst media. Catalysts. 2022. https://doi.org/10.3390/catal12050539.
16. Al-Bawab A, Alshawawreh F, Abu-Dalo MA, Al-Rawashdeh NA, Bozeya A. Separation of soluble phenolic compounds from olive mill wastewater (OMW) using modified surfactant. Fresenius Environ Bull. 2017;26:1949–58.
17. Al-Bawab A, Ghannam N, Abu-Zurayk RA, Odeh F, Bozeya A, Mallouh S, et al. Olive mill wastewater remediation by granular activated carbon impregnated with active materials. Fresenius Environ Bull. 2018;27:2118–26.
18. K Kanaan. coupling activated carbon with surface active materials for olive mill wastewater treatment. Jordan University of Science and Technology; 2017.
19. Abu-Dalo MA, Al-Rawashdeh NAF, Almurabi M, Abdelnabi J, Bawab AAl. Phenolic compounds removal from olive mill wastewater using the composite of activated carbon and copper-based metal-organic framework TI2. Mater. 2023. https://doi.org/10.3390/ma16031159.
20. Odeh F, Bawab A, Fayyad M, Bozeya A. Surfactant enhanced olive oil Mill wastewater remediation. APCBEE Proc. 2013;5:96–101.
21. Odeh F, Abu-Dalo M, Albiss B, Ghannam N, Khalaf A, Amayreh HH, et al. Coupling magnetite and goethite nanoparticles with sorbent materials for olive mill wastewater remediation. Emergent Mater. 2022;5:77–88.
22. Atuga G, Jembe T. Chapter 15 - Constructed wetlands' application for flower farms wastewater treatment in developing countries: Case study in Kenya. In: Stefanakis A, Nikolaou I, editors. Circular economy and sustainability. Amsterdam: Elsevier; 2022.
23. Vymazal J. The Historical Development of Constructed Wetlands for Wastewater Treatment. Land. 2022. https://doi.org/10.3390/land11020174.
24. Ellis JB, Shutes RBE, Revitt DM. Guidance manual for constructed wetlands. Environment Agency; 2003.
25. Varma M, Gupta AK, Ghosal PS, Majumder A. A review on performance of constructed wetlands in tropical and cold climate: Insights of mechanism, role of influencing factors, and system modification in low temperature. Sci Total Environ. 2021;755: 142540.
26. Del Bubba M, Checchini L, Pifferi C, Zanieri L, Lepri L. Olive mill wastewater treatment by a pilot-scale subsurface horizontal flow (SSF-h) constructed wetland. Ann Chim J Anal Environ Cult Herit Chem. 2004;94:875–87.
27. Skrzypiec K, Gajewska MH. The use of constructed wetlands for the treatment of industrial wastewater. J Water Land Dev. 2017. https://doi.org/10.1515/jwld-2017-0058.
28. Achak M, Boumya W, Ouazzani N, Mandi L. Preliminary evaluation of constructed wetlands for nutrients removal from olive mill wastewater (OMW) after passing through a sand filter. Ecol Eng. 2019;136:141–51.
29. Dan A, Fujii D, Soda S, Machimura T, Ike M. Removal of phenol, bisphenol A, and 4-tert-butylphenol from synthetic landfill leachate by vertical flow constructed wetlands. Sci Total Environ. 2017;578:566–76.
30. Tekerlekopoulou AG, Akratos CS, Vayenas DV. Integrated biological treatment of olive mill waste combining aerobic biological treatment, constructed wetlands, and composting. In: olive mill waste. Amsterdam: Elsevier; 2017.
31. Mandi L, Achak M, Ouazzani N. Characterisation of olive mill effluents and treatments essays by sand filters followed by macrophytes systems. Linnaeus Eco-Tech. 2010. https://doi.org/10.1562/Eco-Tech.2010.027.
32. Yalcuk A, Pakdil NB, Turan SY. Performance evaluation on the treatment of olive mill waste water in vertical subsurface flow constructed wetlands. Desalination. 2010;262:209–14.
33. Herouvim E, Akratos CS, Tekerlekopoulou A, Vayenas DV. Treatment of olive mill wastewater in pilot-scale vertical flow constructed wetlands. Ecol Eng. 2011;37:931–9.
34. Kapellakis IE, Paranychianakis NV, Tsagarakis KP, Angelakis AN. Treatment of olive mill wastewater with constructed wetlands. Water. 2012;4:260–71.
35. Michailides M, Tatoulis T, Sultana M-Y, Tekerlekopoulou A, Konstantinou I, Akratos CS, et al. Start-up of a free water surface constructed wetland for treating olive mill wastewater. Hem Ind. 2015;69:577–83.
36. El Ghadraoui A, Ouazzani N, Ahmali A, El Mansour TEH, Aziz F, Hejjaj A, et al. Treatment of olive mill and municipal wastewater mixture by pilot scale vertical flow constructed wetland. Desalin Water Treat. 2020;198:126–39.
37. El Ghadraoui A, Ouazzani N, Saf C, Ahmali A, Hejjaj A, Aziz F, et al. Behaviour of physicochemical and microbiological characteristics of vertical flow constructed wetland substrate after treating a mixture of urban and olive mill wastewaters. Environ Sci Pollut Res. 2021;28:55433–45.
38. Rice EW, Baird RB, Eaton AD, Clesceri LS. Standard methods for the examination of water and wastewater. DC: American public health association; 2012.
39. Leouifoudi I, Harnafi H, Zyad A. Olive mill waste extracts: polyphenols content, antioxidant, and antimicrobial activities. Adv Pharmacol Sci. 2015;2015: 714138.
40. Benny CK, Chakraborty S. Dyeing wastewater treatment in horizontal-vertical constructed wetland using organic waste media. J Environ Manage. 2023;331: 117213.
41. Alwared AI, Jaeel AJ, Ismail ZZ. New application of eco-friendly biosorbent giant reed for removal of reactive dyes from water followed by sustainable path for recycling the dyes-loaded sludge in concrete mixes. J Mater Cycles Waste Manag. 2020;22:1036–46.
42. Al-Balawenah EA. using constructed wetlands to improve wastewater quality in Jordan.
43. Hu Y, He F, Ma L, Zhang Y, Wu Z. Microbial nitrogen removal pathways in integrated vertical-flow constructed wetland systems. Bioresour Technol. 2016;207:339–45.

44. Singh A, Pandey AK. Microalgae: an ecofriendly tool for the treatment of industrial wastewaters and biofuel production. Boca Raton: CRC Press; 2018.
45. Nivala J, Abdallat G, Aubron T, Al-Zreiqat I, Abbassi B, Wu G-M, et al. Vertical flow constructed wetlands for decentralized wastewater treatment in Jordan: optimization of total nitrogen removal. Sci Total Environ. 2019;671:495–504.
46. Abunaser SG, Abdelhay A. Performance of a novel vertical flow constructed wetland for greywater treatment in rural areas in Jordan. Environ Technol. 2020. https://doi.org/10.1080/09593330.2020.1841832.
47. Al-Zreiqat I, Abbassi B, Headley T, Nivala J, van Afferden M, Müller RA. Influence of septic tank attached growth media on total nitrogen removal in a recirculating vertical flow constructed wetland for treatment of domestic wastewater. Ecol Eng. 2018;118:171–8.
48. Silveira DD, Belli Filho P, Philippi LS, Kim B, Molle P. Influence of partial saturation on total nitrogen removal in a single-stage French constructed wetland treating raw domestic wastewater. Ecol Eng. 2015;77:257–64.
49. Ajibade F, Adewumi J. Performance evaluation of aquatic macrophytes in a constructed wetland for municipal wastewater treatment. FUTA J Eng Eng Technol. 2017;11:1–11.
50. Jácome JA, Molina J, Suárez J, Mosqueira G, Torres D. Performance of constructed wetland applied for domestic wastewater treatment: case study at Boimorto (Galicia, Spain). Ecol Eng. 2016;95:324–9.
51. Choi Y-Y, Baek S-R, Kim J-I, Choi J-W, Hur J, Lee T-U, et al. Characteristics and biodegradability of wastewater organic matter in municipal wastewater treatment plants collecting domestic wastewater and industrial discharge. Water. 2017;9:409.
52. Meng X, Wu J, Kang J, Gao J, Liu R, Gao Y, et al. Comparison of the reduction of chemical oxygen demand in wastewater from mineral processing using the coagulation–flocculation, adsorption and Fenton processes. Miner Eng. 2018;128:275–83.
53. Winkler M-KH, Meunier C, Henriet O, Mahillon J, Suárez-Ojeda ME, Del Moro G, et al. An integrative review of granular sludge for the biological removal of nutrients and recalcitrant organic matter from wastewater. Chem Eng J. 2018;336:489–502.
54. Rahimi S, Modin O, Mijakovic I. Technologies for biological removal and recovery of nitrogen from wastewater. Biotechnol Adv. 2020;43: 107570.
55. Ntougias S, Bourtzis K, Tsiamis G. The microbiology of olive mill wastes. BioMed Res Int. 2013;13: 784591.
56. Obied HK, Bedgood D Jr, Prenzler PD, Robards K. Bioscreening of Australian olive mill waste extracts: biophenol content, antioxidant, antimicrobial and molluscicidal activities. Food Chem Toxicol. 2007;45:1238–48.
57. Auchterlonie J, Eden C-L, Sheridan C. The phytoremediation potential of water hyacinth: a case study from Hartbeespoort Dam, South Africa. South Afr J Chem Eng. 2021;37:31–6.
58. Milestone CB, Fulthorpe RR, Stuthridge TR. The formation of colour during biological treatment of pulp and paper wastewater. Water Sci Technol. 2004;50:87–94.
59. Lu J, Guo Z, Kang Y, Fan J, Zhang J. Recent advances in the enhanced nitrogen removal by oxygen-increasing technology in constructed wetlands. Ecotoxicol Environ Saf. 2020;205: 111330.
60. Poor C, Burrill K, Jarvis M. Efficiency of constructed wetlands for nutrient removal. In: World environmental and water resources congress. Reston: American Society of Civil Engineers Reston; 2020.
61. Dordio A, Carvalho AJP. Constructed wetlands with light expanded clay aggregates for agricultural wastewater treatment. Sci Total Environ. 2013;463:454–61.
62. Tatoulis T, Stefanakis A, Frontistis Z, Akratos CS, Tekerlekopoulou AG, Mantzavinos D, et al. Treatment of table olive washing water using trickling filters, constructed wetlands and electrooxidation. Environ Sci Pollut Res. 2017;24:1085–92.
63. Water-Industrial reclaimed wastewater. 2007.
64. Hoffmann H, Platzer C, Winker M, von Muench E. Technology review of constructed wetlands—subsurface flow constructed wetlands for greywater and domestic wastewater treatment. Dtsch Ges Für Int Zusammenarbeit GIZ GmbH Eschborn Ger. 2011;11:35.
65. Wang W, Zhang Y, Li M, Wei X, Wang Y, Liu L, et al. Operation mechanism of constructed wetland-microbial fuel cells for wastewater treatment and electricity generation: a review. Bioresour Technol. 2020;314: 123808.
66. Inc M, Tchobanoglous G, Stensel H, Tsuchihashi R, Burton F. Wastewater engineering treatment and resource recovery. New York: McGraw Hill; 2013.
67. Rana V, Maiti S. Municipal and industrial wastewater treatment using constructed wetlands. Cham: Springer; 2020.
68. Winkler M-KH, Kleerebezem R, de Bruin LMM, Verheijen PJT, Abbas B, Habermacher J, et al. Microbial diversity differences within aerobic granular sludge and activated sludge flocs. Appl Microbiol Biotechnol. 2013. https://doi.org/10.1007/s00253-012-4472-7.
69. Stanković D. Constructed wetlands for wastewater treatment. Građevinar. 2017. https://doi.org/10.1425/JCE.2062.2017.
70. Çeçen F, Aktas Ö. Activated carbon for water and wastewater treatment: integration of adsorption and biological treatment. Hoboken: John Wiley & Sons; 2011.
71. Stottmeister U, Wießner A, Kuschk P, Kappelmeyer U, Kästner M, Bederski O, et al. Effects of plants and microorganisms in constructed wetlands for wastewater treatment. Biotechnol Adv. 2003;22:93–117.
72. Yaragal RR, Mutnuri S. Nitrates removal using ion exchange resin: batch, continuous column and pilot-scale studies. Int J Environ Sci Technol. 2023;20:739–54.

Publisher's Note