Testing a pilot-scale of constructed wetlands for pharmaceutical wastewater treatment using Jordanian zeolitic tuff

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Abstract. A pilot scale of constructed wetlands (CWs) was designed, constructed and operated on August 2022 at pharmaceutical factory in Jordan. This pilot is aiming to remove pharmaceuticals (i.e. antibiotics) from treated industrial wastewater generated from secondary activated sludge system. Jordanian zeolitic tuff (RZT) and its modification (MRZ) were used as the wetland media in all CWs. A tidal flow constructed wetlands (TF) filled with MRZ was used for the first stage treatment followed by a horizontal subsurface flow (HSSF) filled with RZT as the second stage treatment. To date, the system was operated under the hydraulic loading rate 0.32 m/day for 75 days. The average influent concentrations of COD, TN, and TP were 286, 25, 6 mg/l respectively. The removal performance of COD, TN, and TP achieved up to 55%, 67%, and 25% in the CWs pilot. The removal of three key pharmaceutical compounds, i.e., ciprofloxacin, ofloxacin, flumequine was also monitored in the pilot. Over 99% removal efficiency was achieved for ciprofloxacin and ofloxacin. However, the removal efficiency performance of flumequine achieved up to 68%. The pilot results demonstrated a promising performance for innovate nature-based solutions for pharmaceuticals removal, however, the pilot performance should be evaluated over the whole year to (four seasons).
Keywords: Pilot-scale, Jordanian zeolitic tuff, pharmaceutical compounds; constructed wetlands; industrial wastewater.

1. Introduction

Nowadays, constructed wetlands (CWs) are considered as a nature-based solution to treat different types of wastewaters such as agricultural wastewaters, landfill leachate, urban stormwater, and industrial wastewater, including paper and pulp, food processing, chemical, textile, and tannery effluents (Ravikumar et al., 2022). The substrate used in the CWs is a critical component as it helps for biofilm attachment, enhance the plant growth, and provide reactive substances for pollutants transformation. Previous studies used sand or gravel as substrate in treating pharmaceutical wastewater (Ilyas et al., 2020). However, the removal efficiency of gravel is low due to the low capabilities for pollutant entrapment and microorganism attachment. Therefore, there is a crucial need to find a new promising cheap material with high removal efficiency. Therefore, this study aims to evaluate the efficiency of raw zeolitic tuff in constructed wetlands for treating pharmaceutical wastewater at pharmaceutical factory in Jordan.

2. Materials and methods

Jordanian zeolitic tuff was purchased from Agriculture Green Zeolite CO., The local wetland plant, i.e. Typha angustifolia (Typha), was collected from the Zarqa River at Jordan. The hybrid constructed wetlands systems were designed, constructed and operated using 1m3 IBC tanks, with dimensions of 1 m in height, length, and width.

2.2 Zeolitic Tuff Preparation and Characterization

Raw zeolitic tuff (RZT) was modified by hydrophobic modification methodology using HCL (Al-Jammal, N. et al 2019). The modified zeolite was referred as MRZ. The selected size used in this study was 6-10 mm as the wetland media. Powder X-ray diffraction (XRD) patterns of the RZT sample was recorded by XRD (Rigaku Miniflex 600) using copper Kα irradiation (λ = 1.5406 nm) produced at 45 kV and 15 mA. The XRD diffraction patterns were obtained in the 2θ range of 0–50◦. The chemical compositions of the RZT was determined using a sequential X-ray fluorescence (XRF) spectrometer (XRF-S8, Bruker Co., Tiger, Germany).

2.1. Pilot scale setup

A pilot-scale of hybrid constructed wetland system was built at a local pharmaceutical factory in Amman, Jordan (Fig. 1). The two stage-system consists of a tidal flow (TF) and a saturated horizontal subsurface flow (HSSF). The TF tank was filled with MRZT while the HSSF tank was filled with RZT. Both tanks were each comprised of a drainage layer (20 cm in height) at the bottom and a main treatment layer (70 cm in height) at the top. One of the most common wetland plants in Jordan, i.e. Typha angustifolia (Typha), was collected and planted in both systems.

Figure1. Photo of the pilot-scale operated at pharmaceutical industry

2.2. Water quality and pollutant analysis

Water samples were collected from 3 points over 75 days operation. Water samples were collected from the influent and effluent of each stage approximately every two weeks. The pH, electrical conductivity (EC), and turbidity were measured using multi- probes (Multi 9630 IDS WTW, Hach, Germany). The concentrations of chemical oxygen demand (COD), total phosphorus (TP), total nitrogen (TN) were analysed using a spectrophotometer (XD 7000 (VIS), Lovibond, Germany). Pharmaceutical compounds in the water samples were detected using the method developed by Al-Mashaqbeh et al., (2019).

3. Results and discussion

XRD analysis for RZT was carried out to determine the crystalline structure and the results are presented in Figure 2. It is well known that phillipsite, faujasite, diopside, calcite, and anorthite are common mineral components that appear in Jordanian zeolitic tuff (Al Jammal et.al., 2019).

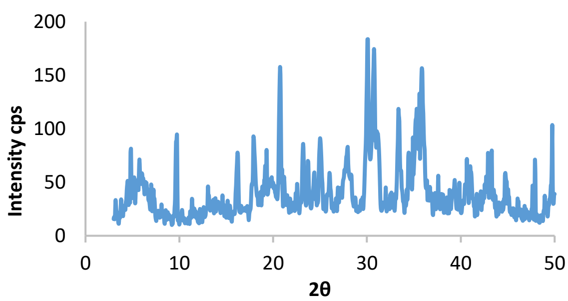

Figure 2. XRD analysis for RZT

Table 1 shows the result of XRF analysis for RZT. The Si/Al ratio of 3.4 was calculated for RZT. The major metal oxides present in the sample are SiO2, Al2O3, Fe2O3, MgO, CaO, K2O, and Na2O. The LOI, which stands for loss on ignition, is considered a common method for determining the organic and carbonate content of samples (Heiri et al., 2001). The LOI shows the volatile portion after the heating of RZT. The loss on ignition percentage of 9.42% for RZT.

Table 1. Result of XRF analysis for RZT

Compound	Metal oxides wt%	Compound	Metal oxides wt%
CaO	9.6	Na2O	1.59
SO3	0.18	Cl	0.09
Fe2O3	15.2	Al2O3	11
SrO	0.12	SiO2	37
TiO2	2.2	MgO	10.7
K2O	1.68	MnO	0.15
P2O5	1	LOI	9.42

The average influent concentration of industrial wastewater for pH, Electrical conductivity (EC), turbidity, COD, TN, TP were 7.57, 2466 (μS/cm), 78 (NTU), 286 (mg/l), 25 (mg/l), 6 (mg/l) respectively as shown in Table 2. Over 126 days, the average flow rate of the hybrid CWs was 119 mL/min with a hydraulic loading rate (HLR) of 1.90 m/d. In addition, the average water temperature was 10.1°C. Table 2 shows the average concentration of COD, TN and TP in the hybrid CWs.

Table 2. The average concentration of water quality parameter at the hybrid CWs

Parameter	Influent	Effluent MRZT tank	Effluent RZT tank
pH	7.57	6.95	6.98
EC (μS/cm)	2466	3077	3621
Turbidity (NTU)	78	8	4
COD (mg/L)	286	165	128
TN (mg/L)	25	10	8
TP (mg/L)	6	5	5

The average overall removal efficiency of COD, TN and TP were estimated and achieved up to 55%, 67%, and 25%. Ravichandran and Philip 2021 reported the removal of COD, TN & PO4 was 73%, 84% & 64% for natural zeolite. The results in this study is lower than those found by Ravichandran and Philip 2021. This difference is due to the variance of experiment conditions such as the mode of operation, operating conditions, and different in the type of wastewater (Lima et al.,2018).

The overall removal efficiency of 3 antibiotic compounds (ciprofloxacin, erythromycin and flumequine) was evaluated at hybrid CWs. The average influent concentration of ciprofloxacin, ofloxacin and flumequine was 818 µg/l, 466 µg/l, 434 µg/l respectively (Table 3). The average overall removal efficiency was observed for ciprofloxacin, ofloxacin and flumequine to be 100%, 100% and 68% respectively.

Table 3. The average concentration of pharmaceutical compounds at the hybrid CWs

Pharmaceutical compounds	Influ ent	Efflue nt MRZT tank	Effl uent RZT tank	Overall removal efficienc y, %
Ciprofloxacin(µg/l)	818	19	4	99
Ofloxacin (µg/l)	466	11	0.3	99
Flumequine (µg/l)	434	252	138	68

The results of this study showed the performance of RZT and MRZT is very high towards antibiotics. Similar trend was reported by Chen et al., (2016) who evaluated the removal of antibiotic using different types of substrates (i.e. oyster shell, zeolite, medical stone, and ceramic). He found that the highest removal was achieved using zeolite.

4. Conclusıon

This study clearly showed that using hybrid CWs is feasible for removing organic, nutrients as well as pharmaceuticals using zeolitic tuff and its modification. The results show a good performance for using hybrid constructed wetland to remove antibiotic (ciprofloxacin, ofloxacin) with over 99% removal and 68% of flumequine. Moreover, the performance of raw zeolitic tuff is similar to its modification which is clealry enough to be used as a substrate in CWs.

Acknowledgment

This work was supported by the Transforming Systems through Partnership (TSP) project sponsored by the UK Royal Academy of Engineering (TSP2021\100376). The project title is "Development of a nature-based solution for pharmaceutical wastewater treatment in Jordan".

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