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Removal of Emerging Pollutants from Industrial Wastewater Using Nature-Based Solution

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Abstract
Three groups of multistage hybrid constructed wetlands (CWs) were evaluated in this study for treating pharmaceutical wastewater in Jordan. In each group, a tidal flow CW (TFCW) was used for the first stage treatment followed by a horizontal subsurface flow CW (HSSF CW) as the second stage treatment. Normal sand, raw zeolitic tuff (RZT), and modified zeolite were used as the wetland media in all TFCWs, however, the second stage HSSF CWs were filled with raw zeolites. To date, the system was operated under the hydraulic loading rate 2.02 m/day in all TFCWs for 3 months. The average influent concentrations of COD, PO4, TN were 366.3, 12.6, 10.3 mg/L respectively. The removal of five key pharmaceutical compounds, i.e. carbamazepine, ciprofloxacin, enrofloxacin, ofloxacin, and diclofenac, was also monitored in the three groups. All groups performed over 99% removal of ciprofloxacin, ofloxacin, and enrofloxacin. However, the removal performances of carbamazepine and diclofenac only achieved up to 27.1% and 32%, respectively, in all groups. The results demonstrated the feasibility of using innovate nature-based solutions for pharmaceuticals removal and provided the data for the further pilot-scale study and implementations.

Keywords
Green technology; modified zeolite; micropollutant; treatment wetlands; water reuse.

INTRODUCTION

Recently, CWs is being successfully implemented in many countries as it is one of the most sustainable and promising alternatives for treating wastewater. The substrate used in the CWs is a critical component as it serves 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, H. et al. 2020). However, gravel removal efficiency 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 works aims to evaluate the efficiency of raw zeolitic tuff, and modified zeolite in constructed wetlands for treating pharmaceutical wastewater at pharmaceutical factory in Jordan.

MATERIALS AND METHODS

Materials

Microcosm-scale constructed wetland systems were designed, constructed and operated using 6 galvanized steel (1.5mm) tanks filled with Jordanian zeolitic tuff Ø6-10 mm.

Zeolite modification

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.

Design and operation of constructed wetlands

Three groups of multistage hybrid CWs were used to treat pharmaceutical wastewater (Fig.1). In each group, a tidal flow CW (TFCW) was used for the first stage treatment followed by a horizontal subsurface flow CW (HSSF CW) as the second stage treatment. Normal sand (Ø5-10 mm), RZT (Ø6-10 mm), and MRZ (Ø6-10 mm), were used as the wetland media in all TFCWs, however, the second stage HSSF CWs were filled with RZT. In the bottom, the larger size of gravel was placed to collect the water. The main media layer (~ 35 cm) was normal sand, RZT and MRZ. Stainless steel pipe with 10 holes (5 mm Ø) was installed at the bottom of the tank to drain the water. The systems were placed outdoor open to the natural environment apart from the precipitation. The systems were stabilized at the beginning for three months to enable the development of biofilms on substrate surfaces and plant growth. Typha one of the most common plant in constructed wetlands was collected from Zarqa River at Jordan. The real industrial wastewater was brought from the local pharmaceutical factory and pumped to the CW systems in winter. Water samples were collected from 7 points after 20 days operation. The systems were operated as followings: the tidal flow system was run under the tidal flow mode (12 hrs fill + 12 hrs draining: pump/pour water into the system and let them stay for 12 hrs, then, open the valve let the water drain and leave them for another 12 hrs.) The systems are operating automatically using timers.

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Figure 1: Microcosm-scale constructed wetland systems operated at Royal Scientific Society, Jordan.

RESULTS AND DISCUSSION

The average influent concentration of industrial wastewater for pH, COD, PO4, TN were 7.68, 366.3, 12.6, 10.3 mg/l respectively (Table 1). The removal performance of COD, PO4, TN achieved up to 36%, 59.8%, 41.4% in all groups.

Table 1: Characterization pH, COD, PO4, TN of and performance of CWs groups.

Parameter	Concentration Influent mg/l	Group 1		Group 2		Group 3	
		Effluent mg/l	% Removal	Effluent mg/l	% Removal	Effluent mg/l	% Removal
pH	7.68	7.82	-	7.98	-	7.72	-
COD	366.3	236.5	36.0	268.8	26.0	225.8	32.9
PO4	12.6	6.7	59.8	6.1	53.4	12.2	20.4
TN	10.3	5.3	41.4	5.0	40.4	5.2	37.9

The results showed that 5 pharmaceutical compounds (Carbamazepine, Ciprofloxacin, Enrofloxacin, Ofloxacin, and Diclofenac) were detected in three groups CWs (Table 2). The overall

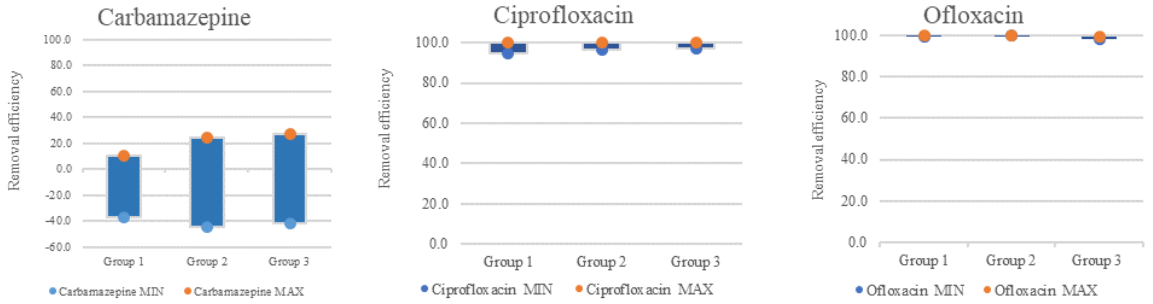
removal efficiencies were evaluated for the three groups. The highest removal efficiencies were recorded for ciprofloxacin, ofloxacin and enrofloxacin in all groups (>99%). The removal efficiencies of Carbamazepine and diclofenac were low ranging from -44% to 27.1%, -23.9% to 32% respectively. The highest removal efficiency of CBZ and Diclofenac were achieved in group 3 (27.1%, 32% respectively). This could be attributed to their large distribution and resistance to degradation, as they present high octanol-water partition coefficient (log Kow) values ranging from 2.45 to 4.5. It is well documented in the literature that log Kow indicates the hydrophilic character of a molecule where the high values of log Kow are reflecting high hydrophobicity (Vargas, J. et al.2021). Moreover, these low results for carbamazepine and diclofenac are consistent with those reported in previous studies (Ilyas, H. et al. 2020).

The impact of modification using HCL was evaluated in this study. The results clearly showed that the uptake of MRZ for most pharmaceutical compounds is higher than RZT than sand. This is explaining the highest overall removal efficiency has been achieved in group 3 (Table 2). It is well documented in the literature that modification of zeolite using hydrochloric acid (HCL) enhance the adsorption capacity by increasing the hydrophobicity of the natural zeolite since the adsorption capacity is directly dependent on their aluminum content, and hydrophobicity increase with an increase in the Si/Al ratio (Wang, B. et al 2021).

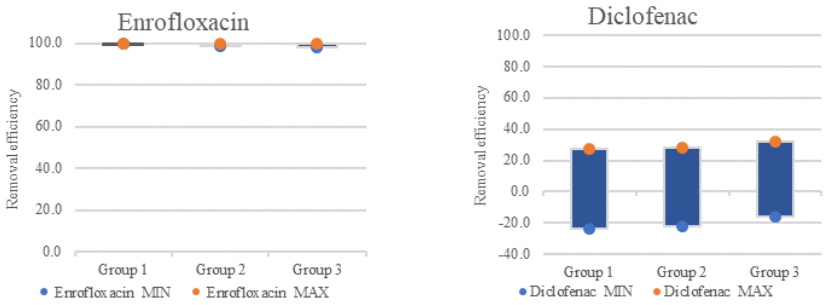
Table 2: Characterization of pharmaceuticals compounds and overall removal of CWs groups.

		Group 1		Group 2		Group 3	
Pharmaceuticals	Average Concentration Influent mg/l	Average Effluent mg/l	% Overall Removal	Average Effluent mg/l	% Overall Removal	Average Effluent mg/l	% Overall Removal
Carbamazepine	476.9	496.4	-10.1	399.7	-0.6	390.9	0.9
Ciprofloxacin	464.8	8.5	97.3	5.4	98.3	4.0	98.7
Enrofloxacin	365.3	0.0	100.0	2.6	99.1	2.8	98.9
Ofloxacin	474.2	1.0	99.7	1.6	99.7	2.4	99.2
Diclofenac	2016.3	1867.6	-0.1	1859.3	-2.4	1774.1	0.5

Figure 2 shows the minimum and maximum overall removal efficiency for 5 pharmaceuticals in all groups. The results showed that the overall removal efficiency at group 3 > group 2> group 1 for most of pharmaceutical compounds. This is mainly due to the high performance of TFCW using MRZ.



(a) (b) (c)



(d) (e)

Figure 2: Minimum and maximum overall removal efficiency for carbamazepine, ciprofloxacin, enrofloxacin, ofloxacin, and diclofenac.

It is important to mention here that the results reported in this paper are very promising since these results representing the collected samples during the winter (temperature = 0 – 10ºC). So, it is expected that the efficiency removal by CWs will be highly increased during the warm weather. Varma, M. et al. 2021 has mentioned that the performance of CW's is highly affected in cold climate due to several limiting factors such as drying up of plants, decline in microbial action, freezing and clogging of pipes resulting in inadequate removal efficiency.

CONCLUSION

The results of starting up stage show a good performance in all groups with over 99% removal of ciprofloxacin, ofloxacin, and enrofloxacin. However, the removal efficiencies of carbamazepine and diclofenac has varied from negative percent to 27.1% and 32%, respectively. The results demonstrated the feasibility of using innovate nature-based solutions for pharmaceuticals removal and provided the data for the further pilot-scale study and implementations. The reported results in this paper are representing the startup operation of CWs groups and during the winter season (from December 2021 until February 2022). So, it is expected that the efficiency removal by CWs will be highly increased during the summer season.

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