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Short communication

BTEX removal in a modified free water surface wetland

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GRAPHICAL ABSTRACT

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ABSTRACT

A pilot scale free water surface (FWS) wetland with provision of additional intermediate berms composed of gravel material was tested for assessing its potential to remediate hydrocarbons present in produced water from a gas field. The average influent BTEX values were as follows: benzene (1.57 mg/L), toluene (0.14 mg/L), ethyl benzene (0.29 mg/L), m and p-xylene (2.01 mg/L) and o-xylene (0.13 mg/L). The FWS wetland removed all monitored hydrocarbons with very good removal efficiencies during the monitoring period: benzene (92.6%), toluene (93.4%), ethyl benzene (98.3%), m and p-xylene (91.3%) and o-xylene (87.4%). Biodegradation was considered to be the main pathway for benzene removal in the studied system. Reaction kinetics were studied and the first-order area based rate coefficient for benzene was 0.13 m/d while for BTEX it was 0.12 m/d. Metagenomic analysis of bacterial community retrieved from the wetland showed majority of sequences were related to phylum *proteobacteria*.

1. Introduction

Constructed wetlands have been successfully used to treat different types of wastewaters including effluents from industrial setups [1]. Both surface flow and subsurface flow constructed wetlands have been used to treat wastewaters containing petroleum hydrocarbons [2]. Pilot and full-scale systems have been developed and operated to treat wastewater containing hydrocarbons in various geographical locations.

A pilot scale subsurface flow wetland consisting of four cells was constructed at the former British Petroleum (BP) Refinery in Casper, Wyoming, USA in 2002 [2]. It was tested to determine benzene, toluene, ethylbenzene, and xylene (BTEX) degradation rates in a cold-climate application. Based on the results of the pilot system, a full-scale wetland was commissioned in 2003 to remediate 6000 m^3/day of hydrocarbon contaminated groundwater [3]. Another interesting project is a full-scale treatment wetland constructed by BP for groundwater

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remediation known as the Wellsville, New York Wetland Treatment system that processes 840 m^3/d of contaminated groundwater. The two systems operate under cold climate conditions and have demonstrated steady removal of hydrocarbons over multi-year periods [4].

In 2010, BAUER commissioned the Nimr Water Treatment Project for treatment of oil-polluted produced water in Oman. It has a capacity to process 45,000 m^3/day of produced water. The project is spread over an area of 600 hectares and includes a surface flow constructed wetland to remediate hydrocarbons. The free water surface constructed wetland covers an area of 234 hectares [5].

Experiments were conducted at the University of Edinburgh, Scotland, UK to investigate benzene removal in vertical flow constructed wetlands [6]. The influent benzene concentration was 1000 mg/L benzene while the mean benzene removal efficiencies were between 72.66% and 89.77%.

Most of the previous studies to assess hydrocarbon removal in constructed wetlands have been conducted in the developed part of the world where temperatures are low, except for the Nimr wetland situated in Oman. The developed constructed wetland is the first of its kind in the oil and gas sector of Pakistan [7]. A pilot scale free water surface (FWS) wetland with a slight design modification was built at a gas field in Sindh province of Pakistan to test whether full scale treatment wetlands could be used to treat produced water containing petroleum hydrocarbons under local environmental conditions. Design modification included provision of additional berms composed of gravel in the FWS cells. The main objectives of this study are as follows:

- To test the performance concerning BTEX removal in a pilot scale free water surface wetland with modified design
- To investigate benzene removal mechanisms
- To study reaction kinetics for benzene and BTEX

2. Materials and methods

2.1. Pilot system design

The pilot FWS wetland consisted of two treatment cells each having a surface area of 50 m^2 and planted with *Phragmites* and *Typha.* A total of 4 berms composed of gravel each having a depth of 12 cm and width of 12 cm were added to the wetland cells. The design flow rate was 3 m^3/day and an operating water depth of 45 cm was maintained so the highest possible load could be applied to the system. Details have been published in Mustafa and Raza [7].

2.2. Monitoring

Monitoring of the wetlands for various monitoring parameters and hydrocarbons started in July 2013 and continued for one year. Water samples were collected from three points: the inlet to FWS wetland, the outlet of cell 1 and outlet of cell 2 for twelve consecutive months. Samples were monitored for benzene-toluene-ethylbenzene-xylene (BTEX) compounds using standard methods [8]. The mean influent and effluent values with standard deviations of the monitored parameters are shown in Table 1.

Removal efficiency was calculated as the percent reduction in the effluent concentration comparative to their respective influent concentrations. The removal efficiency was calculated as follows:

$$\text{Removal efficiency (\%)} = \frac{C_o - C}{C_o} \quad (1)$$

where

C_o = initial influent concentration (mg/L)
C = effluent concentration (mg/L)

The reactions that occur in wetland s are considered to follow the first-order kinetics. The mean areal rate constant k based on an assumed three tanks in series (3TIS) [2] were also calculated for BTEX compounds using the following equation:

$$\frac{C - C^*}{C_i - C^*} = \frac{1}{(1 + k/Pq)^P} \quad (2)$$

where:

C_i = inlet concentration
C = outlet concentration
C^* = background concentration
k = area-based first order rate coefficient, m/d
P = apparent number of TIS
q = hydraulic loading rate, m/d (flow divided by wetland area)

2.3. Metagenomic analysis

Metagenomic DNA was purified from water samples obtained from the wetland using CTAB method for bacterial 16S rDNA metagenomic analysis. PCR amplification of bacterial 16S rDNA using V1–V3 region primers was carried out with purified DNA as template. DNA sequencing using 16S rDNA amplicons was carried out by NGS platform MiSeq (Illumina Inc., USA) according to manufacturer's instructions. Quality of obtained sequence reads was checked by using FastQC program. Sequence reads were filtered by Prinseq program (minimum read length = 150 bp and min quality score = 12). For sequence database searching, the sequence reads were submitted to BlastN [9] against bacterial 16S rDNA sequence database. BlastN results were analysed by MEGAN program [10].

3. Results and discussion

3.1. Removal of BTEX

The commissioned wetland received produced water that had variable influent characteristics (Table 1). As the influent water passed through the wetland, hydrocarbons were removed resulting in significant water quality improvements. The average influent BTEX values were as follows: benzene (1.57 mg/L), toluene (0.14 mg/L), ethyl benzene (0.29 mg/L), m and p-xylene (2.01 mg/L) and o-xylene (0.13 mg/L). The FWS wetland removed all monitored contaminants with good removal efficiencies during the monitoring period: benzene (93%), toluene (93%), ethyl benzene (98%) as shown in Fig. 1 below. Xylene removal was also good; m and p-xylene (91%) and o-xylene (87%). It was interesting to note that the wetland successfully removed hydrocarbons also in winter condition when temperature dropped to a minimum of 7 °C. However, there was decrease in BTEX removal efficiency with a temperature drop. The minimum value of benzene in FWS wetland effluent was 0.005 mg/L while maximum value was 0.28 mg/L. This is in agreement with former studies showing higher benzene removal at higher temperatures [6,11]. Haberl et al. [12] reported on the efficiency of a pilot-scale vertical flow constructed wetlands for removal of hydrocarbon-contaminated groundwater at former Amoco Refinery Site in Casper, Wyoming, USA. The pilot system was operated in an upward vertical flow mode and removal of benzene and BTEX,

Table 1
BTEX concentrations (mg/L) in influent and effluent (mean ± standard deviation) of the modified FWS wetland.

S.No.	Parameters	Influent	Effluent	Removal percentage
1	Benzene	1.573 ± 0.760	0.117 ± 0.099	92.6
2	Toluene	0.144 ± 0.066	0.010 ± 0.006	93.4
3	Ethylbenzene	0.292 ± 0.163	0.005 ± 0.001	98.3
4	M & P-Xylene	2.000 ± 1.266	0.175 ± 0.135	91.3
5	O-Xylene	0.131 ± 0.078	0.0165 ± 0.011	87.4