

Application of Constructed Wetlands with Modified Substrate in Produced Water Treatment

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Abstract- Produced water also known as oilfield brine is one of the largest waste by volume produced during oil and gas exploration activities. Its high volume, complex composition, environmental and health hazards makes it one of the most critical waste in the waste stream of the oil and gas industry. Most wastewater treatment methods employed in the treatment of PW are often energy-intensive, costly, and generate harmful by-products. With more stringent regulations on produced water handling and disposal, there is the need for the application of more efficient yet cost effective, less energy intensive and minimal by-products systems. One of such system is the constructed wetland that mimics nature. To this end, this study investigated the performance of a constructed wetland system with modified substrates for the treatment of produced water, focusing on the removal of heavy metals (Cd, Pb, and Zn) and oil and grease (O&G). A batch scale, three (3) constructed wetland experimental setup arranged in series was established. Gravel, coarse sand, loamy soil, and biochar were used as substrates. *Phragmites australis*, a common reed species was planted in each constructed wetland. Heavy metals were analyzed using Atomic Absorption Spectrophotometer while oil and grease was analyzed by gravimetric method. Results of the study demonstrated appreciable removal efficiencies for heavy metals (Pb: 82%, Cd: 75%, Zn: 74%) and O&G (86%) within a short hydraulic retention time of 45 minutes. This suggest that constructed wetland with a biochar layer can serve as an effective and eco-friendly treatment method for produced water.

Keywords: Constructed Wetlands, Produced water, Biochar, oil and Grease, heavy metals.

I. INTRODUCTION

The exploration and production of fossil fuel are often accompanied by the generation of significant volumes of produced water (PW). PW is a complex mixture of formation water, injection water, and various organic and inorganic compounds [1-3]. It is also referred to as oilfield brine and known to contain oil, grease, heavy metals, radionuclides, treating chemicals, formation solids, salts, dissolved gases, scale products, waxes, microorganisms, and dissolved oxygen [3,4]. The composition and volume of produced water can vary substantially depending on the geological formation, reservoir age, and the type of hydrocarbon produced [5,6]. These complexities pose significant challenges for the oil and gas industry in terms of safely handling and disposing of produced water, which is often a highly regulated and closely monitored process.

The oil-to-water volume ratio during production, is conventionally estimated at 1:3 [7]. This indicates

that for every unit of oil extracted, three units of water are utilized and then discharged as wastewater. The high volume of produced water is one of the critical problem in the waste management of the oil and gas industry [8,9]. Globally, environments around oil and gas exploration activities suffer significant environmental degradation because of generation of produced water among others [10,11]. This has called for proper management of produced water with a focus on cost effectiveness and environmental preservation [12,13].

One management strategy of produced water is injection of produced water into the formation well. Although this is primarily intended to increase oil production it also serves a dual purpose [14,15]. But with the limited availability of injection sites and more stringent regulations in produced water management, produced water disposal has become the last resort for the oil and gas industries. This has led to the exploration of more innovative methods for the treatment of produced water to meet safe limits for disposal into water bodies [16,17].

Some common technologies explored for the treatment of oil produced water before it is disposed into water bodies or reinjected into wells include; biological treatment methods (activated sludge, biological aerated filters, bio-electrochemical treatment, fixed-film treatment, etc.), chemical treatment methods (precipitation, chemical oxidation, coagulation and flocculation, electro-photocoagulation, etc.), and physical treatment methods (filtration, adsorption, flotation, etc.) [7,18,19]. While these methods can effectively remove various contaminants, they often require high operational costs, energy inputs, and may generate toxic byproducts or sludge [20].

Constructed wetlands (CWs) have emerged as a promising, eco-friendly, and cost-effective alternative for wastewater treatment, including produced water [21,22]. CWs are engineered systems designed to mimic the natural processes occurring in wetlands, utilizing wetland vegetation, soils, and associated microbial communities to assist in treating wastewater [23]. This system can effectively remove various pollutants through physical, chemical, and biological processes, such as sedimentation, filtration, adsorption, precipitation, and microbial degradation [21].

Previous studies have investigated the use of constructed wetlands for the treatment of produced water, focusing on the removal of various contaminants [24,25]. However, there is a need for further research to explore the potential of modified constructed wetland systems, incorporating additional substrates or amendments, for enhanced treatment efficiency, particularly concerning heavy metals and oil and grease (O&G) removal. This study investigated the performance of a constructed wetland system designed with modified substrates for the treatment of produced water.

II. MATERIALS AND METHODS

Materials

The materials used in this study were plastic reactors, substrates (gravel, coarse sand, topsoil, and charcoal), wetland vegetation (*Phragmites australis*), and produced water sample obtained from a

terminal station in the Niger Delta region of Nigeria. Plastic reactors were used to avoid metal contamination and serve as impervious layers to prevent water loss through percolation. *Phragmites australis*, a common reed species was selected due to its widespread availability in the local environment, its extensive fibrous root systems with rhizomes, its ability to form extensive stands, spread rapidly through horizontal runners, and thrive in various wetland conditions [26] (Saeed et al., 2021).

Laboratory equipment used for analysis include a multiparameter analyzer for pH and temperature measurements, an Atomic Absorption Spectrophotometer (Agilent Technologies 200 Series AA) for heavy metal analysis and a gravimetric machine for oil and grease measurement. Other materials used were conical flasks, spatulas, and a weighing balance.

National and International Industrial Effluent Discharge Limits

The National Environmental Standards and Regulations Enforcement Agency (NESREA) effluent discharge standards [27], as presented in Table 1, were used to compare the raw and treated produced water samples. For oil and grease, the Department of Petroleum Resources (DPR) Standard for produced water was used, with limits of 10 ppm, 20 ppm, and 40 ppm for inland, onshore, and offshore respectively [28].

Table-1: National Industrial Effluent Discharge Limit

Parameters	Units	NESREA
pH	-	6.5-8.5
Temp.	°C	Ambient
Cd	Ppm	0.01
Pb	Ppm	0.1
Zn	Ppm	0.2

Experimental Setup of Constructed Wetland (CW)

The experimental setup aimed to assess the rate of removal of heavy metals as well as oil and grease from PW is a vertical flow recirculatory system of 3-CWs in series. The reactors were connected using taps, allowing the treated water to flow from one CW reactor to the next and finally into a reservoir for

analysis. Geotextile filter media were embedded at the points where the taps were attached to the reactors to prevent substrate clogging or blockage. The reactors were placed at different elevations to facilitate free flow by gravity as shown in Figure 1.



Figure 1: A 3-reactor constructed wetland in series for produced water treatment

The total depth of each reactor was 29 cm, with a freeboard (ponding height) of about 25% of the total depth. The depths of the topsoil, coarse sand, and silica pebble gravel layers were calculated as 40%, 35%, and 25% of the remaining depth. The substrates were arranged as follows: a bottom layer of silica pebble gravel with a depth of 5.25 cm and weight of 7.1kg, a sub-layer of coarse sand with a depth of 7.7 cm and weight of 9.2kg, and a top layer of topsoil with a depth of 8.8cm and weight of 6.6kg. The various depths were chosen to provide a sufficient soil layer for plant root anchorage and improve pollutant removal through increased contact time between pollutants and the substrates. The retention time required for an effective treatment process was determined by the flow control method. A plastic ball valve tap regulated flow rate and was selected based on its ability to allow one-directional flow and its plastic material composition to avoid rust.

The *Phragmites australis* vegetation was transplanted and allowed to adapt and grow for four weeks, with tap water irrigation every 24 hours. After the four-weeks adaptation period, 330g of

granulated charcoal was added to the topsoil in each reactor, and the biochar was left for three days to mix with the topsoil through irrigation. The loamy soil-to-charcoal ratio (w/w) was 20:1. The selection of charcoal as an amendment substrate was based on its adsorptive potential, chemical stability, availability, and cost-effectiveness.

Prior to transplanting and the treatment of the produced water, the flow rate of the reactors was determined using the volumetric method with distilled water which flowed from the first reactor through the second and third reactors. Treatment of produced water was done by pouring in 10litres of produced water into the first reactor with the valve open, allowing the water to infiltrate from top to bottom layers and pass through to the subsequent reactors. The process was operated under a recirculatory protocol of 3 cycles represented as 1st run, 2nd run, and 3rd run with an overall contact time of 45 minutes. A single cycle was accomplished when the produced water goes through the 3-CWs in series and the permeate collected from the 3rd CW. Consequently, the feed stream of the 1st run was the raw produced water, while the feed stream of the 2nd run was the permeate of the 1st run and the feed stream of the 3rd run was the permeate of the 2nd run.

III. RESULTS AND DISCUSSION

Characteristics of Raw and Treated Produced Water
The characteristics of the raw and the treated produced water are presented in Table 3. Comparing the raw produced water characteristics with the national standard (Table 2), it was observed that, all heavy metals analyzed for the raw water did not meet the discharge standards before treatment. The oil and grease (O&G) analysis of the raw produced water was below the inland, onshore, and offshore limits of 10 ppm, 20 ppm, and 40 ppm respectively as directed by DPR. The low O&G value was achieved by a skimming process prior to the treatment in the CW unit. This is similar to the work of Stefanakis et al. [29] where an oil separator was used to remove more than 85% of oil in water before inflow into the CW.

Comparing results of Table 1 and 2 for the treated produced water, it was observed that the pH of the treated produced water for each of the runs was below the minimum standard value of 6.5. pH value decreased from a slightly alkaline level (7.4) to slightly acidic range (6.07-6.29). The decrease in pH value of the treated produced water may have been due to the adsorption of alkaline earth metals such as Ca²⁺ and Mg²⁺, which are often responsible for high water pH. The adsorptive capacity of the CW unit was evidenced in the removal of Cd, Pb, Zn and O&G.

Table-2: Characteristics of Raw and Treated Produced Water.

Parameter	Units	Raw produced water	Treated produced water		
			1 st Run	2 nd Run	3 rd Run
pH		7.40	6.07	6.29	6.24
Temperature	°C	28.5	28.8	29.6	28.7
Cd	ppm	0.213	0.051	0.043	0.039
Pb	ppm	0.210	0.072	0.063	0.052
Zn	ppm	0.314	0.098	0.091	0.083
O & G	ppm	2.8	2.1	1.7	0.4

Removal Efficiency of Heavy Metals and O&G

Results of the permeate analysis showed that the 3 stage CWs recirculatory system removed selected heavy metals and O&G (Chart 1). The removal efficiencies of heavy metals (Cd, Pb, and Zn) were observed to decrease with the number of runs while that of O&G increased (from 25% to 76%) with the number of runs. This is consistent with the works of Stefankis et al., 2018 [29] and suggests a possible variation in the removal mechanism between heavy metals and O&G. Removal efficiency for heavy metals from the 1st to the 3rd run decreased sharply from 76% to 9% for Cd, from 66% to 17% for Pb, and from 69% to 9% for Zn. An indication of a competitive adsorption of heavy metals in the order: with overall removal efficiencies of 82%, 75%, and 74%, respectively. These removal efficiencies for a contact time of 45 minutes were higher than those

reported in previous study by Khan et al. [30]. The improved performance could be attributed to the inclusion of the biochar layer in the constructed wetland system, which likely enhanced the adsorption process. However, the order and the trend (decrease with the number of runs) of heavy metal removal efficiency were consistent with the work of Si et al. [31]. The removal mechanisms of the heavy metals were attributed to sorption to substrate including biochar, rhizofiltration, and phytostabilization while the main attenuation mechanisms of O&G include sorption and volatilization. The fibrous roots of *Phragmites australis* provides large surface area for sorption, precipitation, complexation or metal valence reduction. The deep penetration of *P. australis* immobilizes and accumulates heavy metals around the root. The results show that Pb and Zn content in the treated permeate were within NESREA permissible limits for discharge.

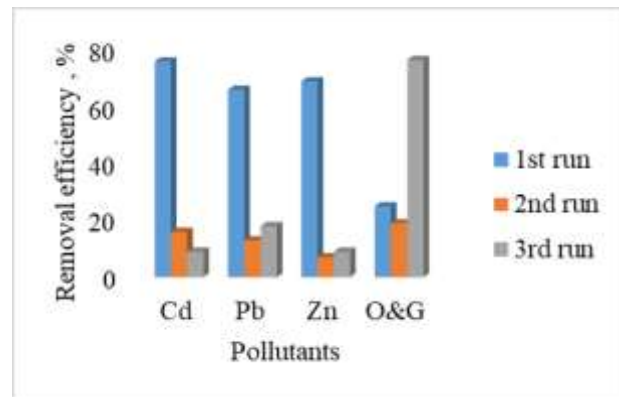


Chart 1: Removal Efficiency of Heavy Metals and O&G from a 3-stage series CW unit

IV. CONCLUSION

This study investigated the treatment of produced water using a constructed wetland system designed with modified substrates, including a biochar layer. The main findings of this study demonstrate the potential of constructed wetlands with a thin biochar layer as an effective and eco-friendly treatment method for produced water, particularly for the removal of Pb, Zn and O&G. The overall removal efficiency for O&G was higher than that for heavy metals within the contact time of 45 minutes.

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