

EFFECTS OF PHYTOREMEDIATION TREATMENT METHOD ON DEGRADATION OF BOD, COD AND TPH IN PETROLEUM REFINERY WASTEWATER

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ABSTRACT

A study was done to remove toxic substances from refinery wastewater using phytoremediation method. The effectiveness of *Eichinochloa pyramidalis* for phytoremediation of refinery wastewater was investigated for an operational period of three months. The design consideration is a batch unit fed with 100 L of refinery wastewater which was properly stirred to attain a uniform solution. The batch unit used was an open drum. *Eichinochloa pyramidalis* was uprooted from

the soil and their roots were washed with tap water and then, with distilled water before they were transferred into the drum containing the wastewater sample. The plant was allowed to grow in the sample and was monitored for a period of 3 months. Analysis was carried out weekly to investigate the effectiveness of *Eichinochloa pyramidalis* on the degradation of Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Petroleum Hydrocarbon (TPH) in the wastewater sample. The BOD, COD and TPH had their highest removal rates on the 12th week. Their values were 87.68%, 95.1% and 98.7% respectively. The phytoremediation treatment method is easy to implement and maintain, does not require the use of expensive equipment or highly specialized personnel and is environmentally friendly. It can therefore, be applied in removing contaminants from wastewater.

KEYWORDS: Phytoremediation, *Eichinochloa pyramidalis*, refinery wastewater.

1. INTRODUCTION

Water is one of the essential enablers of life on earth. Worldwide, 780 million people do not have access to an improved water source.^[1] Large volumes of fresh water are extracted and consumed for use by petroleum industries in the process of refining crude oil and as cooling agent.^[2-4] Waste waters released by these crude oil-processing and petrochemical industries are characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulfides, naphthylenic acids and other chemicals.^[5,6] reported that the produced refinery effluent during processing amounts to 0.4 - 1.6 times the amount of crude oil processed, and that this estimate is based on the yield of 13 million m³ (84 million barrels per day) of crude oil and a total of 5.3 million m³ of effluent is generated globally. Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem.^[7,8]

Conventional methods for treating oil contaminated water include solvent extraction, steam distillation, irradiation as well as chemical techniques such as electrochemical oxidation, reverse osmosis photocatalytic degradation and adsorption on activated carbon, ion exchange resins and silicates.^[9,11] The disadvantage of using any of the above methods is that they are mere phase transfer processes which results in the generation of more wastes during treatment thus, requiring additional treatment steps and costs. Even though the chemical methods appear to be effective, their implementation is usually not economically feasible as the chemicals are required in high dosages. Therefore, there is need to explore other treatment methods with less operational cost and maintenance requirements. The phytoremediation treatment method has been investigated with promising results. Phytoremediation is the process of using green plants or trees to remove, transfer, stabilize, and/or destroy contaminants in the soil, groundwater or wastewater. Analysis of this process is possible using computational intelligence techniques like the artificial neural network. This technique is capable of effective prediction as demonstrated in diverse field (Ref). It is a cost effective method of reducing risk to human and ecosystem health posed by contaminated water.

The essence of this study was to investigate the efficiency of phytoremediation for refinery wastewater treatment over an extended operational period of 3 months.

2. MATERIALS AND METHODS

2.1 Experimental Set-Up and Procedures

The research was conducted in July 2019 until September 2019, at the Department of Chemical Engineering, University of Benin, Nigeria. The wastewater sample was gotten from Warri Refining and Petrochemical Company, Delta State, Nigeria. The materials used in this research were *Echinochloa pyramidalis* (Antelope grass), distilled water, sample bottles, plastic funnel and an open drum.

100 litres of the wastewater was fed into the open drum and stirred properly. The plants were uprooted from the soil and their roots were washed with tap water and then, with distilled water before it was transferred into the drum containing the water sample. The experimental set-up was placed indoors at the Chemical Engineering Department of the University of Benin in Nigeria to avoid high temperature variations but ensuring plenty of natural light at the same time.

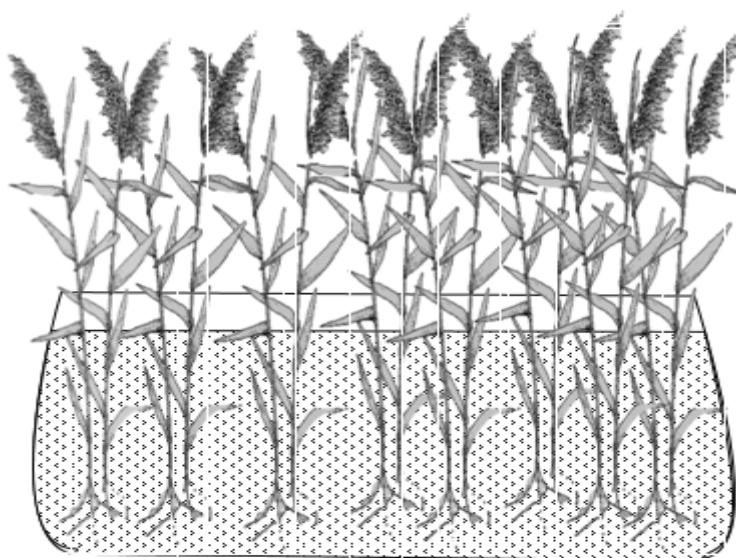


Figure 1: Experimental setup of the lab-scale phytoremediation tank.

2.2 Wastewater Analysis

On day 1 (absence of plant), parameters like pH, temperature, TDS, TSS, conductivity, turbidity, calcium, magnesium, hardness, sodium, potassium, alkalinity, chloride, DO, BOD, COD, sulphate, phosphate, nitrate, Fe, Cr, Zn, Pb, Cu, Cd, Ni, Mn and TPH were analyzed to know the general physiochemical properties of the untreated wastewater from the refinery. All analysis for the physiochemical parameters were carried out using the equipment listed in Table 1.

Table 1: Analytical Equipment and Methods for Characterization of Refinery Effluents.

Parameter	Symbol	Equipment/Analytical Method
pH	pH	HORIBA pH meter
Temperature, °C	T °C	HORIBA pH meter
Electrical conductivity, µS/cm	Ec	HANNA Instrument EC 215
Turbidity, TNU	-	HANNA Instrument LP 2000
Dissolve Oxygen, mg/L	DO	Winkler's Modification Method
Total Suspended Solids, mg/L	TSS	Gravimetric after filtration
Biological Oxygen Demand, mg/L	BOD ₅	5-Day Incubation
Chemical oxygen Demand, mg/L	COD	Dichromate digestion method
Nitrate, mg/L	NO ₃ ⁻ -N	HACH DR/2010 Portable logging spectrophotometer
Phosphate, mg/L	PO ₄ ³⁻ -P	Spectrophotometry 752 UV
Potassium, mg/L	K	Flame Emission Photometric Method
Cadmium, mg/L	Cd	Atomic Absorption Spectrophotometry
Chromium, mg/L	Cr	Atomic Absorption Spectrophotometry
Copper, mg/L	Cu	Atomic Absorption Spectrophotometry
Zinc, mg/L	Zn	Atomic Absorption Spectrophotometry
Iron, mg/L	Fe	Atomic Absorption Spectrophotometry
Lead, mg/L	Pb	Atomic Absorption Spectrophotometry
Nitrate, mg/L	NO ₃ ⁻ -N	HACH DR/2010 Portable logging spectrophotometer
Phosphate, mg/L	PO ₄ ³⁻ -P	Spectrophotometry 752 UV
Potassium, mg/L	K	Flame Emission Photometric Method

Subsequently, at intervals of seven days (one week) for a total of 84 days (twelve weeks), samples were collected from the phytoremediation tank, the water characteristics were determined by analyzing the physiochemical parameters of interest like TPH, BOD and COD. The sample collection containers were thoroughly rinsed three times with the sample before samples were taken. Samples were collected using a 1 litre capacity borosilicate glass bottles.

3. RESULTS AND DISCUSSION

The physiochemical analysis that was carried out on day 1 before the plants were introduced into the phytoremediation tank included pH, temperature, TDS, TSS, conductivity, turbidity, calcium, magnesium, hardness, sodium, potassium, alkalinity, chloride, DO, BOD, COD, sulphate, phosphate, nitrate, Fe, Cr, Zn, Pb, Cu, Cd, Ni, Mn and TPH. Table 2 shows the concentration of the physiochemical contaminants of the influent solution as compared with the FEPA standard.^[12] Notice that BOD, COD and TPH results are above the FEPA standard. If the wastewater is discharged into the rivers without being treated, it will disrupt life in the water and damage the environment.

Table 2: Concentration of the Physiochemical Contaminants on day 1 (Influent Solution) and the FEPA Standard for Streams and Rivers.^[12]

S/N	PARAMETERS	UNITS	RESULTS	FEPA Standard for Streams and Rivers
1	pH		6.79	6 – 9
2.	Temperature	⁰ C	29.8	30
3	TDS	mg/l	49	200
4	TSS	mg/l	34	30
5	Conductivity	μS/cm	98	300
6	Turbidity	NTU	30.74	10
7	Calcium	mg/l	7.70	200
8	Magnesium	mg/l	1.56	200
9	Hardness	mg/l	25.62	300
10	Sodium	mg/l	17.45	200
11	Potassium	mg/l	3.52	12
12	Alkanility	mg/l	15.25	17
13	Chloride	mg/l	17.76	600
14	DO	mg/l	0.80	>2.0
15	BOD	mg/l	110	30
16	COD	mg/l	308	40
17	Sulphate	mg/l	5.65	500
18	Phosphate	mg/l	0.33	5
19	Nitrate	mg/l	5.49	20
20	Fe	mg/l	0.82	20
21	Cr	mg/l	0.02	<1
22	Zn	mg/l	0.48	<1
23	Pb	mg/l	0.03	<1
24	Cu	mg/l	0.15	<1
25	Cd	mg/l	0.00	<1
26	Ni	mg/l	0.04	<1
27	Mn	mg/l	0.28	5
28	TPH	mg/l	1022.23	30

3.1 Pollutants Removal Calculation

The removals rates of COD, BOD and TPH were calculated using the formula below:

$$\text{Degradation Efficiency} = \frac{C_o - C_t}{C_o} \times 100$$

Where C_o and C_t are initial and instantaneous concentration concentrations respectively

3.2 BOD (Biological Oxygen Demand or Biochemical Oxygen Demand)

Figure 2 shows the effect of phytoremediation treatment time on the percentage degradation of BOD. For a duration of 12 weeks, the BOD removal efficiency was observed to increase appreciably. BOD increased from a degradation efficiency of 10.36% to 87.68%. A similar

trend was reported in the literature by^[19] that, as treatment increased, there was a significant increase in the percentage degradation of BOD.

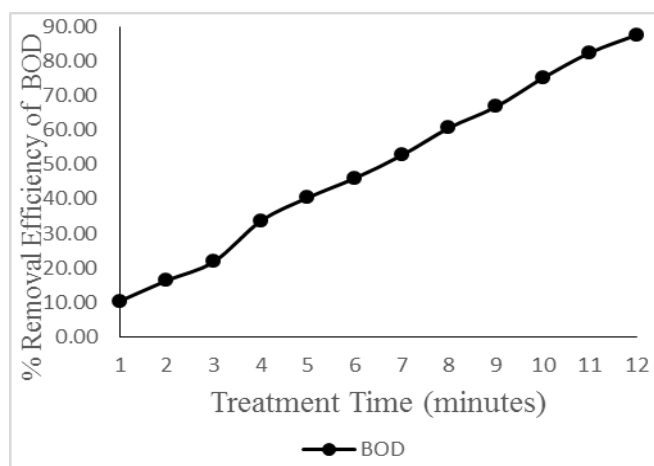


Figure 2: Variation of Percentage Efficiency of BOD with Treatment Time.

Table 3 shows the BOD collated results obtained from analysing the wastewater and their percentage degradation values. BOD is the amount of dissolved oxygen required by microorganisms, to breakdown organic materials present in a given water sample at certain temperature over a specific period of time. The BOD affects the amount of dissolved oxygen in water bodies. The higher the BOD, the more rapidly oxygen is depleted in the water body and that can negatively affect the aquatic organisms. They become stressed, suffocate, and die. The final BOD value of the sample (13.55mg/L) fell below maximum value of 30 mg/L stipulated by the regulatory agency, FEPA during the study period of 84 days.^[12]

Table 3: Effect of Treatment Time on Percentage Degradation for Phytoremediation (BOD Parameter Table).

Treatment Time (Weeks)	BOD (mg/L)	BOD (% Degradation)
0	110.00	
1	98.60	10.36
2	92.00	16.36
3	86.00	21.82
4	73.00	33.64
5	65.56	40.40
6	59.32	46.07
7	52.01	52.72
8	43.25	60.68
9	36.53	66.79
10	27.31	75.17
11	19.26	82.49
12	13.55	87.68

3.3 COD (Chemical Oxygen Demand)

Figure 3 and Table 4 indicate the performance of *Eichinochloa pyramidalis* in the wastewater sample within the operational period of 12 weeks. COD is the total amount of oxygen needed to oxidize chemically organic materials, both biodegradable and biologically degradable to CO_2 and H_2O ,^[20] (Boyde, C.E., 1998). The degradation efficiency of COD with treatment time is illustrated in Figure 3. It was observed that the degradation efficiency of COD was directly proportional to the treatment time (1 – 12weeks). As the treatment time increased, the degradation efficiency increased from of about 16.23% to 95.1%. The trend from Table 4 shows that there was a steady decrease of COD in the wastewater as time progressed from week 1 to week 12.

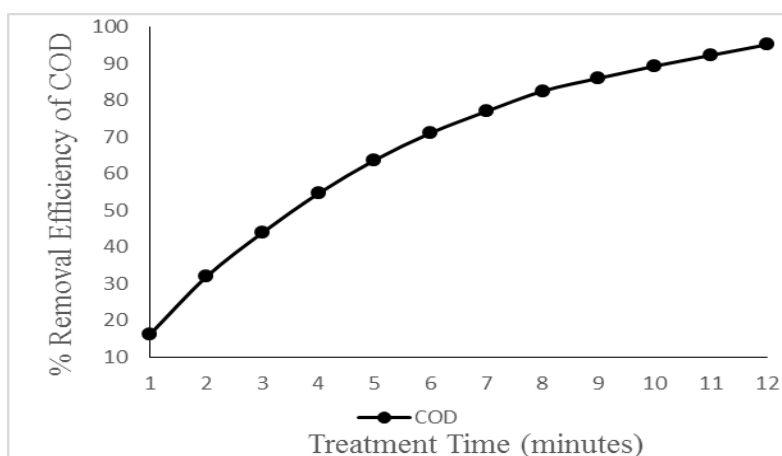


Figure 3: Variation of Percentage Degradation Efficiency of COD with Treatment Time.

Table 4: Effect of Treatment Time on Percentage Degradation for Phytoremediation (COD Parameter Table).

Treatment Time (Weeks)	COD (mg/L)	COD (% Degradation)
0	308.00	
1	258.00	16.23
2	210.00	31.82
3	173.00	43.83
4	140.00	54.55
5	112.08	63.61
6	89.30	71.01
7	71.04	76.94
8	54.10	82.44
9	43.21	85.97
10	33.05	89.27
11	23.98	92.21
12	15.08	95.10

3.4 TPH (Total Petroleum Hydrocarbon)

Figure 4 and Table 5 show the removal efficiency of TPH in this study by using phytoremediation technique. From Table 5, the TPH values decreased from week 1 to week 12. TPH is one of the major pollutants found in refinery effluents. There was a significant TPH reduction of 98.7% at the end of the treatment process. As the treatment time increased, the degradation efficiency increased from of about 3.89% to 98.7%. This is an indication of the degradation of the crude oil in the contaminated water which makes it possible for more air to permeate into the water.^[21]

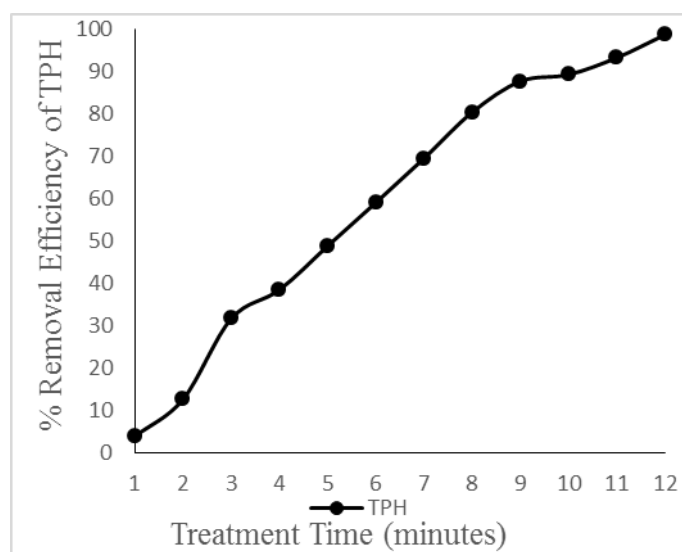


Figure 4: Variation of Degradation Efficiency of TPH with Treatment Time.

Table 5: Effect of Treatment Time on Percentage Degradation for Phytoremediation (TPH Parameter Table).

Treatment Time (Weeks)	TPH (mg/L)	TPH (% Degradation)
0	1022.28	
1	982.50	3.89
2	892.80	12.67
3	698.54	31.67
4	629.05	38.47
5	523.14	48.83
6	418.54	59.06
7	311.53	69.53
8	200.39	80.40
9	125.72	87.70
10	109.65	89.27
11	68.91	93.26
12	13.22	98.71

CONCLUSION

The use of phytoremediation as a strategy for cleanup of refinery waste water was studied for a period of twelve (12) weeks. The following conclusions can be drawn: The results obtained showed that there was a BOD, COD and TPH removal efficiency of 87.68%, 95.1% and 98.7% respectively; the final removal efficiency values of BOD, COD and TPH fell within the acceptable limit stipulated by the regulatory agency FEPA. The implication of these results is that the treated wastewater could be safely discharged into rivers and streams without posing any threat to the aquatic ecosystem; phytoremediation is easy to implement and maintain, does not require the use of expensive equipment or highly specialized personnel and is environmentally friendly and aesthetically pleasing to the public. In future research, prediction of results obtained for BOD, COD and TPH can be analysed further using soft computing (SC) techniques. This has been successfully demonstrated in other field of research.^[13-18] The use of the SC technique will help fine-tune results for better performance in terms of removal efficiency values.

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