

## Treatment of Refinery Wastewater using Vertical Flow Constructed Wetlands

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### Abstract

Pilot scale constructed wetlands were used to treat refinery wastewater. The experimental set up consisted of four vertical flow constructed wetlands (CW) with different plants and media packed in precast concrete pots. Diameter and height of each CW was 300 mm and 450 mm respectively and consisted of 10 cm of 24 cm layer of plant growing media (sand) followed by gravel (10 – 20 mm) in the bottom layer. CW 1 was planted with common reed (*Phragmites karka*), CW 2 was planted with *Phragmites karka* plus additional layer of sludge over the media, CW 3 was planted with narrow-leaved cattail (*Typha angustifolia*) plus additional layer of sludge over the media while CW 4 was planted with *Typha angustifolia*. Experiment was conducted at Karachi (Pakistan) with a warm humid summer (38°C) and a normal cold winter (10°C). After acclimatization period, wastewater from a local refinery was added manually to maintain a hydraulic loading rate of 85 mm/d. The average influent values were as follows: turbidity (181 NTU), suspended solids (283 mg/l), oil and grease (1146 mg/l), COD (746 mg/l), BOD (328 mg/l), sulphate (164 mg/l), chloride (34 mg/l) and total phenol (1.7 mg/l). The four CW removed all monitored pollutants with good removal efficiencies during the initial monitoring period of 3 months: turbidity (91%, 72%, 96%, 95%); suspended solids (87%, 86%, 86%, 73%), oil and grease (77%, 80%, 60%, 83%), COD (57%; 47%; 53%, 72%); BOD (37%, 49%, 33%, 36%); sulphate (62%, 77%, 85%, 76%), chloride (96%, 95%, 98%, 98%) and total phenol (68%, 98%, 98%, 97%). Overall CW 4 showed the best performance in removing pollutants. For phenol removal, CW 2 and CW 3 performed better than CW 1 and CW 4. With regard to type of plant species, wetlands with *Typha angustifolia* performed better than those planted with *Phragmites karka*.

### Keywords

Constructed wetland, phenol, sludge, refinery wastewater, vertical flow

## INTRODUCTION

Crude oil and condensate refineries produce huge amounts of wastewater. The characteristics of refinery wastewater vary in a complex pattern depending on the type of crude oil and treatment processes involved. Refinery wastewater consists of macro pollutants as well as micropollutants. Macropollutants are usually inorganic compounds like nitrate compounds, sulfate compounds etc. and micropollutants are organic compounds like benzene, toluene, phenols and hydrocarbons. The operation and design of refinery wastewater treatment plants is challenging and technology driven. Oil refineries are now highly motivated to choose simple, cheaper, cleaner and safe treatment technologies that are reliable, cost efficient and time saving to ensure that they meet the required regulatory limits set by the respective environmental agencies. Refinery wastewater has attracted researchers to use biological processes for treatment. Refinery wastewater and its major components like BTEX and phenol can be treated through aerobic, anaerobic, anoxic or combination of all three processes.

Many of the processes in crude oil refineries use water and the contaminated water is either sent for treatment to wastewater treatment facility located at site or pretreated and conveyed to local publically owned treatment plant. The conventional methods for the treatment of refinery

wastewater encompass various physical and chemical processes with subsequent biological treatment. The physical and chemical processes for refinery wastewater treatment encompass chemical oxidation, flocculation, coagulation, chlorination, solvent extraction, reverse osmosis, ion exchange, adsorption and ozonation. These processes create problems in the secondary effluent due to formation of toxic compounds such as cyanates, chlorinated phenols, hydrocarbons etc. Constructed wetland systems are accepted as low-tech, economical, green, efficient and sustainable systems that are capable of treating different types of wastewater. Globally, they have been successfully used to treat different types of wastewaters including effluents from industrial establishments (Vymazal, 2011). There are wide arrays of physical, chemical and biological mechanisms that transform and distribute pollutants in the multiple abiotic and biotic components of wetland systems. The use of constructed wetland as a biological treatment method for refinery wastewater is an attractive option due to the potential of complete biodegradation of low molecular weight hydrocarbons with no disadvantages posed by other processes. Constructed wetland produces harmless end products, have low operating and capital cost, and maintain organic components concentration below toxic limits if properly designed and maintained.

In Pakistan most of the oil refineries employ conventional methods of wastewater treatment like trickling filters followed by sand filtration. Over the past few years, constructed wetlands have been widely accepted as an economical and feasible alternative worldwide for wastewater treatment. This research is carried out in the climatic condition of Karachi as climate has a profound effect on performance of constructed wetland system. The results of this research work will help in developing the full scale applications of this technology under local conditions. This research will promote the idea of pollutant removal from refinery wastewater which is expensive to treat using conventional treatment methods.

The main objectives of this study are as follows:

To compare refinery wastewater treatment performance of four pilot scale vertical flow constructed wetlands

To investigate the effect of plant species on refinery wastewater treatment

To study the effect of sludge on refinery wastewater treatment

## METHODS

### Experimental setup

The experimental set up consisted of four vertical flow constructed wetlands (CW) with different plants and media packed in precast concrete pots. Diameter and height of each CW was 300 mm and 450 mm respectively. Each CW consisted of 24 cm layer of plant growing media (sand) followed by 10 cm of gravel (10 – 20 mm) in the bottom layer. A PVC valve (38 mm diameter) was fitted at the bottom to collect samples.

CW 1 was planted with common reed (*Phragmites karka*), CW 2 was planted with *phragmites karka* and had an additional layer of sludge over the media, CW 3 was planted with narrow-leaved cattail (*Typha angustifolia*) and had an additional layer of sludge over the media while CW 4 was planted with *Typha angustifolia*. The sludge was obtained from the secondary level of a nearby activated sludge wastewater treatment plant treating domestic wastewater. Young plant seedlings of *Phragmites karka* and *Typha angustifolia* were collected from a natural wetland in soil tubes and planted before the start of experimentation. Initially five (05) number of plant seedlings were planted in each CW. Immediately after the plantation all the CW were submerged with tap water up to the top surface to allow the plants to establish. During the establishment period (Figure 1a), tap

water was added regularly to supplement water losses by evapotranspiration. After one month of establishment, refinery wastewater was fed to pilot scale CW in order to acclimatize the plants. The plants grew well during the acclimatizing period from 0.6 m to 1.5 m (Figure 1b). The primary treated refinery wastewater was transferred from a refinery located in Karachi, Pakistan to the research site in PVC vessels. The refinery wastewater was added manually. Wastewater was added on daily basis to maintain a hydraulic loading rate of 85 mm/d. CW were operated on a pulse load regime (intermittent and saturated flow mode). Experiments were conducted at Karachi (Pakistan) with a warm humid summer (38°C) and a normal cold winter (10°C).



**Figure 1.** Vertical Flow Constructed Wetlands CW (a) initial plantation period (b) during acclimatization period.

#### **Influent characteristics**

The primary treated refinery wastewater was fed to each of the four CW. The average values for various physico-chemical parameters including pH, turbidity, suspended solids, oil and grease, chemical oxygen demand, biochemical oxygen demand, sulphate, chloride, ammonia-nitrogen and phenol were 8.1, 181 NTU, 283 mg/l, 1146 mg/l, 746 mg/l, 328 mg/l, 164 mg/l, 34.1 mg/l, 6.7 mg/l and 1.7 mg/l, respectively. The mean influent values with standard deviations are shown in Table1.

#### **Wastewater testing**

Influent added to CW was refinery wastewater. The CW effluent samples were collected from PVC valve fitted at the bottom of each treatment system. The collected samples were tested for various physical and chemical parameters including pH, turbidity, suspended solids (SS), oil and grease, chemical oxygen demand (COD), 5 days at 20°C biochemical oxygen demand (BOD), sulphate, chloride, and total phenol. Wastewater testing for all the above described parameters except phenol was carried out in Water Quality Laboratory of Department of Environmental Engineering NED University of Engineering and Technology. Phenol was tested by PERAC Research and Development (PRD) Laboratories. Sample testing was performed using American Public Health Association (APHA) standard methods unless stated otherwise. The sampling was carried out from October to December 2013 and samples were collected every two weeks.

**Table 1.** Characteristics (mean  $\pm$  standard deviation) of influent into Vertical Flow Constructed Wetlands.

Parameters	pH	Turbidity (NTU)	SS (mg/l)	Oil and Grease (mg/l)	COD (mg/l)	BOD (mg/l)	Sulfate (mg/l)	Chloride (mg/l)	Ammonia-nitrogen (mg/l)	Total phenol (mg/l)
Values	8.1 $\pm$ 0.60	181 $\pm$ 59.90	283 $\pm$ 20.14	1146 $\pm$ 641.41	746.2 $\pm$ 290.85	328.3 $\pm$ 25.83	164 $\pm$ 22.76	34.1 $\pm$ 1.37	6.7 $\pm$ 0.77	1.71 $\pm$ 1.01

## RESULTS AND DISCUSSION

### Pollutant removal in CW

#### General parameters

The mean effluent values and removal efficiencies are represented in Table 2. The pH of the influent was slightly basic while mean effluent pH values for CW1, CW2, CW3 and CW4 were 7.1, 7.2, 7.4 and 7.1, respectively. The results indicate that effluent pH is above neutral and all the four wetland treatment systems are effective in neutralizing the pH to normal range. The CW moderated and buffered the pH variations which are the capability of treatment wetlands (Kadlec and Wallace, 2009). Turbidity removal was also good with removal efficiencies of >90% for all CWs except for CW 2 that had a removal efficiency of 72%. For CW2, the effluent turbidity values in the first monitoring month were high however results of latter monitored samples showed better performance. All CWs showed good suspended solids removal except for CW4 which demonstrated a slightly lower removal 73% as compared to > 85% for the other three wetlands. In CW, suspended solids are removed through capture and settling (Kadlec and Wallace, 2009). The different layers (sand and gravel) of the system capture solids and retain them. Table 2 also indicates that all four wetland systems removed oil and grease. CW 1 and CW 4 performed better in removing oil and grease than CW 2 and CW 3. Overall results of CW 4 effluent indicate that it demonstrated better removal for oil and grease. Mashuri et al. 2000 reported that physical processes such as leaching, evaporation, sedimentation and sorption assist in the removal of mineral oils in wetlands. Moreover, various aerobic, anoxic and anaerobic processes occur in wetlands in which microorganisms play a vital role in pollutant removal. CW 4 showed the best removal performance and it is suspected that conditions favourable for microbially mediated removal processes in this system were more functional along with physical removal processes and this might have resulted in better performance of this system in terms of oil removal.

**Table 2.** Mean effluent concentrations (removal efficiency %) for Vertical Flow Constructed Wetlands.

Parameter	Unit	Effluent			
		CW 1	CW 2	CW 3	CW 4
pH	-	7.1	7.2	7.4	7.1
Turbidity	NTU	16.6(91)	51.1(72)	6.2(96)	9.8(95)
SS	mg/l	35.4(87)	38.4(86)	40.6(86)	76.1(73)
Oil and grease	mg/l	263.8(77)	226.5(80)	467.3(60)	203.1(83)
COD	mg/l	320.2(57)	393.8(47)	346.8(53)	309(72)
BOD	mg/l	208.1(37)	167.9(49)	221.9(33)	211.7(36)

Sulphate	mg/l	63.1(62)	37.1(77)	24.8(85)	39(76)
Chloride	mg/l	1.3(96)	1.6(95)	0.4(98)	0.6(98)
Ammonia-nitrogen	mg/l	1.4(79)	3.7(45)	1.7(75)	2.2(67)
Total phenol	mg/l	0.55(68)	0.03(98)	0.03(98)	0.04(97)

#### COD removal

The mean COD removal efficiencies for the four wetlands were 57%, 47%, 53% and 72% respectively. Figure 2 shows the COD removal performance of the four treatment systems. First three readings for all wetland systems followed almost the same pattern and illustrate smooth removal of COD. However, changes were observed in the COD effluent concentrations in the later monitoring period. This may be due to anaerobic degradation of organic matter in the lower portion of CW. The anaerobic conditions may have developed due to high loading rates resulting in lowering of oxygen concentration in parts of CW. One more reason for this fluctuation is the high variability in influent characteristics (Table 1), standard deviation for COD was 290.85 mg/l. Removal efficiency in terms of COD removal for the studied CW is as follows: CW4> CW1> CW3> CW2. Ratio of BOD<sub>5</sub>/COD for influent (refinery wastewater) was 0.42 while ratios for effluent from CW1, 2, 3 and 4 were 0.65, 0.42, 0.63 and 0.68, respectively. Results indicate that treatment of refinery wastewater in CW enhances biodegradability for all CW except for CW 2. This anomaly may be due to development of anaerobic conditions in parts of CW2.

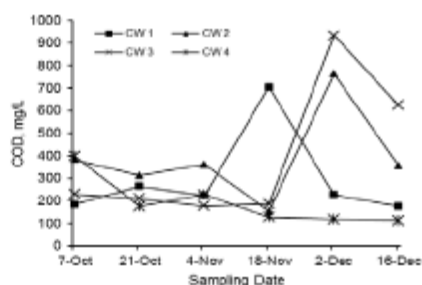


Figure 2. Effluent COD concentration versus time during monitoring period.

#### Phenol removal

All CW successfully removed total phenol. The mean influent phenol concentration was 1.57 mg/l while the mean effluent phenol concentrations for CW 1, CW 2, CW 3 and CW 4 were 0.55 mg/l, 0.03 mg/l, 0.03 mg/l and 0.04 mg/l, respectively (Figure 3). Phenol removal was lesser (68%) in CW 1 as compared to other 3 CWs (>96%). In wetlands phenols are removed through a number of different processes including microbial degradation, sorption, plant uptake and volatilization (Imfeld et al., 2009). Among the processes enumerated, microbial degradation is considered to be the most effective pathway for removal of phenolic compounds (Liu et al., 2009). It is suspected that CW 1 did not develop level of microbial growth that could have improved its performance and make it comparable to the other 3 CWs. Moreover, anaerobic degradation of benzene produces intermediates including phenols (Ulrich et al. 2005). There may be parts of CW 1 in which conditions might have developed that favoured anaerobic degradation. This may be the reason for poorer performance of CW 1.

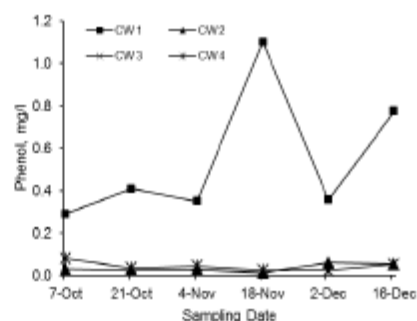


Figure 3. Variations in effluent phenol concentration during monitoring period.

#### Impact of plant species

For phenol removal, CW 2 (*Phragmites* + sludge) and CW 3 (*Typha* + sludge) performed better than CW 1 (*Phragmites*) and CW 4 (*Typha*). And for COD removal CW4 (*Typha*) showed the highest removal efficiency followed by CW1 (*Phragmites*) and CW 3 (*Typha* + sludge) while CW2 (*Phragmites* + sludge) demonstrated the lowest removal efficiency. For wetland plants, time for establishment is an element that may impact contaminant removal (Brisson and Charenzec, 2009). The plants in this study are relatively younger (5 months) and this factor might have underestimated the actual efficiency of the studied plant species. Vymazal and Kropfelova, 2005 have reported that it takes approximately 3 years for *Phragmites australis* to reach maturity. During the initial monitoring period, it was observed that plants were generally healthy. In the second month, most of the bottom shoots of *Phragmites* began to turn yellow. By comparing the two plant species, it was observed that *Typha* were healthier than *Phragmites*. Higher ammonia removal (>75%) was observed in CW 1 (*Phragmites*) and CW 3 (*Typha* + sludge). However, CW2 (*Phragmites* + sludge) and CW4 (*Typha*) had lower removal rates. Gagnon et al., 2012 while studying the effect of plant species on water quality of a sludge treatment wetland found that nitrogen removal varied with plant species. They found that higher TKN and ammonia removal was observed in wetlands planted with *Phragmites* as compared to those with *Typha* and *Scirpus*. They also found that *Phragmites* sequestered up to 25% of the nitrogen input. These results also showed that impact of plant species on nitrogen removal varied with time. Overall for the current study with regard to type of plant species, wetlands with *Typha angustifolia* performed better in removing the monitored pollutants than those planted with *Phragmites karka*.

#### Impact of sludge

CW without sludge (CW1 and CW 4) performed better than CW in which sludge was added (CW 2 and CW 3) for the same plant species. However, for phenol removal CW with sludge performed better than those without sludge. As microbial degradation is considered the most effective pathway so addition of sludge might have provided the necessary nutrients required by the microbes and stimulated their growth and reproduction. The addition of sludge had an influence on the plants; increased number of plants, 25 for *Phragmites* and 14 for *Typha* as compared to CW without sludge, 20 for *Phragmites* and 10 for *Typha*. Moreover, sludge addition also increased plant height, 1.98 m for *Phragmites* and 1.37 m for *Typha* as compared to CW without sludge, 1.77 m for *Phragmites* and 1.22 m for *Typha*. With regard to overall pollutant removal CW 3 (*Typha* + Sludge) performed better than CW 2 (*Phragmites*+ Sludge). Gagnon et al., 2012 showed that *Typha* was as effective as *Phragmites* in removing the monitored pollutants except for nitrogen removal which was higher in *Phragmites*.

#### CONCLUSIONS

Vertical flow constructed wetlands successfully removed the monitored pollutants from refinery wastewater

Out of four, 3 vertical flow constructed wetlands demonstrated excellent phenol removal efficiencies (>96%)

Wetlands with *Typha angustifolia* performed better than those planted with *Phragmites karka* in removing the monitored pollutants

Wetlands without sludge performed better than those with sludge except for removal of phenol