Effectiveness of Constructed Wetlands for Oil-Refined Wastewater Purification

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Abstract: Oil-refined wastewater coming from the Maoming Petro-Chemical Company, China Petro-Chemical Corporation contains high concentrations of organic and inorganic pollutants and therefore cannot be discharged directly unless a treatment of purification is conducted. Four herbaceous plants, Vetiveria zizanioides, Phragmites australis, Typha latifolia, and Lepironia articulata were planted in simulated constructed wetlands made in large-scaled pots for the purposes of testing their efficiencies in the purification of oil-refined wastewater and their growing performances in oil-refined wastewater wetlands. The purifying rates of constructed wetlands for oil-refined wastewater were all very high at the beginning, which removed over 97.7% of ammoniac N, 78.2% of COD, over 91.4% of BOD, and 95.3% of oil in the first batch of highlyconcentrated wastewater (HCW), and over 97.1% of ammoniac N, 71.5% of COD, over 73.7% of BOD, and 89.8% of oil in the first batch of low-concentrated wastewater (LCW). But the performance of wetlands became a littler poorer as time passed. The removing efficiencies of wetlands to ammoniac nitrogen, COD, BOD, and oil were always in order of ammoniac N > oil > BOD > COD. At the beginning, the purifying function of plants was quite weak, but it gradually increased with acceleration of plants growth and increase of biomass. However, the removal efficiencies of different species assumed only a little disparity, and they were not significantly different. The four tested species all had better growth in wetlands with two wastewaters than in those with clean water, but the tiller numbers of the former three species in HCW were fewer than those in LCW, whereas L. articulata was on the contrary, inferring that HCW might damage the former three species, and promote the growth of L. articulata. During the phase of clean water cultivation, the new tiller producing rate of V. zizanioides was the lowest among the four species, but it gradually rose during the phase of cultivation in wastewater, while the tiller-producing rates of the other three species were distinctly lowered, suggesting that V. zizanioides might have a stronger adaptation to the harsh environment than other species tested in the experiment.

Water is the source of life, and is the basic condition of human survival. The severe water pollution and insufficient water source are nowadays two thorny problems about the water environment around the globe. In China, the water problem is more prominent. There is only 2500 m³ water resource per capita in China, less than one-fourth of the world's average. In 1999, the total wastewater discharge amount in China was 40.1 billion tons, and COD in the wastewater was 13.9 million tons, but the treatment rate was only 29.65%. As a result, about 80% of waters, including 45% of ground water and 90% of cities' drinking water, have been polluted at varying degrees (Wang *et al.*, 2001; Qin *et al.*, 2002).

Guangdong is one of the most developed provinces in China, but its pollution, especially industrial pollution, is also quite severe. For example, the Maoming Petro-Chemical Company (MPCC), China Petro-Chemical Corporation lied in Guangdong discharged 13.12 million tons of oil-refined wastewater and 7.48 million tons of ethylene-produced wastewater in the year 1999 alone; therefore she has the very onerous work of wastewater treatment every year. Although the company has attached lots of importance on the environmental protection, and invested lots of funding in building up new purifying factories and in enlarging the capacity of old factories, which have made the present ability of the company to treat wastewater become much stronger than before. However, there was still only 63.4% of oil-refined

wastewater reaching the effluent standard in 1999, indicating that the company still has lots of work to do with special reference to wastewater purification (The inner reference material coming from the Company).

Wetland is regarded to be very effective in the aspect of environmental protection, especially for wastewater treatment. For example, Knight *et al.*(2000) found out, through a statistic calculation to more than 1300 data, that the mean purifying rates of constructed wetlands for livestock wastewater were 65% for BOD, 53% for TSS, 48% for NH₄-N, 42% for TN, and 42% for TP. Due to its low expense, low energy-consuming, high effectiveness and sustainability, wetland treatment systems are regarded as a promising wastewater-treating technique, and are being used by more and more countries and regions, especially by developing nations (Dunbabin and Bowmer, 1992; Campbell and Ogden, 1999; Kivaisi, 2001; Xia, 2002). Constructed wetlands also have been used to treat petroleum industry effluents, but they are still concentrated mainly on the remove of COD, suspended solids, and heavy metals (Knight *et al.*, 1999). There have been very poor documents so far about the purification of constructed wetlands for the main pollutants of petroleum industry effluents, such as oil, phenol, and benzene.

Many experiments and observations have confirmed that vetiver grass (Vetiveria zizanioides (L.) Nash) has excellent effects in erosion control, extreme soil amelioration, wastewater purification, and other environmental uses (Kantawanichkul et al., 1999; Truong and Hart, 2001; Xia et al., 2001). For example, Summerfelt et al. (1999) ever found that vetiver established in wetland could effectively remove extra solids and nutrients in aquaculture sludge, and the removal rates to suspended solids, total COD, total kjeldahl N, total P, and dissolved P were 96-98%, 72-91%, 86-89%, 82-90%, and 92-93%, respectively. Xia et al. (2002) found that this species could purify over 87% of ammoniac N and 74% of total P of garbage leachate. Phragmites australia (Cav.) Trin. ex Steudel and Typha latifolia L., the two common species in South China as well as in tropical and subtropical regions of the globe, have also been strongly proved to be effective with regard to their ability to remove pollutants (Taylor and Crowder, 1984; Li and Hu, 1995; Kern and Idler, 1999; Ye et al., 2001). Lepironia articulata Rich., a local species of South China and a potential pollutant-purifying plant, grows mainly on natural wetlands nearby minetailings or industrial pollution areas, but there has not been any report on its effectiveness for wastewater purification. By and large, there have been hardly documents so far introducing the purification of wetland systems constructed with the four above-mentioned species for industrial wastewater, especially oil-refined wastewater. It is hoped, therefore, that the present study could yield information related to abilities of the four plants to purify oil-refined wastewater by using constructed wetlands, which aims to screen out the highly effective pollutant removing species and then to provide an economical and effective pollutant purifying method for industrial wastewater, especially for oil-refined wastewater.

1 MATERIALS AND METHODS

1.1 Experimental Materials

The experimental spot was set up in the wastewater-treating station of MPCC, and mimic constructed wetlands were used in this experiment. The soil used in the wetlands was dug from a local nursery; it is sandy loamy soil, and its chemical features are listed below.

Table 1 Soil chemical characteristics used in constructed wet	lano	ls
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pН	Organic matter	Total N	Total P	Total K	Total S	Available N	Available P	Available K
	(%)	(%)	(%)	(%)	(%)	(mg/kg)	(mg/kg)	(mg/kg)
4.57	0.61	0.033	0.032	0.54	0.011	30	29	90

The tested wastewaters in the trial consisted of the highly concentrated wastewater (HCW) and the low concentrated wastewater (LCW). The former was called flotation wastewater, having the highest concentration of pollutants during the process of physical and chemical purification; the latter was the discharge water coming from flotation wastewater that had been physically and chemically cleansed. Of the tested 4 herbaceous species, *V. zizanioides*, *P. australis*, and *T. latifolia* were collected in the nursery of South China Institute of Botany (SCIB), among them the former had been growing in the xeric environment, and the latter two in the hydrophytic one; *L. articulata* was collected from a natural wastewater discharging channel beside the oil-shale waste dump in Maoming, which was very similar to an artificial wetland of wastewater purification.

1.2 Trial Designs and Arrangements

Simulated artificial wetlands were constructed in large-scale porcelain pots, and then wastewaters were loaded into for purification. The experiment was arranged 3 water treatments (HCW, LCW, and clean water (CW)) and 4 plant treatments (V. zizanioides, P. australis, T. latifolia, and L. articulata). In addition to these, 2 groups of control were arranged, which were HCW wetlands without plants and LCW wetlands without plants, respectively. All treatments and controls were three duplicates. During the process of plant growth and wastewater purification, the pots were all concentrated under a large cloth canopy. When it rained, the canopy was covered with cloth to prevent rainwater from entering the pots; when it did not rain, the cloth was put aside to let plants grow in the sunshine or natural environment. The trial operation was carried out as follows: first, large-scale pots with the height of 70 cm and diameter of 90 cm were made to measure, and then the fully mixed soil was put into pots, 87.1 kg (DW) for each pot; thereafter the above 4 species were planted into pots, 9 pots for each species and 18 clumps for each pot. In view of big differences of stem diameter among different species, T. latifolia, P. australis, V. zizanioides, and L. articulata were planted 1 tiller, 2, 3, and 5 tillers, respectively, for each clump and furthermore their tops and roots were all pruned to 30 cm and 5 cm, respectively, in order to make each species have as identical as possible biomass when planting. After planting, clean water was loaded into the pots until the water level was higher 10 cm than the soil surface. Thus, the construction of simulated treatment wetlands were finished. The survival rates were investigated and new slips were planted in stead of the dead ones after wetlands were constructed for 15days. During the period of cultivation, clean water was added to pots once every 2-4 days to supplement water reduced by transpiration and evaporation, but the amount added each time was no more than that removed. 2 months later, clean water was no longer added until the soils became almost dry, then the above-mentioned 3 kinds of water were loaded, 55 kg for each pot. Samples of wastewater were collected for chemical analysis 8 days after loading. Thereafter all wastewaters were discharged and pots were open incubation until the soil become almost dry, then the second and third batches of wastewater were loaded, and the same management, sample collection and chemical analysis as the first batch were conducted 8 days after each batch of wastewaters was loaded.

1.3 Observations and Analysis

1.3.1 Situations of plant growth in wetlands

The observation included the survival rate, plant height and tiller number. The latter two items were made twice, which were prior to loading wastewater (July 16) and in the end of the experiment (September 9), respectively.

1.3.2 Purification of constructed wetlands for oil-refined wastewater

The analytical items contained pH, ammoniac nitrogen (AN), oil, sulfide, volatile phenol (VP),

1.4 Analytical Methods

pH was measured with an acidmeter. COD values were acquired through measuring the consumption of dissolved oxygen while the wastewaters were oxidized with KMnO₄; and BOD was also referred to as the consumption of dissolved oxygen after the wastewaters were incubated 5 days at 20_ in an incubator. Ammoniac N was determined with direct distillation; VP and sulfide were measured by colorimetry; oil was determined by ultraviolet spectrophotometry; and benzene by gas chromatography (He, 2001).

2 RESULTS AND ANALYSIS

2.1 Water Quality of Wastewaters and Purifying Efficiencies of the Physical and Chemical Method

Table 2 is the water quality of wastewaters collected from the wastewater-purifying station. It shows that the concentrations of six observed items, AN, COD, BOD, oil, VP, and benzene in HCW, no matter which batch, were higher than the Second Grade Standard (SGD) of Wastewater Discharge Limits (WDL) in Guangdong (DB44/26—2001), but pH, and sulfide made an exception. After purifying, the contents of these items significantly decreased, and almost all of them reached SGD with the exception of AN, and oil in the second batch; some of them, such as BOD, VP, and benzene were even lower the First Grade Standard. This indicated that the physical and chemical purifying efficiencies were good, from the lowest, round 30% for AN to the highest, nearly 100% for benzene. Considering that acidity and sulfide in HCW completely met the discharge standard, and VP and benzene were almost all purified by the physical and chemical method in the first and second analyses, therefore the four items were not any more investigated in the third analysis and only the left 4 items, AN, COD, BOD and oil were investigated. In addition, it can be seen from Table 2 that the water quality of wastewaters is quite changeable everyday and the physical and chemical removal rates are also unstable. For example, VP in HCW was 1.8 mg/L in the first batch and become into 8.48 mg/L in the second, increasing by nearly 4 times; BOD had the similar changes.

pН	AN	COD	BOD	Oil	Sulfide	VP	Benzene		
Water quality of the first batch of wastewaters at the time of loading (17 July 2002)									
7.10	22	132	41	36	0.18	1.80	8.972		
7.22	17	87	8.2	6.0	0.08	0.07	0.005		
/	22.7	34.1	80.0	83.3	55.5	96.1	>99.9		
Water quality of the second batch of wastewaters at the time of loading (6 August 2002)									
7.21	29	196	26	47	0.46	8.48	9.30		
7.02	18	67	6.7	13	0.05	0.05	0.005		
/	37.9	65.8	74.2	72.3	89.1	99.3	>99.9		
ity of the	third batch o	of wastewat	ers at the ti	ime of load	ing (21 Aug	gust 2002	2)		
/	50	174	78	61	/	/	/		
/	34	78	9.2	5.4	/	/	/		
/	32.0	55.2	88.2	91.1	/	/	/		
Wastewater Discharge Limits in Guangdong Province, China (DB44/26–2001) ^b									
6-9	15	120	30	8	1.0	0.5	2.5		
6-9	10	60	20	5	0.5	0.3	2.0		
	pH ality of th 7.10 7.22 / ity of the s 7.21 7.02 / ity of the / / / vater Disch 6-9 6-9	pHANality of the first batch 7.10 22 7.22 17 / 22.7 ity of the second batch 7.21 29 7.02 18 / 37.9 ity of the third batch of/ 50 / 34 / 32.0 vater Discharge Limits $6-9$ 10	pHANCODality of the first batch of wastewa 7.10 22 7.22 17 7.22 17 7.22 17 7.22 17 7.22 17 7.21 29 7.21 29 7.02 18 67 7.02 18 67 7.02 18 67 7.02 18 7.9 65.8 ity of the third batch of wastewat $7.32.0$ 7.9 <t< td=""><td>pH AN COD BOD ality of the first batch of wastewaters at the 7.10 22 132 41 7.22 17 87 8.2 / 22.7 34.1 80.0 ity of the second batch of wastewaters at the 7.21 29 196 26 7.02 18 67 6.7 7 / 37.9 65.8 74.2 1 ity of the third batch of wastewaters at the trip / 50 174 78 / 34 78 9.2 / 32.0 55.2 88.2 vater Discharge Limits in Guangdong Provin 6-9 15 120 30 30 6-9 10 60 20 30 30 30 30</td><td>pH AN COD BOD Oil ality of the first batch of wastewaters at the time of loa 7.10 22 132 41 36 7.10 22 132 41 36 7.22 17 87 8.2 6.0 / 22.7 34.1 80.0 83.3 ity of the second batch of wastewaters at the time of loa 7.21 29 196 26 47 7.02 18 67 6.7 13 $/$ 37.9 65.8 74.2 72.3 ity of the third batch of wastewaters at the time of load $/$ 37.9 65.8 74.2 72.3 ity of the third batch of wastewaters at the time of load $/$ 34 78 9.2 5.4 $/$ 32.0 55.2 88.2 91.1 vater Discharge Limits in Guangdong Province, China ($6-9$ 15 120 30 8 $6-9$ 10 60 20</td><td>pH AN COD BOD Oil Sulfide ality of the first batch of wastewaters at the time of loading (17 Jul 7.10 22 132 41 36 0.18 7.10 22 132 41 36 0.18 7.22 17 87 8.2 6.0 0.08 / 22.7 34.1 80.0 83.3 55.5 ity of the second batch of wastewaters at the time of loading (6 Aug 7.21 29 196 26 47 0.46 7.02 18 67 6.7 13 0.05 / 37.9 65.8 74.2 72.3 89.1 ity of the third batch of wastewaters at the time of loading (21 Aug / 34 78 9.2 5.4 / / 32.0 55.2 88.2 91.1 / / 32.0 55.2 88.2 91.1 / / 32.0 55.2 88.2 91.1 / /</td><td>pH AN COD BOD Oil Sulfide VP ality of the first batch of wastewaters at the time of loading (17 July 2002) 7.10 22 132 41 36 0.18 1.80 7.22 17 87 8.2 6.0 0.08 0.07 / 22.7 34.1 80.0 83.3 55.5 96.1 ity of the second batch of wastewaters at the time of loading (6 August 2000 7.21 29 196 26 47 0.46 8.48 7.02 18 67 6.7 13 0.05 0.05 / 37.9 65.8 74.2 72.3 89.1 99.3 ity of the third batch of wastewaters at the time of loading (21 August 2002 / 50 174 78 61 / / / 32.0 55.2 88.2 91.1 / / / 32.0 55.2 88.2 91.1 / / / 32.0 55.2 88.2 <t< td=""></t<></td></t<>	pH AN COD BOD ality of the first batch of wastewaters at the 7.10 22 132 41 7.22 17 87 8.2 / 22.7 34.1 80.0 ity of the second batch of wastewaters at the 7.21 29 196 26 7.02 18 67 6.7 7 / 37.9 65.8 74.2 1 ity of the third batch of wastewaters at the trip / 50 174 78 / 34 78 9.2 / 32.0 55.2 88.2 vater Discharge Limits in Guangdong Provin 6-9 15 120 30 30 6-9 10 60 20 30 30 30 30	pH AN COD BOD Oil ality of the first batch of wastewaters at the time of loa 7.10 22 132 41 36 7.10 22 132 41 36 7.22 17 87 8.2 6.0 / 22.7 34.1 80.0 83.3 ity of the second batch of wastewaters at the time of loa 7.21 29 196 26 47 7.02 18 67 6.7 13 $/$ 37.9 65.8 74.2 72.3 ity of the third batch of wastewaters at the time of load $/$ 37.9 65.8 74.2 72.3 ity of the third batch of wastewaters at the time of load $/$ 34 78 9.2 5.4 $/$ 32.0 55.2 88.2 91.1 vater Discharge Limits in Guangdong Province, China ($6-9$ 15 120 30 8 $6-9$ 10 60 20	pH AN COD BOD Oil Sulfide ality of the first batch of wastewaters at the time of loading (17 Jul 7.10 22 132 41 36 0.18 7.10 22 132 41 36 0.18 7.22 17 87 8.2 6.0 0.08 / 22.7 34.1 80.0 83.3 55.5 ity of the second batch of wastewaters at the time of loading (6 Aug 7.21 29 196 26 47 0.46 7.02 18 67 6.7 13 0.05 / 37.9 65.8 74.2 72.3 89.1 ity of the third batch of wastewaters at the time of loading (21 Aug / 34 78 9.2 5.4 / / 32.0 55.2 88.2 91.1 / / 32.0 55.2 88.2 91.1 / / 32.0 55.2 88.2 91.1 / /	pH AN COD BOD Oil Sulfide VP ality of the first batch of wastewaters at the time of loading (17 July 2002) 7.10 22 132 41 36 0.18 1.80 7.22 17 87 8.2 6.0 0.08 0.07 / 22.7 34.1 80.0 83.3 55.5 96.1 ity of the second batch of wastewaters at the time of loading (6 August 2000 7.21 29 196 26 47 0.46 8.48 7.02 18 67 6.7 13 0.05 0.05 / 37.9 65.8 74.2 72.3 89.1 99.3 ity of the third batch of wastewaters at the time of loading (21 August 2002 / 50 174 78 61 / / / 32.0 55.2 88.2 91.1 / / / 32.0 55.2 88.2 91.1 / / / 32.0 55.2 88.2 <t< td=""></t<>		

Table 2 Water quality of wastewaters at the time of loading ^a

^a The unit of all observed data is mg/L, but pH value has not unit; 0.005 is the instrument-measured bottom limit of

benzene. ^b Issued by Guangdong Provincial Bureau of Environmental Protection on 20 August 2001

2.2 Purifying Benefits of Constructed Wetlands to the First Batch of Wastewaters

The water quality of the first batch of wastewaters staying in wetlands for 8 days is showed in Table 3, which indicated that: 1) apart from a little rise of pH, all other items assumed a distinct drop, and furthermore AN, VP, and benzene all dwindled to their respective instrument-measured bottom limits, and parts of BOD and sulfide also dwindled to the bottom limits, namely instruments could not measure their contents due to their too low concentrations; 2) compared HCW with LCW, the dwindling scope of pollutants was higher in the former than in the latter, which was obviously related to the higher original concentration of HCW; and 3) the purifying rates of wetlands for AN, COD, BOD, and oil were all in the sequence of AN > oil > BOD > COD, no matter in which type of wastewaters, LCW or HCW. The reasons why there is the highest purifying rate for constructed wetlands to AN are probably due to the strong volatility of AN on the one hand, and the easy uptake feature by plants on the other hand (Xia et al., 2002). Kantawanichkul et al. (1999) found, too, that TKN and NH₃-N was removed over 90% by constructed wetlands with V. zizanioides. It is interesting that the removal of AN was the lowest by using the physical and chemical method (Table 2), whereas it became the highest by using the method of wetland systems (Table 3). The removal rates of oil by constructed wetlands were also quite high, up to 89.8% in LCW and 95.3% in HCW. The newest report coming from Ji et al. (2002) pointed out that the removal efficiencies of reed beds to mineral oil were 88~96%. In addition to these, there was another phenomenon that the treatments with plants had the almost same purifying efficiencies as those without plants (controls), inferring that the purifying efficiency of plants was not very prominent in the beginning. This point is revealed more clearly in Table 4.

Treatment	pН	AN	COD	BOD	Oil	Sulfide	VP	Benzene		
	Water quality and removal rates of HCW									
СК	8.51	0.5 (97.7)	32 (75.8)	4.1 (90.0)	1.80 (95.0)	0.11 (38.9)	0.02	0.005		
V. zizanioides	7.57	0.5 (97.7)	31 (76.5)	4.4 (89.3)	1.30 (96.4)	0.11 (38.9)	0.02	0.005		
T. latifolia	7.92	0.5 (97.7)	26 (80.3)	3.8 (90.7)	2.40 (93.3)	0.01 (94.4)	0.02	0.005		
P. australis	7.86	0.5 (97.7)	32 (75.8)	3.3 (91.9)	0.85 (97.6)	0.03 (83.3)	0.02	0.005		
L. articulata	7.82	0.5 (97.7)	23 (82.6)	2.0 (95.1)	2.10 (94.2)	0.07 (61.1)	0.02	0.005		
Mean purifying rate (%)	/	97.7	78.2	91.4	95.3	63.3	/	/		
_			Water quality	y and removal ra	ates of LCW					
СК	8.10	0.5 (97.1)	26 (70.1)	2.8 (65.9)	0.55 (90.8)	0.02 (75.0)	0.02	0.005		
V. zizanioides	7.82	0.5 (97.1)	29 (66.7)	2.0 (75.6)	0.93 (84.5)	0.02 (75.0)	0.02	0.005		
T. latifolia	7.96	0.5 (97.1)	25 (71.3)	2.0 (75.6)	0.77 (87.2)	0.01 (87.5)	0.02	0.005		
P. australis,	7.59	0.5 (97.1)	28 (67.8)	2.0 (75.6)	0.31 (94.8)	0.02 (75.0)	0.02	0.005		
L. articulata	7.88	0.5 (97.1)	16 (81.6)	2.0 (75.6)	0.51 (91.5)	0.02 (75.0)	0.02	0.005		
Mean purifying rate (%)	/	97.1	71.5	73.7	89.8	77.5	/	/		

Table 3 The water quality of the first batch of wastewaters 8 days after staying in mimic wetlands*

^aThe units of all observed data are the same as those in Table 2; data in parentheses are purifying rates (%); mean purifying rate is the average value of purifying rates in each column; 0.5, 2.0, 0.02, and 0.005 are the instrument-measured bottom limits of AN, BOD, VP, and benzene, respectively.

Many a research has indicated that plants are a main pollutant-removing element in wetland systems. However, the effectiveness of plants for pollutant purification in the present experiment was not so distinct in the beginning of the experiment (Table 4). The net purified amounts coming from plants were very low, and some of them were even negative, which seemed that the purifying effectiveness of the treatments with plants was even poorer than that without plants. It is also noted clearly in Table 4 that the purifying benefits of different treatments were quite close, and there were no significant differences among them. Therefore, it seemed that plants in wetlands could not reveal strong purifying ability at the beginning, which was probably due to the relatively lower biomass and the relatively poorer adaptation to the wastewater environment at the beginning; as a result, they had not yet shown strong purifying ability. All in all, the purifying effectiveness of *L. articulata* was slightly better compared with other 3 species.

Treatment	Species	COD	BOD	Oil
HCW	V. zizanioides	1	-0.3	0.50
	T. latifolia	6	0.3	-0.60
	P. australis	0	0.8	0.95
	L. articulata	9	2.1	-0.30
LCW	V. zizanioides	-3	0.8	-0.38
	T. latifolia	1	0.8	-0.22
	P. australis	-2	0.8	0.24
	L. articulata	10	0.8	0.04

Table 4 The net removing amounts of plants to COD, BOD and oil in the first batch of wastewaters*

*Concentrations are expressed by mg/L; "-" indicates an increase of pollutants after being "purified" by plants

2.3 Purifying Benefits of Constructed Wetlands to the Second Batch of Wastewater

The second batch of wastewaters was loaded 11 days after the first batch was discharged, and then collected samples for analysis 8 days later (Table 5). The changes of observed items were basically consistent with the first time: 1) pH still become higher, while other items showed them a decrease at varying degrees, among them VP and benzene of all treatments went down to their respective instrument-measuring bottom limits and AN and sulfide of parts of treatments did so. That is to say that wetlands yielded very high removing rates to these pollutants, of which the highest value was to benzene in HCW, up to over 99%; 2) the removing rates of wetlands to AN, COD, BOD and oil still presented in order of AN > oil > BOD > COD; 3) most purifying rates of this batch dwindled in comparison with those of the first batch, among them those in LCW assumed higher a dropping scope, especially COD in LCW, which dropped to 35.8%. This is perhaps because the purifying ability of wetlands decreases with their operation; 4) overall purifying benefits of wetlands to high-concentrated pollutants (in HCW) were better than to lowly-concentrated pollutants (in LCW), except for AN that did not conform itself to the phenomenon; and 5) purifying efficiency of plants still was not very conspicuous, namely the purifying rates were apart very small between treatments with plants and without plants.

Table 5 The water quality of the second batch of wastewaters 8 days after staying in mimic wetlands*

Treatment	pН	AN	COD	BOD	Oil	Sulfide	VP	Benzene

СК	8.65	2.9 (90.0)	66 (66.3)	9.8 (62.3)	3.5 (92.6)	0.04 (91.3)	0.02	0.005		
V. zizanioides	7.70	1.5 (94.8)	49 (75.0)	6.7 (74.1)	2.2 (95.3)	0.02 (95.7)	0.02	0.005		
T. latifolia	8.02	2.1 (92.8)	59 (69.9)	7.9 (69.7)	2.4 (94.9)	0.04 (91.3)	0.02	0.005		
P. australis	7.83	1.3 (95.5)	53 (73.0)	5.7 (77.9)	2.9 (93.8)	0.03 (93.5)	0.02	0.005		
L. articulata	7.98	0.9 (96.9)	50 (74.5)	2.9 (89.0)	2.4 (94.9)	0.04 (91.3)	0.02	0.005		
Mean purifying rate (%)	/	94.0	71.7	84.6	94.3	92.6	/	/		
Water quality and removal rates of LCW										
СК	8.12	1.3 (92.8)	41 (38.8)	2.1 (68.7)	2.4 (81.5)	0.01 (80.0)	0.02	0.005		
V. zizanioides	7.95	0.5 (97.2)	44 (34.3)	2.0 (70.1)	1.6 (87.7)	0.01 (80.0)	0.02	0.005		
T. latifolia	8.14	0.5 (97.2)	50 (25.4)	3.2 (52.2)	1.6 (87.7)	0.01 (80.0)	0.02	0.005		
P. australis,	7.78	1.3 (92.8)	45 (32.8)	2.4 (64.2)	1.7 (86.9)	0.01 (80.0)	0.02	0.005		
L. articulata	8.20	0.5 (97.2)	35 (47.8)	2.6 (61.2)	1.9 (85.4)	0.01 (80.0)	0.02	0.005		
Mean purifying rate (%)	/	95.4	35.8	63.3	85.8	80.0	/	/		

^aThe units of all observed data are the same as Table 2. Data in parentheses are purifying rates (%), and mean purifying rate is the average value of purifying rates in eaach column; 0.5, 2.0, 0.02, and 0.005 are the instrument-measured bottom limits of AN, BOD, VP, and benzene, respectively.

Table 6 showed that the net removing amounts of treatments with plants to COD, BOD and oil in HCW were all positive values, indicating that they assumed stronger purifying ability than CK. This result suggests that wetlands with plants are more beneficial to HCW purification first. Compared with the those values in HCW, the net removing amounts to pollutants in LCW were lower, close to 0 or even negative, inferring that the purifying ability of plants were still unstable in this stage. As regarding the purifying effects, it was still *L. articulata* which performed slightly better, *V. zizanioides* and *P. australia* second, and *T. latifolia* a little bit poorer, but they did not reveal a large discrepancy in this aspect, namely the four species assumed similar purifying abilities to wastewater.

Treatment	Species	AN	COD	BOD	Oil
HCW	V. zizanioides	1.4	17	3.1	1.3
	T. latifolia	0.8	7	1.9	1.1
	P. australis	1.6	13	4.1	0.6
	L. articulata	2.0	16	6.9	1.1
LCW	V. zizanioides	0.8	-3	0.1	0.8
	T. latifolia	0.8	-9	-1.1	0.8
	P. australis	0	-4	-0.3	0.7
	L. articulata	0.8	6	-0.5	0.5

Table 6 The net removing amounts of plants to COD, BOD and oil in the second batch of wastewaters^{*}

*The data are expressed with mg/L. "-" indicates an increase of pollutants after being "purified" by plants

2.4 Purifying Benefits of Constructed Wetlands to the Third Batch of Wastewaters

The third batch of wastewaters was loaded 7 days after the second batch of wastewater was discharged. The investigated results of water quality and purifying efficiencies 8 days after staying in

wetlands are presented in Table 7. The purifying abilities of wetlands to the 4 pollutants were still ranked as AN > oil > BOD > COD, further inferring that AN was one of the most easily bio-removed elements from wastewater while COD was one of the hardest bio-removed elements. In comparison to the purifying rates of the second batch, these of the third batch did not have a clear increase or decrease, suggesting that wetlands began to enter a relatively stable state. Generally speaking, the purifying rates to the third batch of wastewaters still kept a quite high level, over 50% with the exception of COD in LCW. In addition, the purified extent of HCW by wetlands was higher than that of LCW as the first two batches of wastewater.

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Wastewater type	Treatment	AN	COD	BOD	Oil	Mean purifying rate (%)
HCW	СК	2.2 (95.6)	81.3 (53.3)	8.7 (88.8)	3.1 (94.9)	83.2
	V. zizanioides	1.0 (97.9)	63.7 (63.4)	5.6 (92.8)	2.9 (95.2)	87.3
	T. latifolia	1.1 (97.8)	51.0 (70.7)	4.1 (94.7)	2.1 (96.6)	89.9
	P. australis	1.2 (97.7)	53.7 (69.2)	5.1 (93.4)	1.9 (96.9)	89.3
	L. articulata	1.1 (97.7)	61.3 (64.8)	5.2 (93.3)	2.3 (96.2)	88.0
Mean purifyi	ng rate (%)	97.3	64.3	92.6	96.0	87.5
LCW	СК	0.7 (98.0)	59.7 (23.5)	4.9 (46.4)	2.0 (63.0)	57.7
	V. zizanioides	0.5 (98.5)	45.7 (41.4)	2.3 (74.6)	1.7 (68.5)	70.7
	T. latifolia	0.5 (98.5)	40.0 (48.7)	2.5 (72.5)	1.2 (77.0)	74.2
	P. australis	0.5 (98.5)	43.0 (44.9)	2.3 (75.0)	1.5 (71.5)	72.5
	L. articulata	0.5 (98.5)	47.7 (38.9)	2.4 (74.3)	1.3 (75.3)	71.8
Mean purifyi	ng rate (%)	98.4	39.6	68.6	71.1	69.5

Table 7 The water quality of the third batch of wastewaters at the time of loading and 8 days after staying in constructed wetlands*

^{*}The units of all measured data are mg/L. Data in parentheses are the purifying rates, and mean purifying rate is the average value of purifying rates in each column; 0.5 is the instrument-measured bottom limits of AN.

In the aspect of net purifying ability of plants, the four species began to produce net removing rates to all pollutants in any kind of wastewaters, except for *P. australis* to AN in LCW. Combining with purification of plants to the first two batches of wastewater, it can be suggested that the purifying capacity of plants in wetland systems gradually increases with wetland's running. This is obviously associated with that plants gradually grow and develop in wetland and their biomass gradually increases, and also associated with that they gradually adapt themselves to the wastewater environment. It is positive, therefore, that the purifying ability of plants in wetlands would become stronger and stronger as time passed. In addition, it has been inferred from Table 5 and 7 that the purifying ability of wetland systems had basically trended to stable, but the net purifying ability of plants was gradually becoming stronger and stronger, which means that the purifying abilities of soil and other elements in wetland systems were slowly becoming weaker and weaker. However, there still was not a legible rule for the purifying benefits among different species to same pollutant or same species to different pollutants. On the whole, the purifying rate of *T. latifolia* was slightly higher, *L. articulata* was second, and *P. australia* and *V. zizanioides* were slightly lower. It is inferred, therefore, that wetland covered by several plant species might be superior to that by single species with reference to removal efficiency of pollutants (Xia, 2002).

Wastewater type	Species	AN	COD	BOD	Oil
HCW	V. zizanioides	1.2	17.6	3.1	0.2
	T. latifolia	1.1	30.3	4.6	1.0
	P. australis	1.0	27.6	3.6	1.2
	L. articulata	1.1	20.0	3.5	0.8
LCW	V. zizanioides	0.2	14.0	2.6	0.3
	T. latifolia	0.2	19.7	2.4	0.8
	P. australis	0.0	16.7	2.6	0.5
	L. articulata	0.2	12.0	2.5	0.7

Table 8 The net removing amounts of plants to COD, BOD and oil in the third batch of wastewaters^{*}

*Concentrations are expressed in mg/L.

2.5 Growth situations of plants in wetlands

On the 15th day after planting, the surviving rates were investigated; as a result, they were all 100% for V. zizanioides, P. australis, and L. articulata, but only 91.3% for T. latifolia, inferring the last species is difficult to be transplanted. As to the growth situation, the four species all grew better in wetlands with two types of wastewater than in those with clear water with regard to plant height and tiller number (Table 9). This means that wastewater produced a promotion to the growth of plants because there were some nutrients in wastewater promoting the growth of plants. In view of the growth situations of same species in different types of wastewater, V. zizanioides, P. australis, and T. latifolia grew a little poorer in HCW than in LCW, particularly their tiller numbers that all decreased slightly. This is perhaps because that the highly-concentrated floatation wastewater had phyto-toxicity to the three species as compared to the lowconcentrated discharge wastewater. L. articulata was different from them, and it grew better in HCW than in LCW, inferring that this species might be more tolerant to pollution than the above 3 species. Considering the original habitats of the four species, V. zizanioides, P. australis, and T. latifolia were taken from the nursery of SCIB with a good habitat condition, while only L. articulata was from a leachate-discharging wetland near the oil shale residue dump, and furthermore it grew out naturally, not to be planted artificially. That is to say that only the original habitat of L. articulata was closest to that of the experiment. Therefore, it is probably this reason that made L. articulata perform stronger tolerance than other three species. Moreover, that the stronger removing efficiency of L. articulata as shown in Table 4 and 6 is perhaps due to this reason, too. Many plants, such as T. latifolia, assume adaptive tolerance, meaning that plants generally produce or increase tolerance to one harsh environment after they grow for a section of time in the special environment (McNaughton et al., 1974; Taylor and Crowder, 1984; Ye et al., 1997). For example, T. latifolia from metal-contaminated sites accumulates considerably more metals, up to nearly twice as much Zn and Pb and three times as much Cd, in roots than those from the uncontaminated sites (Ye et al., 1997).

Table 9	Growth situations	of the four	herbaceous	plants tested in	n constructed	wetlands

		First i	nvestigation	Second	investigation
Species	Water treatment	Plant height Number of tillers		Plant height	Number of tillers
		(cm)	(No./clump)	(cm)	(No./clump)
V. zizanioides	CW	102.9±10.9	4.5±1.4	110.7±9.8	5.4±1.5
	LCW	104.3 ± 8.7	$4.7{\pm}1.9$	136.8 ± 8.5	8.8 ± 2.5
	HCW	104 5+7 0	4 9+2 2	136 9+10 5	8 4+3 1

T. latifolia	CW	84.7±9.2	3.4±1.5	120.2±17.3	4.3±2.0
	LCW	83.3±13.3	3.3±1.0	133.2±19.2	6.2 ± 2.0
	HCW	84.6±11.6	3.6±1.3	125.8±19.3	5.8 ± 2.5
P. australis	CW	$81.8{\pm}16.2$	4.2 ± 1.4	87.7 ± 17.9	4.9±2.1
	LCW	74.3±12.7	3.9±2.0	106.3 ± 18.5	6.4±3.0
	HCW	82.1±10.3	4.3±1.3	113.1±10.8	6.3±3.5
L. articulata	CW	82.2±7.9	15.9 ± 4.1	101.9 ± 9.0	17.7 ± 5.9
	LCW	81.1±7.0	17.3±4.1	126.7 ± 7.7	28.8±7.6
	HCW	86.1±6.1	16.9 ± 3.4	129.8±6.5	33.3±7.8

The tillering rate is used to express the tiller-forming speed of a plant, which is referred to the ratio of tiller number observed in last time and that observed in this time (Xia *et al.*, 1994). Obviously the higher the tillering rate is, the faster the tiller-forming speed is. The tillers each clump of *V. zizanioides*, *P. australis*, *T. latifolia*, and *L. articulata*, were 3, 2, 1, and 5, respectively at the time of planting. Combined with Table 9, therefore, it can be calculated out that the tillering rates of the four grasses prior to loading wastewater and after loading wastewater (Table 10). At the stage of clean water, the tillering rate of *V. zizanioides* was the lowest, indicating that its speed yielding new tillers was the slowest. This might be influenced negatively by the change of habitat from the xeric to hydrophytic environment. The seedlings of other three species were all collected from hydorphytic habitat. At the stage of wastewater, the tillering rates of *P. australis*, *T. latifolia*, and *L. articulata* tangibly decreased, and those of *V. zizanioides* assumed a trend of increase. This reveals that *V. zizanioides* can acclimatize itself to the hydrophytic environment after it is domesticated in the this environment for a while. At this time, it can present quite strong adaptation and thus produce quite rapid tiller-forming speed even it is in wastewater. It might be inferred, thereby, that the tillering speed of *V. zizanioides* would become faster and faster relative to other three species as time passed despite the fact that it is not a hydorphyte but the other three species are.

Stage	V. zizanioides		P. australia		T. latifolia		L. articulata					
	CW	LCW	HCW	CW	LCW	HCW	CW	LCW	HCW	CW	LCW	HCW
Clean water stage	1.50	1.57	1.63	2.10	1.95	1.70	3.40	3.30	3.60	3.18	3.46	3.38
Wastewater stage	1.20	1.87	1.71	1.17	1.64	1.47	1.26	1.88	1.61	1.11	1.66	1.97

Table 10 Tillering rates of the four plants before and after wastewater irritation

3 CONCLUSION

It might be concluded from the foregoing results:

1) The concentrations of pollutants in oil-refined wastewater were quite high, especially HCW, whose pollutants tested in the experiment exceeded the second grade of WDL in Guangdong, China. Therefore, HCW could not be directly discharged but should be further treated. The tested indices of LCW that came from HCW through physical and chemical purification, almost all have met wastewater WDL. In general, the removing rates of physical and chemical methods for oil-refined wastewater were high in spite of the phenomenon that the concentrations of pollutants continuously changed and the removal efficiencies were also relatively unstable.

2) At the beginning, the wetlands could remove almost all pollutants in wastewaters, but their performance became a littler poorer and then became relatively stable as time passed. During the period of wastewater treated with wetlands, the purifying efficiencies of wetlands to AN, COD, BOD, and oil were

rated as AN > oil > BOD > COD.

3) At the beginning, the purifying function of plants was quite weak. The purifying rates of some wetlands with plants were even lower than those without plants. As time passed, however, the function of plants gradually increased with acceleration of plant growth and increase of biomass. But there were a very disparities among purifying abilities of different species, and they were not significant different.

4) All tested species, *V. zizanioides*, *P. australis*, *T. latifolia*, and *L. articulata* had better growth in wetlands with any type of wastewaters than in wetlands with clean water. However, the tiller numbers of the former three species in HCW were fewer than those in LCW, but *L. articulata* was on the contrary, inferring that HCW may not be very suitable to the growth of the former three species due to too high concentrations, but still suitable to the growth of *L. articulata*. This phenomenon was perhaps related to the original habitat of *L. articulata* that was a natural effluent wetland of oil-shale waste dump in the locality, very similar to the habitat condition of the experiment. *V. zizanioides*, *P. australis*, and *T. latifolia* were collected from the nursery having different growing conditions however.

5) During the phase of clean water cultivation, the new tiller producing rate of *V. zizanioides* was lowest among the four species tested. This was also associated probably with their original habitats, as *V. zizanioides* was sampled from the xeric environment while other three species were from the hydrophytic one similar to the condition of the experiment. During the phase of cultivation in wastewater, the tiller-producing speed of *V. zizanioides* gradually rose whereas that of the other three species was distinctly lowered, indicating that *V. zizanioides* possesses stronger tiller-producing ability than the other three species after it has acclimatized itself to the hydrophytic environment. Judging from these results, *V. zizanioides* might have a stronger adaptation to the environment than other species tested in the experiment.

Acknowledgments

This study was supported by The Vetiver Network and Maoming Petro-Chemical Company, China Petro-Chemical Corporation.

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