人工湿地处理炼油废水的生态效益研究

夏汉平1, 柯宏华2, 邓钊平2, 谭 鹏2, 刘世忠1

(1. 中国科学院华南植物研究所,广州 510650; 2. 中国石油化工股份有限公司茂名分公司,广东 茂名 525011)

摘要: 来自茂名石化公司的炼油废水含有较高浓度的污染物, 超过广东省规定的排放标准, 未经处理不能直接排放。4 种草本植物, 香根草、芦苇、宽叶香蒲和蒲草被用来测试建植人工湿地的效果以及所建植的人工湿地处理炼油废水的效果。在为期 2 个月的处理过程中, 人工湿地在前期对炼油废水的净化效率很高,它们对第一批高浓度废水中氨氮、COD、BOD 和油的去除率分别是 97.7%、78.2%、91.4% 和 95.3%, 对第一批低浓度污水分别是 97.1%、71.5%、73.7% 和 89.8%。但是, 随着时间的推移, 湿地的净化效果会有一定程度的下降, 然后逐渐趋于稳定。湿地对氨氮、COD、BOD 和油类的去除效率始终表现为氨氮>油类>BOD> COD, 但植物对它们的净去除量却是 COD> BOD> 氨氮和油类。湿地建植之初, 植物的净化功能很弱, 但随植物的生长和生物量的增加而逐渐增强。然而, 不同植物种对废水的净化率很接近, 基本上无显著性差异。被测试的 4 种植物在污水湿地中的生长表现都好过在清水湿地中的, 但香根草、芦苇和宽叶香蒲在高浓度废水的分蘖数比在低浓度的废水少些, 而蒲草相反, 表明高浓度污水相对于低浓度污水而言已经对前面 3 个种产生了伤害, 却仍促进蒲草生长。在清水培养阶段, 香根草产生分蘖的速度是 4 个种中最低的; 进入污水培养阶段, 香根草的分蘖速度升高, 而其他 3 种的却下降, 这意味着香根草对恶劣环境的适宜性, 特别是经较长时间的适应后, 可能比其他 3 个种更强。

关键词: 人工湿地; 废水处理; 植物净化; 炼油废水

Ecological effectiveness of constructed wetlands in treating oil refined wastewater

XIA Han-Ping¹, KE Hong-Hua², DENG Zhao-Ping², TAN Peng², LIU Shi-Zhong¹ (1. South China Institute of Botany, Chinese A cadeny of Sciences, Guangzhou 510650, China; 2 SIN OPEC M aon ing Ref ining & Chen ical Co Ltd., Macming, Guangdong 525011, China). Acta Ecologica Sinica, 2003, 23(7): 1344~ 1355

Abstract W astew ater produced from the oil refinery of the M aoming Petro-Chemical Company, China Petro-Chemical Corporation contains high concentrations of organic and inorganic pollutants, therefore it cannot be discharged directly into river or sea unless being treated first. Four plant species, V etiveria zizanioides, Phragmites australis, Typha latifolia, and Lepironia articutala were planted in large containers as constructed vertical flow wetland to test their efficiencies in the purification of oil refined

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作者简介: 夏汉平(1966~), 男, 湖南汉寿县人, 博士, 研究员, 主要从事恢复生态学与环境生态工程研究。 Email: xiahanp@scib. ac cn

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w astew ater and their grow th in wetlands soaked with oil refined wastewater. The results gotten from a 2month treatment indicated that the purifying rates of constructed wetlands for oil refined wastewater were all very high at the beginning, which removed 97.7% of ammonia N, 78.2% of COD, 91.4% of BOD, and 95.3% of oil in the first batch of highly-concentrated wastewater (HCW), and 97.1% of ammonia N, 71.5% of COD, 73.7% of BOD, and 89.8% of oil in the first batch of low-concentrated wastewater (LCW). But the performance of wetlands was decreased and became basically stable as time passed. The efficiency of wetlands in removing the pollutants was always in order of ammonia N > oil > BOD > COD, but the net removal of plants to them was ranked as COD > BOD > oil and ammonia N. In the beginning, the purifying function of plants was quite weak, but it gradually increased with the acceleration of plants grow the However, there was almost no significant difference in the removal efficiencies among the four species The four tested species produced better grow th in wetlands with HCW or LCW than with clean water, but V. zizanioides, P. australis, T. latifolia produced fewer tillers in HCW than those in LCW, while this was contrary to L. articutala This inferred that HCW might damage the first three species, and promote the growth of L. articutala During the period 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 period of treatment water soak, while the tiller-producing rates of the other three species were distinctly lowered It was therefore suggested that V. zizanioides might have a stronger adaptation to the harsh environment than other species tested in the experiment, especially in the situation of long time of adaptation to the environment However, the above results remains to be further verified due to the limited observation time of only two months

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W ater is the source of life, and is the basic condition of human survival. The severe water pollution and insufficient supply are now adays two difficult problems about the water environment around the globe. In China, the water problem is more prominent and urgent. 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 [1,2].

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 in Southwest Guangdong, discharged 13.12 million tons of oil refined wastewater and 7.48 million tons of ethylene-produced wastewater in the year 1999 alone. A lthough the company has strongly recognized the importance of environmental protection, and invested substantially in building up new purifying plants and in enlarging the capacity of old plants, 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 reached the effluent standard in 1999, indicating that the company still has a major task with special reference to wastewater purification.

Wetland is regarded to be very effective in the field of environmental protection, especially for wastewater treatment. For example, Knight $et\ al$, through statistic calculation to a set of more than 1300 data, showed 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^[3]. Due to its low expense, low

energy-consumption, 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, particularly by developing nations^[4-7]. Constructed wetlands also have been used to treat petroleum industry effluents, but they are still concentrated mainly on the removal of COD, suspended solids, and heavy metals^[8]. There has been very poor documentation to date on the purification of constructed wetlands for the main pollutants of petroleum industry effluents, such as oil, phenol, and benzene

M any experiments and observations have confirmed that vetiver grass (Vetiveria zizanioides (L.) Nash) has excellent effects in erosion control, amelioration of harsh soil conditions, wastewater purification, and other environmental uses[9-11]. For example, 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%, $82\% \sim 90\%$, and $92\% \sim 93\%$, respectively^[12]. This species can also purify over 87% of ammonia N and 74% of total P from landfill leachate [13]. Phragm ites australia (Cav.) Trin ex Steudel and Typha latif olia 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 [14-17]. Lep ironia articutala Rich, a local species of South China and a potential pollutant-purifying plant, grow s mainly on natural wetlands nearby mine tailings or industrially polluted areas, but there has been no any report on its effectiveness for wastewater purification. In general, there are very few documents on the purification of wetland systems using the above four species for industrial wastewater, especially oil refined wastewater It is hoped, therefore, that the present study would provide information, firstly to demonstrate the ability of the four plants in purifying wastewater from oil refinery by using constructed wetlands, secondly to screen out the highly effective pollutant removing species, and thirdly to offer an economical and effective pollutant purifying method for industrial wastewater, especially for oil-refined wastewater

1 Materials and Methods

1.1 Experimental materials

The experiment was set up at the wastewater treatment station of MPCC, and simulated 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).

Table 1 Chemical characteristics of soil used in constructed wetlands

pН	O rganic matter (g/kg)		Total P (g/kg)	Total K (g/kg)	Total S (g/kg)		A vailable P (mg/kg)	A vailable K (m g/kg)
4. 57	6 10	0. 33	0. 14	4. 48	0.11	30 0	12. 7	74. 7

The tested wastewater in the trial consisted of a highly concentrated wastewater (HCW) and a low concentrated wastewater (LCW). The former was the flotation wastewater, having the highest concentration of pollutants; the latter was the HCW after having been physically and chemically treated Of the tested 4 herbaceous species, V. zizanioides, P. australis, and T. latifolia were collected from the nursery of South China Institute of Botany (SCB), among them the first had been growing in the xeric environment, and the latter two in the hydrophytic one; L. articutala was collected from a natural wastewater discharging channel beside the oil-shale waste dump in M aoming, which was very similar to an artificial wetland of wastewater purification

1.2 Trial designs and arrangements

Simulated artificial wetlands were constructed in large earthen containers, filled with wastewater for © 1995-2005 Tsinghua Tongfang Optical Disc Co., Ltd. All rights reserved.

purification Three water treatments (HCW, LCW, and clean water (CW)) and 4 plant treatments (V. zizanioides, P. australis, T. latifolia, and L. articutala) were used In addition, 2 groups of control were also included in the trial, which were HCW wetland without plants and LCW wetland without plants All treatments and controls had three replicates During the trial period all the containers were all grown in open air under an open frame which was covered by a large cloth canopy when it rained to prevent rainwater from entering the containers

Large earthen containers, 70 cm high and 90 cm in diameter, with an outlet drain for each one on the bottom were custom made for the trial Each container was then filled with 87.1 kg (DW) of soil and then was planted with 18 slips of one of the above 4 species. Due to the big differences of stem diameter among different species, T. latifolia, P. australis, V. zizanioides, and L. articutala were planted with 1 tiller, 2, 3, and 5 tillers, respectively, for each slip in order to make each species have as identical as possible biom ass when planting Prior to planting, their tops and roots were all pruned to 30 cm and 5 cm, respectively. A fter planting, clean water was loaded into the pots until the water level was 10 cm higher than the soil surface. The survival rates were recorded and dead slips were replaced 15 days later. During the period of establishment, clean water was added to the containers once every 2~4 days to supplement water loss by evaportranspiration. At the end of the 2 months establishment period, the soil was let to dry up, then the 3 treatment waters were loaded, 55 kg for each container. Samples of wastewater were collected from the drains for chemical analysis 8 days after loading. After each test was over, all wastewaters were discharged and containers were let open until the soil become almost dry, then the second and third batches of wastewater were loaded, and the same operation as the first batch was repeated 8 days after each batch of wastewaters was loaded Concretely speaking, the three batches of wastewaters lasted in constructed wetlands from July 17th ~ 25th, August 6th ~ 14th, August 21st ~ 29th, respectively. Obviously, the experiment can be divided into two stages: the stage of clean water cultivation, which was from May 4th to July 16th; and the stage of treatment water cultivation, which was from July 17th to September 9th.

- 1.3 Observations and analysis
- 1 3 1 Plant growth in wetlands The observation included the survival rate, plant height and tiller number. The latter two data were made twice, which were prior to loading treatment water (July 16) and in the end of the experiment (September 9), respectively.
- 1 3 2 Analyses of wastewater The analyses included pH, ammonia nitrogen (AN), oil, sulfide, volatile phenol (VP), benzene, COD, and BOD. pH was measured with a pH meter COD values were measured through measuring the consumption of dissolved oxygen while the wastewaters were oxidized with KM nO4; BOD was also referred to as the consumption of dissolved oxygen after the wastewaters were incubated 5 days at 20 in an incubator Ammonia N was determined with direct distillation; VP and sulfide were measured by colorimetry; oil was determined by ultraviolet spectrophotometry, and benzene by gas chromatography^[18].

2 Results and D iscussion

2.1 Quality of wastewaters at loading time and purifying efficiency of the physical and chemical method. The levels of AN, COD, BOD, oil, VP, and benzene in wastewaters before (HCW) and after (LCW) being treated by the physical and chemical methods at the wastewater treatment plant are listed in Table 2. It showed that the concentrations of these pollutants, except for pH and sulfide, in HCW, irrespective of which batch wastewater, were almost all higher than the Second Grade Standard (SGD) of Wastewater Discharge Limits (WDL) in Guangdong (DB44/26-2001). After HCW was physically and

chem ically treated, the contents of these pollutants in LCW 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 than 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 (Table 2). Considering that acidity and sulfide in HCW completely met the discharge standard, and VP and benzene were almost all removed by the physical and chemical methods in the first and second analyses, these four pollutants were not measured any longer in the third analysis. In addition, it can be seen from Table 2 that the water quality of wastewaters is quite changeable and the physical and chemical removal rates are also unstable. For example, VP in HCW was $1.8 \, \text{mg/L}$ in the first batch and became into $8.48 \, \text{mg/L}$ in the second, increasing by nearly 4 times; BOD and other pollutants had the similar changes

Table 2 Quality of wastewaters at the different loading stages^a

W astewater type	pН	AN	COD	BOD	O il	Sulfide	VP	Benzene			
W ater	quality of t	he first bate	h of wastew	aters at the	time of loa	ding (17 Jul	y 2002)				
HCW	7. 10	22	132	41	36	0.18	1. 80	8 972			
LCW	7. 22	17	87	8 2	6.0	0.08	0 07	0 005			
Purifying rateb(%)	-	22 7	34. 1	80.0	83. 3	55. 5	96 1	> 99. 9			
W ater quality of the second batch of wastewaters at the time of loading (6 August 2002)											
HCW	7. 21	29	196	26	47	0.46	8 48	9. 30			
LCW	7. 02	18	67	6.7	13	0 05	0 05	0.005			
Purifying rate (%)	-	37. 9	65. 8	74. 2	72 3	89. 1	99. 3	> 99. 9			
W ater o	uality of the	third batch	of wastewa	iters at the t	ime of load	ing (21 Aug	ust 2002)				
HCW	-	50	174	78	61	-	-	-			
LCW	-	34	78	9. 2	5. 4	-	-	-			
Purifying rate (%)	-	32 0	55. 2	88 2	91. 1	-	-	-			
W a	stew ater Di	scharge L im	its in Guang	dong Provin	ice, China	(DB 44/26-20	01)c				
Second grade	6~ 9	15	120	30 8	3	1. 0	0.5	2 5			
First grade	6~ 9	10	60 2	20 5	i	0.5	0.3	2 0			

a The unit of all data is m g / L; 0 005 is the instrument measuring lowest limit of benzene; b Referred to as purifying rates of the physical and chemical method; c Issued by Guangdong Provincial Bureau of Environmental Protection on 20 August 2001

2.2 Purifying benefits of constructed wetlands in the first batch of wastewaters

The quality of the first batch of wastew aters after being treated in wetlands for 8 days is shown in Table 3, which indicated that: 1) apart from a small rise in pH, all other pollutants dropped sharply, and furthermore AN, VP, and benzene all reached the instrument measuring lowest limits, and parts of BOD and sulfide also reached their respective lowest limits; 2) comparing HCW with LCW, the drop of pollutant levels was higher in the former than in the latter; and 3) the purifying rates of wetlands for AN, COD, BOD, and oil were all in the order of AN > oil > BOD > COD, irrespective of the type of wastew aters, LCW or HCW. The reasons for the highest purifying rate for AN were probably due both to its strong volatility and the easy transformation feature into nitrate N or N $_2^{[13]}$. Kantaw anichkul *et al* also found that TKN and NH₃-N were removed over 90% by constructed wetlands with *V*. $_2$ iz an ioid $_2$ is interesting that the removal of AN was the lowest by using the physical and chemical method (Table 2), whereas it was the highest by 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 latest report pointed out that the removal efficiencies of reed beds to mineral oil were 88% \sim 96% [19]. In addition to these, there

was another phenomenon in Table 3 that treatments with plants had the almost same purifying efficiencies as those without plants (controls), which is revealed more clearly in Table 4

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, namely the purifying effectiveness of the treatments with plants was even poorer than controls. This was probably due to the relatively smaller biomass and the relatively poorer adaptation to the wastewater environment at the beginning. Table 4 also shows that there were almost no significant differences among different species with regard to their purifying efficiencies to pollutants, except for parts of COD (P > 0.05). Overall the purifying effectiveness of L. articutala was slightly better compared with other 3 species

Table 3	Quality of	the first batch of	wastewaters after 8	3 days treatment	in wetlands*
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T reatm en t	pН	AN	COD	BOD	O il	Sulfide	VP	Benzene
		W ater qu	ality and remo	val rates of H	CW			
СК	8 51 ± 0 16	0 5 (97. 7)	$32\ 1 \pm 4\ 4$ (75. 8)	4.1 ± 0.7 (90.0)	1. 80 ± 0. 09 (95. 0)	0 11 (38 9)	0 02	0.005
V. zizanioides	7. 57 ± 0.05	0 5 (97. 7)	30.9 ± 5.9 (76.5)	4. 4 ± 1. 1 (89. 3)	1. 30 ± 0. 37 (96 4)	0 11 (38 9)	0 02	0 005
T. latif olia	7. 92 ± 0.09	0 5 (97. 7)	$26\ 4 \pm 6\ 6$ $(80\ 3)$	3.8 ± 0.8 (90.7)	2 40 ± 0 10 (93 3)	0 01 (94 4)	0 02	0. 005
P. australis	7. 86 ± 0 18	0 5 (97. 7)	31. 7 ± 1. 1 (75. 8)	3.3 ± 0.4 (91. 9)	0.85 ± 0.07 (97. 6)	0 03 (83 3)	0 02	0.005
L. articutala	7. 82 ± 0 15	0 5 (97. 7)	23.5 ± 3.3 (82.6)	2 0 (95. 1)	2 10 ± 0 15 (94 2)	0 07 (61. 1)	0 02	0. 005
M ean purifying	rate (%)	97. 7	78 2	91. 4	95. 3	63. 3	-	-
		W ater qu	ality and remo	val rates of L	CW			
CK	$8\ 10 \pm 0\ 05$	0 5 (97. 1)	26.0 ± 5.4 (70.1)	28 ± 01 (65. 9)	0.55 ± 0.02 (90.8)	0 02 (75 0)	0 02	0.005
V. z iz an ioid es	7. 82 ± 0.22	0 5 (97. 1)	28.5 ± 2.7 (66.7)	2 0 (75. 6)	0.93 ± 0.07 (84.5)	0 02 (75 0)	0 02	0. 005
T. latif olia	7. 96 ± 0 27	0 5 (97. 1)	24.6 ± 2.0 (71.3)	2 0 (75. 6)	0 77 ± 0 10 (87. 2)	0 01 (87. 5)	0 02	0. 005
P. australis,	7. 59 ± 0 11	0 5 (97. 1)	27. 7 ± 1. 4 (67. 8)	2 0 (75. 6)	0 31 ± 0 02 (94 8)	0 02 (75 0)	0 02	0.005
L. articutala	7. 88 ± 0 11	0 5 (97. 1)	16 4 ± 4 2 (81. 6)	2 0 (75. 6)	0.51 ± 0.03 (91.5)	0 02 (75 0)	0 02	0.005
M ean purifying	rate (%)	97. 1	71. 5	73. 7	89. 8	77. 5	-	-

^{*} The units of all observed data (parts are means ± SD) 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, 0.01, 0.02, and 0.005 are the instrument measuring lowest limits of AN, BOD, sulfide, VP, and benzene, respectively. When the measured data are smaller than the instrument measuring lowest limits, they are treated as the instrument measuring lowest limits

2.3 Purifying benefits of constructed wetlands in the second batch of wastewater

The second batch of wastew aters was loaded after the first batch was discharged for 11 days, and then collected samples for analysis 8 days later (Table 5). The changes of concentrations were basically consistent with the first batch (1) pH values slightly increased (2) All pollutants decreased at varying degrees, among them VP and benzene of all treatments went down to their respective instrument

measuring lowest limits, so did parts of AN and sulfide This further indicates that wetlands provided very high removal rates of these pollutants, the highest of which was benzene in HCW, up to over 99%. (3) The removal rates of wetlands to AN, COD, BOD and oil still presented in order of AN > oil > BOD > COD. (4) Most purifying rates of this batch were lower in comparison with those of the first batch, but those in LCW had a higher reduction rate, especially COD, which dropped to 35.8%. This is perhaps because the purifying ability of wetlands decreases with age (5) Overall purifying effectiveness of wetlands to high concentration

Table 4 The net removal of COD, BOD and oil by plants in the first batch of wastewaters*

T reatm en	t	Species	COD	BOD	O il
HCW	V.	z iz an ioid es	1. 2	- 0.3	0 50
	T.	la tif ol ia	5. 7	0.3	- 0.60
	P.	australis	0.4	0.8	0.95
	L.	articu ta la	8 6	2 1	- 0.30
LCW	V.	z iz an ioid es	- 25	0.8	- 0.38
	T.	la tif ol ia	1. 4	0.8	- 0.22
	P.	australis	- 1.3	0.8	0 24
	L.	articu ta la	9. 6	0.8	0.04

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

pollutants (in HCW) was better than to low concentration pollutants (in LCW), except for AN. (6) Purifying efficiency of plants still was not very high, namely the difference of purifying rates was very small between treatments with plants and without plants (CK).

Table 5 Quality of the second batch of wastewaters after 8 days treatment in wetlands*

Treatment	pН	AN	COD	BOD	O il	Sulfide	VP	Benzene
		W ater qu	ality and remo	val rates of H	ICW .			
CK	8 65 ± 0 06	2 9 ± 0 1 (90 0)	65. 9 ± 8. 8 (66. 3)	9.8 ± 0.7 (62.3)	3.53 ± 0.08 (92.6)	0 04 (91 3)	0 02	0 005
V. zizanioides	7. 70 ± 0. 10	1. 5 ± 0. 3 (94. 8)	49. 4 ± 6. 6 (75. 0)	6. 7 ± 1. 1 (74. 1)	$2 \ 22 \pm 0 \ 34$ (95. 3)	0 02 (95 7)	0 02	0.005
T. latifolia	$8 \ 02 \pm 0 \ 25$	2.1 ± 0.4 (92.8)	58.6 ± 2.3 (69. 9)	7. 9 ± 1. 0 (69. 7)	2 37 ± 0 31 (94 9)	0 04 (91 3)	0 02	0 005
P. australis	7. 83 ± 0. 11	1. 3 ± 0.1 (95. 5)	53.3 ± 5.0 (73.0)	5. 7 ± 0. 2 (77. 9)	290 ± 0.07 (93.8)	0 03 (93 5)	0 02	0 005
L. articutala	7. 98 ± 0. 34	0 9±0 1 (96 9)	50 1 ± 8 3 (74 5)	2.9 ± 0.4 (89. 0)	240 ± 015 (94.9)	0 04 (91 3)	0 02	0 005
M ean purifyin	g rate (%)	94. 0	71. 7	84. 6	94. 3	92 6	-	-
		W ater qu	ality and remo	val rates of L	CW			
CK	8 12 ± 0 11	1. 3 ± 0.3 (92.8)	40 6 ± 7. 0 (38 8)	2 1 ± 0 1 (68 7)	244 ± 020 (81. 5)	0 01 (80 0)	0 02	0 005
V. zizanioides	7. 95 ± 0. 20	0 5 (97. 2)	43.6 ± 2.9 (34.3)	2 0 (70 1)	1. 59 ± 0. 4. 3 (87. 7)	0 01 (80 0)	0 02	0 005
T. latif olia	8 14 ± 0 07	0 5 (97. 2)	49.5 ± 0.9 (25. 4)	3.2 ± 0.2 (52.2)	1. 61 ± 0. 33 (87. 7)	0 01 (80 0)	0 02	0 005
P. australis,	7. 78 ± 0.05	1. 3 ± 0. 4 (92. 8)	45.2 ± 4.7 (32.8)	2.4 ± 0.1 (64.2)	1. 68 ± 0 08 (86 9)	0 01 (80 0)	0 02	0 005
L. articutala	8 20 ± 0 10	0 5 (97. 2)	35. 2 ± 3. 5 (47. 8)	2.6 ± 0.4 (61. 2)	1. 85 ± 0.13 (85. 4)	0 01 (80 0)	0 02	0 005
M ean purifyin	g rate (%)	95. 4	35. 8	63. 3	85. 8	80. 0	-	_

^{*} The units of all observed data are the same as Table 2, and others have the same meanings as Table 3

Table 6 showed that the net removing amounts of treatments with plants to AN, COD, BOD and oil in HCW were all positive values, indicating that plants began to produce purifying efficiency to these pollutants in the second batch of wastewaters. This result also suggests that wetlands with plants were more effective in treating HCW than LCW, because the net removing amounts to pollutants in LCW were

lower, close to 0 or even negative. This inferred that the purifying ability of plants were still unstable at this stage. Regarding the purifying effectiveness among different species, it was still L. articutala, which performed slightly better than V. zizanioides, P. Australia, and T. latifolia. On the whole, the four species had similar purifying abilities to wastew ater.

2.4 Purifying benefits of constructed wetlands in the third batch of wastewater

The third batch of wastewaters was loaded after the second batch of wastewater was discharged for 7 days. The 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

Table 6 The net removal of AN, COD, BOD and oil by plants in the second batch of wastewaters*

T reatm en	ıt	Species	AN	COD	BOD	O il
HCW	V.	z iz an ioid es	1. 4	16 5	3. 1	1. 31
	T.	la tif ol ia	0.8	7. 3	1. 9	1. 16
	P.	australis	1. 6	12 6	4. 1	0 63
	L.	articu ta la	2 0	15. 8	69	1. 13
L CW	V.	z iz an ioid es	0.8	- 3.0	0 1	0.85
	T.	la tif ol ia	0.8	- 89-	1. 1	0.83
	P.	australis	0	- 4.6	0.3	0.77
	L.	articutala	0.8	5. 4 -	0. 5	0.59

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

purifying rates of the second batch, those of the third batch did not have a clear increase or decrease, suggesting that wetlands began to enter a relatively stable state. In general, the purifying rates of the third batch of wastewaters were still quite high, over 50% with the exception of COD in LCW. In

Table 7 Quality of the third batch of wastewaters after 8 days treatment in wetlands*

W astew ater type	T reatm ent	AN	COD	BOD	O il	M ean purifying rate(%)
HCW	СК	2 2 ± 0 2 (95. 6)	81. $3 \pm 4 \ 0$ (53. 3)	8 7 ± 1. 7 (88 8)	3 10 ± 0 13 (94 9)	83 2
	V. z iz an ioid es	1. 1 ± 0. 1 (97. 9)	63. 7 ± 7. 9 (63. 4)	5.6 ± 0.3 (92.8)	2.85 ± 0.56 (95. 2)	87. 3
	T. latif olia	1. 1 ± 0. 3 (97. 8)	$51. \ 0 \pm 5. \ 8$ (70. 7)	4.1 ± 0.7 (94.7)	2 13 ± 0 07 (96 6)	89. 9
	P. australis	1. 2 ± 0. 4 (97. 7)	53. 7 ± 2. 1 (69. 2)	5.1 ± 0.7 (93.4)	1. 89 ± 0 89 (96 9)	89. 3
	L. articutala	1. 1 ± 0. 2 (97. 7)	61. 3 ± 5. 0 (64. 8)	5. 2 ± 0. 8 (93. 3)	$\begin{array}{c} 2 \ 35 \pm 0 \ 44 \\ (96 \ 2) \end{array}$	88 0
M ean pu	urifying rate (%)	97. 3	64. 3	92 6	96.0	87. 5
LCW	СК	0 7 ± 0 1 (98 0)	59.7 ± 1.4 (23.5)	4.9 ± 0.3 (46.4)	$2 03 \pm 0 04$ $(63 0)$	57. 7
	V. z iz an ioid es	0 5 (98 5)	45. 7 ± 3. 6 (41. 4)	23 ± 03 (74.6)	1. 67 ± 0 04 (68 5)	70 7
	T. latif olia	0 5 (98 5)	40.0 ± 1.0 (48.7)	25 ± 04 (72.5)	1. 25 ± 0. 77 (77. 0)	74. 2
	P. australis	0 5 (98 5)	43.0 ± 8.8 (44.9)	23 ± 01 (75. 0)	1. 52 ± 0. 44 (71. 5)	72 5
	L. articutala	0 5 (98 5)	47. 7 ± 7. 8 (38. 9)	2.4 ± 0.1 (74.3)	1. 30 ± 0. 09 (75. 3)	71. 8
M ean pu	urifying rate (%)	98 4	39. 6	68. 6	71. 1	69. 5

^{*} The units of all observed data are the same as Table 2, and others have the same meanings as Table 3

addition, the purified effect of HCW by wetlands was higher than that of LCW similar to the first two batches of wastewater

Regarding the net purifying ability of plants, the four species began to produce net removing rates to all pollutants in both types of wastewaters (Table 8). Furthermore the removed amounts of the four elements were COD > BOD > oil and AN, which was completely contrary to the order of their removal rates by wetlands (Table 3, 5, and 7). Combined with purification of plants in the first two batches of wastewater, it was found that the purifying capacity of plants in wetland systems gradually increased with wetland's running. This was obviously associated with gradual growth and development of the plants resulting in a gradual increase of biomass, and also they gradually adapted them selves to the wastewater environment as they grew in wetlands. It is positive, therefore, that the purifying ability of plants in wetlands became stronger and stronger as plants grew up. In addition, there still was no clear distinction of the purifying benefits among the 4 species to same pollutant or same species to different pollutants. On the whole, the effectiveness of T. latif olia was best, L. articutala was second, and P. australia and V. zizanioides were last. It was suggested, therefore, that wetland covered by several plant species might be superior to that by single species with reference to removal efficiency of pollutants

2.5 Survival and grow th of plants in wetlands

On the 15th day after planting, the survival rates by plants in the third batch of wastewaters* were investigated, 100% were recorded for V. V zizanioides, P. australis, and L. articutala, but only 91.3% for T. latifolia, indicating the last species was difficult to be transplanted For growth, the four species all grew better in wetlands with two types of wastewater than in those with clear water in tems of plant height and tiller number (Table 9). This was probably due to the presence of some nutrients in wastewater It was also found from Table 9 that V. zizanioides, P. australis, and T. latif olia produced less grow th in HCW than in LCW,

Table 8 The net removal of AN, COD, BOD and oil

W astew ater type		Species	AN	COD	BOD	O il
HCW	V.	z iz an ioid es	1. 2	17. 6	3. 1	0 2
	T.	la tif ol ia	1. 1	30, 3	4. 6	1. 0
	Р.	australis	1. 0	27. 6	3 6	1. 2
	L.	articutala	1. 1	20 0	3. 5	0.8
LCW	V.	z iz an ioid es	0.2	14. 0	2 6	0.3
	T.	la tif ol ia	0.2	19. 7	2 4	0.8
	Р.	australis	0.2	16 7	2 6	0.5
	L.	articutala	0. 2	12 0	2 5	0.7

^{*} Concentrations are expressed in mg/L

particularly their tiller numbers This is perhaps because that HCW contained higher levels of phyto-toxic materials to the three species than LCW. L. articutala 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 other 3 species Considering the original habitats of the four species, V. zizanioides, P. australis, and T. latifolia were taken from the nursery of SCB under a good habitat condition, whereas L. articutala was from a leachate-discharging wetland near the oil shale residue dump where it established naturally Therefore L. articutala original habitat was closest to that of the experiment, and probably due to this reason that L. articutala grew better than other three species Moreover, the stronger removing efficiency of L. articutala as shown in Table 4 and 6 was probably also due to this reason Many plants can assume adaptive to lerance, meaning that plants generally produce or increase to lerance to one harsh environment after growing for some time in the special environment [16,20]. For example, T. latifolia from metalcontaminated 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 [21].

	***	First investi	gation (July 16 th)	Second inves	stigation (Sep. 9 th)
Species	W ater treatment	Plant height (cm)	Number of tillers (Num. /clump)	Plant height (cm)	Number of tillers (Num. /clump)
V. z iz an ioid es	CW	102 9 ± 10 9	4. 5 ± 1. 4	110 7 ± 9. 8	5. 4 ± 1. 5
	LCW	104. 3 ± 8. 7	4. 7 ± 1. 9	136 8±8 5	88 ± 25
	HCW	104. 5 ± 7 . 0	4.9 ± 2.2	1369 ± 105	8 4 ± 3. 1
T. latif olia	CW	84. 7 ± 9. 2	3. 4 ± 1. 5	$120\ 2 \pm 17.\ 3$	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 ± 16 2	4. 2 ± 1. 4	87. 7 ± 17. 9	4.9 ± 2.1
	LCW	74. 3 ± 12. 7	3.9 ± 2.0	$106 \ 3 \pm 18 \ 5$	64 ± 30
	HCW	82 1 ± 10 3	4. 3 ± 1. 3	113 1 ± 10 8	6 3 ± 3 5
L. articutala	CW	82 2 ± 4. 4	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

Table 9 Growth of the four plants tested in constructed wetlands

The tillering rate is the ratio of tiller number observed in the last time to the current number [22]. The tiller numbers of each slip of V. zizanioides, P. australis, T. latif olia, and L. articutala, were 3, 2, 1, and 5, respectively at the time of planting And then combined with Table 9, the tillering rates of the four grasses in different stages, clean water cultivation and treatment water cultivation stages, are calculated in Table 10 At the establishment stage in clean water, the tillering rate of V. zizanioides was the lowest, inferring it was affected negatively by the change of habitat from the xeric to hydrophytic environment The slow growth of V. zizanioides in the beginning could be explained by the gradual increase in parenchyma density in both root and shoot of vetiver plant as it changes from dry land to wetland conditions. The other three species were all collected from hydorphytic habitat, as a result they were hardly influenced by the wetlands environment At the treatment water phase, the tillering rates of P. australis, T. latifolia, and L. articutala tangibly decreased, whereas those of V. zizanioides increased This revealed that V. zizanioides could acclimatize itself to the hydrophytic environment after it was transferred to the new one This was probably because that the size and number of air chambers in the leaves of V. zizanioides gradually became larger, and furthermore air chambers accumulated ergastic substance when it was transplanted from dryland to wetland [23]. Ergastic substance is possibly related to the storage of contam inants from the wetland Once adapted, V. zizanioides can produce quite rapid tiller forming rate 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 it matures although it is not a hydrophyte as the other three species

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

g.	V.	z iz an io	id es	P.	austra	lia	T	. latif o	lia	L	articu	ta la
Stage	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
Treatment water 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

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3 Conclusion

It m ight be concluded from the foregoing results:

- (1) The concentrations of pollutants in oil refined wastewater were quite high, especially in HCW; they exceeded the second grade of WDL in Guangdong, China The tested indices of LCW that came from HCW after physical and chemical purification, almost all met WDL.
- (2) In general, the pollutants removal rates of physical and chemical methods for oil-refined wastewater were high despite the continuously changing concentrations of the pollutants and the relatively unstable removal efficiencies
- (3) In the beginning, the wetlands could remove almost all pollutants in wastewaters, but their efficiencies became slower and then became relatively stable with time. The purifying efficiencies of wetland were in order of AN > oil > BOD > COD.
- (4) At the start of the trial the purifying function of plants was quite weak. As time passed, however, the function of plants gradually increased with acceleration of plant growth and increase of biomass. But there were only small variations among purifying abilities of different species. The net removed amounts of plants to pollutants ranked as COD > BOD > oil and AN.
- (5) All tested species, V. zizanioides, P. australis, T. latifolia, and L. articutala had better grow the in wetlands with any type of wastewaters than in wetlands with clean water. However, the tiller numbers of the first three species in HCW were fewer than those in LCW, except for L. articutala, This result was perhaps related to the natural habitat of L. articutala, which was a natural effluent wetland of oil-shale waste dump in the locality and very similar to the habitat of the experiment; whereas the other three species were collected from the nursery having different growing conditions

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