Research on Phosphorus Removal in Artificial Wetlands by Plants and Their Photosynthesis

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ABSTRACT

Urban rainfall runoff pollution has become a major reason for water eutrophication problem in the process of urbanization in China, while phosphorus is a significant restrictive factor that influences primary productivity of freshwater system. It's rather significant to conduct phosphorus control in waste water with engineering measures. This research, based on material balance research of phosphorus in artificial wetlands, HRT (hydraulic retention time) and analysis of wetland plant photosynthesis and removal rate of phosphorus, simulates purification of phosphorus in urban runoff sewage by artificial wetland system. Experiment shows that removal rate of total phosphorus in urban runoff sewage by artificial wetland system reaches 42.23%-60.89%, and contribution rate in removal of phosphorus which is assimilated and absorbed by plants is 14.74%; contribution rate in removal of phosphorus which is accumulated and absorbed by substrates is 43.22%; contribution rate in removal of phosphorus which is absorbed by means like microorganisms is 2.93%. Pollutant absorption by substrates is a process of dynamic equilibrium. With extension of HRT, phosphorus removing effect of wetlands present an increasing and then decreasing tendency; Net photosynthetic rate and TP removal rate of canna and reed have significant positive correlation, and correlation coefficients are respectively 0.941(P<0.001) and 0.915(P<0.05). Substrates and plants are main pathways for phosphorus removal of artificial wetlands, covering 95% of the total removing effect.

Key words: Artificial Wetlands; Plants; Photosynthesis; Phosphorus

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INTRODUCTION

With rapid development of urbanization in China, urban rainfall runoff pollution are becoming increasingly serious, thus becoming a major source of water eutrophication and the main reason fir deterioration of water quality and water environment in urban areas. What's more, USEPA has already listed overland runoff of urban areas into one of the three major pollution sources that result in river and lake pollution throughout U.S [1]. Hence, it's has important practical significance to improve current water resource pollution situation and promote recycle of urban rainwater resources in China urban areas by taking effective technical measures. At the moment, many sewage treatment systems have been applied to treating pollutants in sewage. Artificial wetlands system, an artificial ecosystem that simulates natural wetlands, realizes purification of sewage by using the compound ecosystem: plants-substrates-microorganism. The system, as featured by low cost of investment, simple operation and maintenance, stable decontamination effect and a certain ornamental value, etc., has attracted many scholars to conduct researches, and it's used to treat sewages of different types [2]. Santos O et al used artificial wetlands system to treat sewages of aquaculture [3], Xian Q et al used floating0beds system of aquatic plants to dispose sewages from pig breeding system [4], Calheiros C S C et al applied artificial wetlands system to disposing sewages from leather processing [5], and Wu H et al used artificial wetlands system to purify polluted river water [6]. At present, researches on artificial wetlands disposing urban runoff pollution and influence of plants and their photosynthesis on decontamination by artificial wetlands are not common yet, so it's necessary to conduct an in-depth research.

This research takes rainfall runoff in Xi'an City as the background and phosphorus in sewage as research object with bench-scale experiment. Main research targets: (1) determine removing effect of phosphorus in rainfall runoff in Xi'an City by artificial wetlands; (2) quantify contribution in phosphorus removal of plants in artificial wetlands; (3) explore and analyze relation between phosphorus removing effects of photosynthesis and plants.

MATERIALS AND METHODS

Experimental Facility and Design
The experimental site is located inside the outdoor experimental Field (34°15′17″N, 108°59′10″E) of Xi'an University of Technology which belongs to semi-humid continental monsoon climate in warm temperate zone with four distinct seasons. The annual average temperature is 13. 0℃~ 13. 7℃ and annual precipitation is 522. 4~ 719.5mm. Experimental period is from April to July of 2014, and experimental facility is bench-scale facility of surface-flow artificial wetlands (see Figure 1), it's a self-made open organic glass box of 40cm×40cm×60cm, a hole-type drain pipe with pipe diameter 20cm is installed at the bottom of the box, outside pipe is covered by geotechnical cloth which can prevent substrates in the experiment from entering the porthole to generate blocking. Side wall of the facility is connected with a right-angle capillary tube with diameter being 6mm or so, a dividing ruler is set beside the tube to measure water yield of evapotranspiration. A perforating water distribution pipe which is identical with drain pipe at the height of 35cm of the side wall, valve outside the tube is connected to inflow rubber hose used for even inflow in the experimental process. Out of consideration of convenience, economical efficiency and applicability of material drawing of substrates, substrates in glass box select a combination of silver sands, zeolums and gravels, from the bottom up, fill gravels （10~30mm）, zeolums (3~5mm) and silver sands 0.1~0.25mm) (major constituents: Si_2O_3, Al_2O_3, Fe_2O_3) from the heights of 10, 15 and 20cm. 10cm water depth is sustained on the silver sand layer.
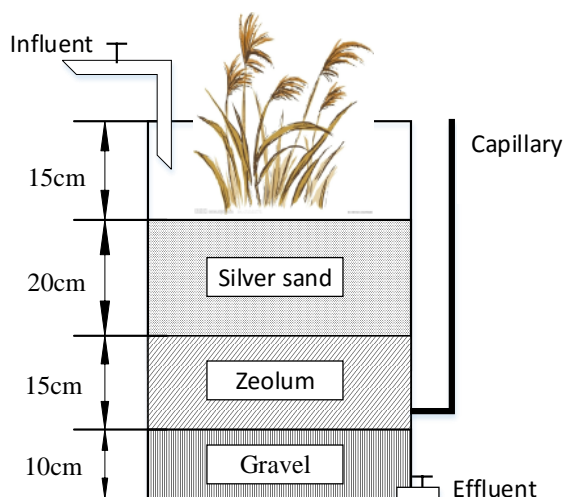
Figure.1 Figure of Experimental Facility

In order to try to avoid problems like runoff frequency burstiness and instable concentration faced by urban rainfall runoff, the experiment uses sewage to analyze and conduct an actual measurement of surface runoff water quality in Xi'an City mainly by multiple collections of samples. As urban runoff pollution is too great in the early phase and out of consideration of resource of rainwater in the middle and later phase [7], the experiment simulates key pollutants ammonia nitrogen, total nitrogen and total phosphorus in sewage and adopts sewage manually compounded by tap water and chemical medicine to simulate urban surface runoff in Xi'an City. The main chemical medicines compounding the sewage include: nitrate （KNO_3）, ammonium chloride (NH_4CL) and monopotassium phosphate (KH_2PO_4), etc. Compounded sewage will be drawn into the bucket at the high altitude by a water pump, and come out of the water valve through the bucket to control water flow. Table 1 gives concrete inflow pollutant concentration in the experiment.

Table 1 - Table of Inflow Pollutant Concentration

Parameter	Mean concentration	Stand deviation
TN(mg/L)	7.62	0.73
NH$_4$-N(mg/L)	2.00	0.23
TP(mg/L)	0.71	0.16

Selection of Aquatic Plants
By looking up relevant literatures and comparing with practical situation, for wetland plants, we select reed and canna which are easy to get and
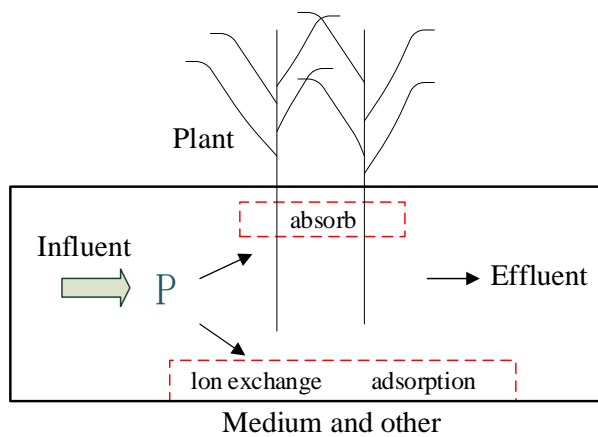
with better effect of decontamination, for planting pattern, we select mixed plantation of the two with planting density being 17 plant/ m^2, and a control group without plants is set. Before the experiment is started, select seedlings with similar growth momentum and size to conduct mixed plantation, firstly use tap water to cultivate them, after they survive, add them into sewage to be measured for several weeks, and the experimental will be started after they grow stable. The experiment adopts batch-type inflow and uses distilled water to compensate for each wetland unit, and HRT is selected as 7 days.

Sampling and Chemical Analysis
From April to July of 2014, collected water quality samples at 12:00 each day (respectively corresponding to HRTs of seven different days), measured content of water quality-P in the lab, and measuring method referred to the fourth edition of Monitoring & Analysis Methods of Water and Sewage. In addition, select days with fine weather and sufficient sunshine to measure photosynthetic rate of wetland plants, used LI6400 portable photosynthesis tester (U.S, LI-COR) to measure growth parameters every other 2h within 8:00~18:00. Selected 2-3 mature leaves which are healthy, intact and sunny in the middle-upper part of plants with good growth momentum when the measurement was conducted, repeated the measurement on each leaf for three times. Simultaneously, conducted the water quality test and calculated corresponding removal rates. When the experiment was started and ended, respectively selected intact plants to clean and dry them. Conducted total phosphorus analysis through micro-plant grinder by dried plants going through a 10-mesh screen.

Mass Balance Calculations
Regard artificial wetland as a system, circulation of phosphorus in artificial wetlands system conforms to principle of substance conservation, namely input phosphorous and output phosphorus in the system shall keep a balance (Figure 2). Phosphorus input by the system is that in sewage, and that output by the system includes: (1) Outflow phosphorus in artificial wetlands system; (2) Phosphorus absorbed and held back in the substrates; (3) Phosphorus absorbed by plants; (4) Phosphorus consumed by microorganism and other reactions.

$$P_{\text{plant}} = C_{\text{TP plant, out}} W_{\text{plant, out}} - C_{\text{TP plant, in}} W_{\text{plant, in}}$$
(5)

In the equation, $C_{\text{TP plant, in}}$ and $C_{\text{TP plant, out}}$ respectively represent phosphorus concentration （mg/L） of plant bodies when they are immigrated into and emigrated from artificial wetlands system. $W_{\text{plant, in}}$ and $W_{\text{plant, out}}$ respectively represent biomass （g） of plant bodies when they are immigrated into and emigrated from artificial wetlands system;

$$P_{\text{medium}} = C_{\text{TP, medium out}} W_{\text{medium, out}} - C_{\text{TP medium, in}} W_{\text{medium, in}}$$
(6)

In the equation, $C_{\text{TP medium, in}}$ and $C_{\text{TP, medium out}}$ respectively are phosphorus concentration （mg/L） of substrates in artificial wetlands system at the beginning and in the end of the experiment.

RESULTS AND DISCUSSION

Experimental Situation Analysis
During the whole period of the experiment, growth momentums of plants inside the experimental facility are all good without no demise or malnutrition phenomena. See results of wetland system with plants and that without plants in Table 2, from which it can be seen that artificial wetlands system can effectively remove phosphorus in the sewage, phosphorus absorption in sewage by wetland system with plants and that without plants are respectively 12.89 mgP/m²day and 8.94 mgP/m²day with their removal rates reaching 60.89% and 42.23%, so removal rate of total phosphorus by wetland system with plants is higher than that by wetland system without plants. Contribution rate of plants to removing P-pollutants can reach 3.95 mgP/m²day, covering 30.6% of total P-removing quantity by artificial wetlands, while the rest 69.1% pollutants removing quantity are done by other means like substrates and microorganisms. The results indicate that during the process of artificial wetlands removing P-pollutants, phosphorus removed by other means like substrates and microorganisms cover most proportion of wetlands removing phosphorus. Similar to researches of many scholars, Gagnon V et al [8] verified that P-pollutants are mainly distributed in substrates and wetland system with plants has higher efficiency

Figure 2. Equilibrium Diagram of Phosphorus Migration and Transformation in Artificial Wetlands

Material balance model of phosphorus in artificial wetlands is as follows:

$$P_{\text{influent}} = P_{\text{output}} \quad (1)$$

In the equation, P_{influent} represents input flux of phosphorus of pollutants in the system, and P_{output} represents output flux of phosphorus of pollutants in the system;

$$P_{\text{influent}} = \sum_{i=1}^{n} C_{\text{TP influent } i} V_{\text{influent } i} \quad (2)$$

In the equation, $C_{\text{TP influent } i}$ represents inflow phosphorus concentration （mg/L） in the ith experimental period, and $V_{\text{influent } i}$ represents inflow volume (L) in the ith experimental period;

$$P_{\text{output}} = P_{\text{effluent}} + P_{\text{plant}} + P_{\text{medium}} + P_{\text{other}} \quad (3)$$

In the equation, P_{effluent} represents phosphorus in effluent water, P_{plant} represents phosphorus （mg） absorbed by plants, P_{medium} represents phosphorus （mg） absorbed and stored by substrates, and P_{other} represents phosphorus lost by other means;

$$P_{\text{effluent}} = \sum_{i=1}^{n} C_{\text{TP effluent } i} V_{\text{effluent } i} \quad (4)$$

In the equation, $C_{\text{TP effluent } i}$ represents effluent phosphorus concentration （mg/L） in the ith experimental period, and $V_{\text{effluent } i}$ represents effluent volume (L) in the ith experimental period;

in removing total phosphorus; Chung A K C et al [9] figured out that removal rate of total phosphorus by artificial wetlands is 52 while P-accumulation in plant body is not 5% enough; Wu H et al [10] also believed that efficiency of artificial wetlands removing P-pollutants is 67% and maximum P-removing efficiency of plants reaches 34.17%. All of which may be related to multiple factors like different plants and substrate types and different pollutant concentrations, Konnerup D et al [11] found that the lower content of total phosphorus in sewage is, the more obvious the P-removing effect by artificial wetlands will be. Chen Y C et al [12] found that higher concentration of nutrients will result in lower removing rate.

Table 2 -Removing Effect of P-Pollutants in Xi'an Rainfall Runoff by Artificial Wetlands

Wetland Type	influent	Absorption by Artificial Wetlands	effluent	Removal Rate of Artificial Wetlands
	（mg P/m^2 day）			
With Plants	21.17	12.89	8.28	60.89%
Without Plants		8.94	12.23	42.23%

According to experimental results, relationship between removal rates of HRT and TP is as shown in Figure 3. It can be seen that 6 days before the experimental period, HRT has a positive correlation with removing effect of TP. The longer HRT is, the better removing effect of TP will be. Average removal rates of average removal rate of TP when HRT is 1, 2, 3, 4,5 and 6 days are respectively 47.01%, 48.66%, 49.35%, 54.29%, 61.82% and 65.50%, which is mainly because prolonging of HRT increases time of reaction between plants, microorganisms and substrates in artificial wetlands and pollutants in sewage, and this has promoted absorption of pollutants by artificial wetlands. However, on the 7th day, removal rate of TP in artificial wetlands decreases to a certain degree which means rising of TP pollutant concentration in sewage, which may be because removal of phosphorus in sewage by substrates is mainly by means of absorption. Absorption is a reversible physical change. When TP concentration in sewage is low, a small proportion of substrates will flow back to the system, resulting in reduction of removal rate of TP.
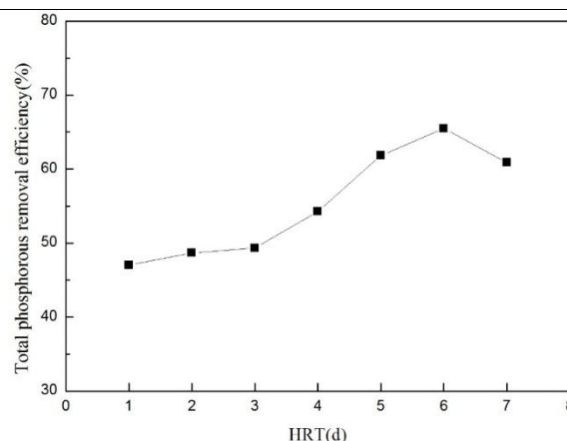
Figure 3 -Relation Curve Between HRT and TP Removing Effect

Analysis of Phosphorus Mass Balance
Conduct a mass balance analysis based on the experimental data, and thus obtaining phosphorus balance analysis results in artificial wetlands and contribution proportions of different removing pathways (Table 3 and Figure 4). TP input and output in wetlands system is 21.17mg P/m^2 day. In wetlands system with plants, effluent amount of phosphorus with sewage is 8.28 mg P/m^2 day and removing contribution ratio is 39.11%; Phosphorus amount assimilated and absorbed by plants is 3.12 mg P/m^2 day and removing contribution ratio is 14.74%; Phosphorus amount accumulated and absorbed by substrates is 9.15mg P/m^2 day and removing contribution ratio is 43.22%; Phosphorus amount absorbed by other means is 0.62 mg P/m^2 day and removing contribution ratio is 2.93%.It can be seen that

storage by substrates and assimilation & absorption by plants are main pathways for phosphorus removal by artificial wetlands, and absorption by microorganism has the least removing contribution. Compared with wetlands system without plants, TP accumulated and absorbed by substrates and TP absorbed by microorganism and other means have increased to a certain degree, which indicates that plants' P-pollutant removal in wetlands system is not only through their absorption of phosphorus but also through influencing substrates and microorganism to boost absorption of pollutant TP by wetlands.

It's generally believed that interlaced root systems of plants in wetlands have enlarged contact area between substrates and phosphorus, which is more beneficial for physical and chemical reaction between substrates and phosphorus [13].

Parameter	Wetlands	Input load （mg P/m^2 day）	Out point （mg P/m^2 day）			
		influent	effluent	Plant uptake	medium	others
TP	With Plants	21.17	8.28	3.12	9.15	0.62
	Without Plants		12.39	0	8.7	0.08

Table 3 - P-Balance Analysis in Artificial Wetlands
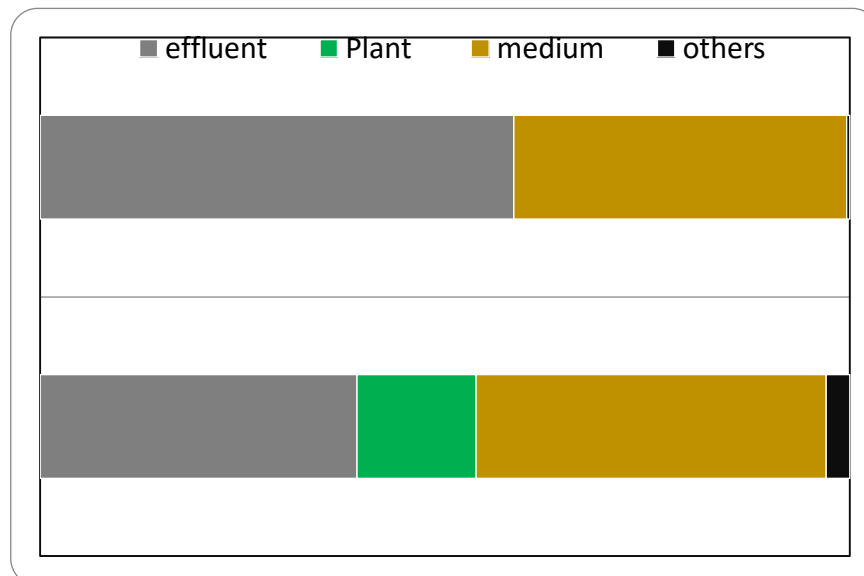
Figure 4 - Contribution Proportions of Different P-Removing Pathways in Artificial Wetlands

Influence of Plant Photosynthesis on TP Removal
Plant photosynthesis is a process in which plants use solar energy to produce plant biomass. Through researching on the relation between plant photosynthesis and TP removal rate of wetlands system, the experiment has found that pollutant removal rate by wetlands system with plants presents periodical diurnal variation (there is no obvious change in wetlands system without plants). Maximum net photosynthetic rates of reed and canna rise gradually from morning and reach the maximum value during 12:00-14:00 respectively reaching $20.99 \mu molCO_2/(m^2s)$ and $15.2 \mu molCO_2/(m^2s)$, and then gradually decrease in the afternoon. Variation of phosphorus removal rate of wetlands system with plants is similar to plant net photosynthetic rate, reaching the maximum value 78.18% at 14:00. Respectively

conduct Pearson correlation analysis on net photosynthetic rates and TP removal rates of reed and canna, and result shows that net photosynthetic rates have positive correlation with TP removal rates of reed and canna with correlation coefficients respectively being 0.941（P<0.001）and 0.915（P<0.05）and the result is identical with the research result conducted by Zhu L et al [14] that plant growth amount as positive correlation with nitrogen &

phosphorus accumulation in plant bodies, which is mainly because assimilation & absorption of P-pollutant by plants are mainly applied to compound of energy substances (ATP, phosphatide, etc.) and genetic materials. Plant photosynthesis is right in the phase in which plants compounding energy and substances. Hence, photosynthetic rate of plants has a certain correlation with absorption of phosphorus.

Table 4 - Relationship Between Net Photosynthetic Rate and TP Removal

Time	Net Photosynthetic Rste $\mu molCO_2/(m2s)$		TP Removal Rate
	Canna	Reed	
8:00	7.85	5.3	31.43%
10:00	9.58	13.29	38.96%
12:00	14.96	20.99	72.47%
14:00	15.2	20.59	78.18%
16:00	14	16.9	72.21%
18:00	5.64	5.22	38.44%
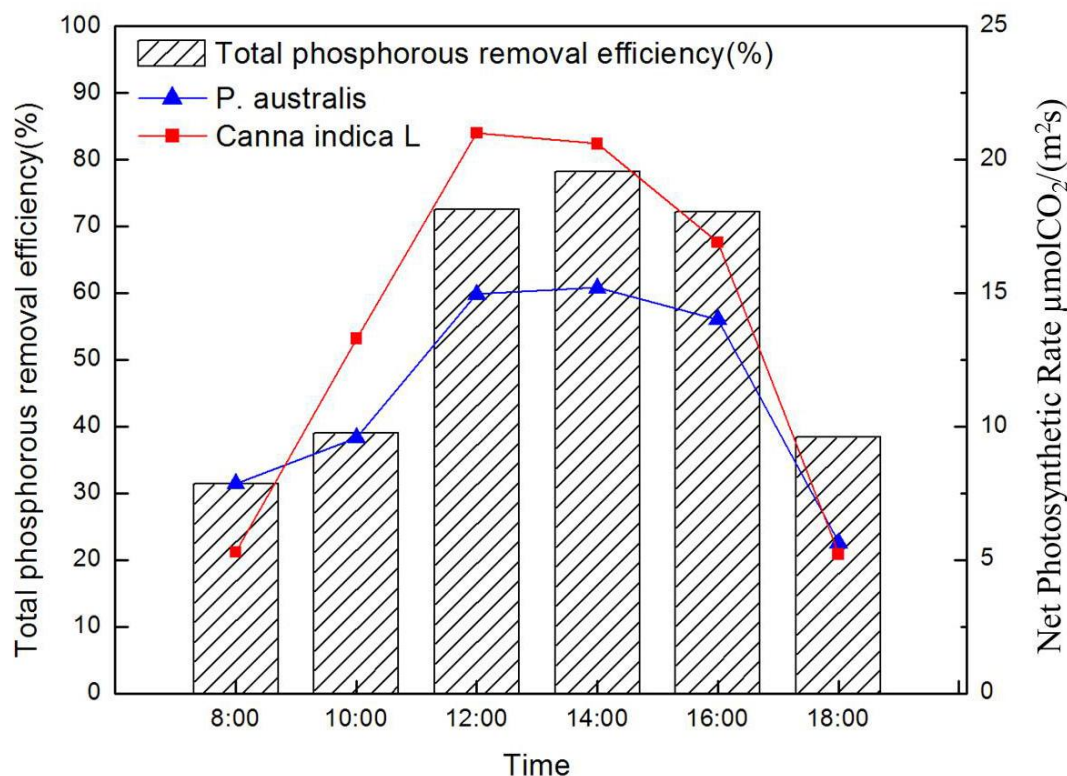
Figure 5 - Relation Graph Between Net Photosynthesis and TP Removal in Artificial Wetlands

CONCLUSIONS

According to the experimental results, it can be considered that:

(1)TP removing effect of artificial wetlands system in rainfall runoff in Xi'an can reach 42.23%-60.89%, so it's believed that artificial wetlands system can effectively remove TP contents in sewage. In the meantime, it's found that compared with wetlands system without plants, wetlands system with plants has better phosphorus removing effect, and phosphorus removing contribution rate by plants covers 18.66% in the whole wetland.

(2)TP removal in sewage in the artificial wetlands system mainly rely on absorption by plants and substrates, and phosphorus effect of the two covers more than 95% of the total removing effect. Mass balance analysis of wetlands finds that phosphorus removing contribution made by wetlands not only presented in absorption by themselves but also in boost of absorption and reaction of TP by substrates and microorganism as their physiological properties can generate additional gaining effect on artificial wetlands. As HRT is prolonged, phosphorus removing effect of wetlands correspondingly increases, but it reduces in the 7th day as influenced by substrates;

(3)Net photosynthetic rates and TO removal rate of canna and reed have positive correlation, and correlation coefficients are respectively 0.941（P<0.001）and 0.915（P<0.05）. P-pollutant removal by plants is mainly based on phosphorus absorption used for compound of energy substances (ATP, phosphatide, etc.) and genetic materials, and plant photosynthesis is right in the phase of plants compounding energy and substances.

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