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Performance of modified one-stage Phoredox reactor with hydraulic up-flow in biological removal of phosphorus from municipal wastewater

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ABSTRACT

Nowadays, eutrophication is considered as one of the disturbing environmental phenomena, which its main cause is the discharge of nutrients into receiving waters. The main problematic chemicals in this regard are nitrogen and phosphorus. Considering the undesirable effects of these two nutrients on the receiving waters, the application of a biological process with high removal efficiency, such as modified Phoredox, is essential to ensure the removal of nitrogen and phosphorus. In this context, a pilot plant (made of Plexiglas) with wall thickness of 0.5 cm and dimensions of 100 × 20 × 20) along with four sample valves and a dual valve were provided and utilized in order to allow the entrance of flow and the discharge of the reactor for the purpose of flexibility in operation. With regard to the structure of modified one-stage Phoredox reactor, in this study, 20% of the total volume of the reactor was dedicated to the anaerobic region which was embedded on the base of the reactor with the help of a porous network by assuming an up-flow. Investigating the data obtained in the present research revealed that the modified one-stage Phoredox reactor was able to provide the highest removal of chemical oxygen demand (COD) (95.5%) at the organic loading rate of 400 mg/L, inlet phosphorus concentration of 10 mg/L, hydraulic retention time (HRT) of 8 h, and media filling rate of 60%, while the biochemical oxygen demand $(BOD)_5$ removal efficiency by studied system was 94.9%. The remaining COD in this optimized phase was 15.04 mg/L. Moreover, the highest total phosphorus (TP) removal by this system was obtained to be 96.5 at organic loading rate of 500 mg/L and the inlet TP of about 15 mg/L, the HRT of 8 h and filling rate of 60% filling. The remaining TP in this optimized phase was obtained 0.54 mg/L which was extremely lower than the standard limit specified by the Department of Environment for discharging the sewage into the environment. This low rate indicates the effective performance of the modified one-stage Phoredox reactor to achieve environmental standards.

Keywords: Phoredox; Phosphorus; Biofilm; Nutrient; Biological treatment

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1. Introduction

Phosphorus compounds are potential pollutants of receiving waters, incorporating these chemicals via various types of wastewater [1–3]. Phosphorus is one of the main live micronutrients, which is found in Adenozin three phosphate, cell membranes, teeth and bones. The average concentration of total phosphorus (TP) value in raw municipal wastewater is 8–10 mg/L, 40% of which is organic and the rest of it is inorganic. Furthermore, approximately 10% of this phosphorus concentration is removed in the initial natural sedimentation, and 10%–20% is removed in biologic purification. Nevertheless, the 70% of phosphorus is often discharged through secondary treatment output [4].

Fertilizers consumed in agriculture, natural rainfalls, domestic and industrial wastewaters, and natural run-off is the major sources of phosphorus in receiving waters [5,6]. Chemically, the high levels of nitrogen (nitrite and nitrate) and phosphorus (phosphate and polyphosphate) in wastewaters result in eutrophication in the environmental (e.g., in rivers and lakes), particularly, in water resources [7,8]. This can cause the excessive growth of plants and microalgae, which reduces the water quality, damages the plants and animals and stops the direct consumption of water [4,5,9,10]. In most cases, phosphorus, rather than nitrogen, is considered as a limiting factor in the emergence of this phenomenon, because the nitrogen fixation naturally occurs by diazotrophs. Accordingly, the majority of recent studies on nutrient removal have focused on phosphorus removal [9–11].

Eutrophication affects water quality through dissolved oxygen consumption and aquatic life destruction. As a result, phosphorus removing from industrial and domestic wastewater is of utmost importance to achieve the discharge standard limits and eutrophication control. US federal government established the standard of 0.01–0.1 mg/L as acceptable amount of phosphate in freshwater. In addition, according to Iran environmental protection standards, the maximum allowable of residual concentration of phosphorus in treated domestic wastewater before its discharge is 1 mg/L [12]. The cheap and common methods employed for removal of nutrient and adjustment of their concentration to the standard discharge limits are physical, chemical and biological methods [13–19]. The physical methods, e.g., filtration, ultrafiltration, reverse osmosis and ion exchange are expensive and sometimes inefficient [6,10,20–22]. The chemical methods such as chemical sedimentation (using iron and aluminium salts) and adsorption are associated with the drawbacks including high sludge production and operation costs besides and pH changes [23].

However, biological methods have been more welcome at industrial level due to their efficiency, lower production of extra materials, and cost-effectiveness. Investigations in this field have led to the appearance of different methods of biological nutrient removal (BNR). For enhanced phosphorus uptake, the anaerobic/oxic (A/O) or Phoredox processes have been used. In the first process, the essential features of the process are an anaerobic zone followed by an aerobic zone (A/O process). Operation of the process with modified Phoredox sequencing provides favourable conditions for the enrichment of the sludge with Bio-P microorganisms. In the second, Phoredox process incorporates both biological and chemical removal of phosphorus. The benefits of this system are the simultaneous removal of phosphorus and carbonated organic materials, the production of alkalinity for nitrification, the production of sludge with good sedimentation and energy saving [24,25].

Cost management, reduction of operational difficulties, improving the performance of the wastewater purification systems without increasing the time or cost required, and other technical issues have urged environment managers to create new processes in the wastewater treatment engineering. In this regard, biofilm systems with moving beds have gained great attention as one of the active sludge expressions. The principal idea of introducing this system was to develop a process having the following advantages: (i) compactness, (ii) shock acceptance, (iii) simple operation and backwash [12], even if it was associated with some disadvantages such as (i) media blockage, (ii) significant gas-phase pressure drop, (iii) need for vast ground, etc. In this process, biomass is formed as the biofilm on the support media moving freely throughout the reactor. Therefore, sludge sedimentation and recirculation are not essential for sludge separation or the maintenance of biomass in the bioreactor, respectively [26–28].

Numerous studies have been conducted on the biological removal of phosphorus from municipal wastewater. In this sense, Nikimalekie [29] applied the anaerobic-aerobic process in closed consecutive reactors using hydraulic retention time (HRT) of 7 d to remove phosphorus from synthetic municipal wastewater and recorded the removal efficiency of 90%. Rashed and Massoud [30] performed a study on the impact of microorganisms on enhanced biological phosphorus removal in a modified contact stabilization system. The results of this study showed that the reason for the high phosphorus removal capability using this pilot plant is the high performance of the microorganisms in the accumulation of phosphorus. Finally, the removal efficiency of chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and TP in this study were 93%, 93% and 90%, respectively. Rashed et al. [31] conducted a study on the application of contact stabilization activated sludge in the advanced removal of phosphorus from domestic wastewater via the biologic method. The results of this study indicated that the removal efficiency of COD, BOD_5 and TP were 94%, 85.44% and 80.54%, respectively. Seyedsalehi et al. [8] performed another study about the effect of the ratio of propionic acid to acetic acid on the nitrogen and phosphorus removal using anaerobic-aerobic process. Their investigation has demonstrated that the ratio of propionic acid to acetic acid in the initial wastewater influences the conversion and change of cell stocks such as poly-hydroxyvalerate and polyhydroxybutyrate (PHB), glycogen, phosphorus and nitrate in the anaerobic stage. The removal efficiency was improved at ratios lower than 2. The removal efficiencies of total nitrogen and phosphorus were observed to 94% and 68% using the ratio of 1, while their removal efficiencies were increased to 97% and 82% using ratio of 2. With regard to the appropriate features of systems containing media (such as high removal efficiency, easy operation, lack of clogging, etc. [25]), the present study aims to investigate and modify up-flow Phoredox.

2. Materials and methods

2.1. Experimental device

This study was conducted on a pilot scale. The pilot was set up in Batab Sanat Ojan Co., in Tehran and all of the experiments were performed in the Water and Wastewater Laboratory of Sheikh-e Bahai Laboratory at Islamic Azad University, Science and Research Branch, Tehran, Iran. The experiments were carried out on the guidelines presented in the standard method for the examination of water and wastewater and were selected by taking into account the equipment in the laboratory [32].

The pilot plant was made using Plexiglas material with a wall thickness of 0.5 cm. Bioreactor dimensions were 100 × 20 × 20 cm (40 L capacity). Four sample valves were provided to taking the sample and a dual valve was considered to enter the flow and to discharge the bioreactor for the purpose of flexibility in operation. The useful volume of the bioreactor was 36 L by considering the free board. Table 1 shows the dimensions of the modified Phoredox bioreactor used in this research.

To ensure that the pilot is well-sealed, it was filled with water for one week. It should be mentioned that considering the structure of the modified Phoredox reactor, in this study, 20% of the total volume of the bioreactor was dedicated to the anaerobic region which was embedded on the base of the reactor with the help of a porous network. Moreover, one of the sample valves was installed in this region. 60% of the aerobic section of the bioreactor, which was steered by the biofilm method, was filled with Kaldnes K3 media (the Norwegian brand), while the remaining 40% of the aerobic volume of the bioreactor was considered as the working volume. The moving media was Kaldnes K3 which was made of polyethylene with high resistance and each of the K3 medium had a total surface area of 584 m^2/m^3. The aeration system of the bioreactor was installed in the oxic section by using a diffuser embedded on the floor of the oxic region of the bioreactor. Furthermore, the aeration of the bioreactor was done using a piston air pump (aqua) with a theoretical capacity of 20 L/h. The pilot plant had a control system; this system includes a digital control circuit in which all cycles related to operating conditions of the pilot plant were programmed. All tanks were controlled by the selected cycle and the program which was previously installed in the control system. Fig. 1 shows the schematic of the pilot plant used in the work.

Table 1
Dimensions of the modified Phoredox bioreactor used in the work (plexiglass material was used in the bioreactor fabrication)

Parameter	Values
Wall thickness, cm	0.5
Internal length, cm	20
Internal width, cm	20
Height of the bioreactor, cm	100
Height of free space, cm	10
Total bioreactor volume, L	40
Useful volume of the bioreactor, L	36
Percentage of filling with media, %	60

The modified Phoredox bioreactor modified by the biofilm system is a reactor with the continuous hydraulic flow. It is a modified version of Phoredox process. The traditional system of Phoredox, which is an advanced purification system with an emphasis on the removal of nutrient (nitrogen and phosphorus), was previously run with the help of active sludge and unstable against the organic and quality shocks. In this study, the hydraulic flow of the system was up-flow. The following parameters including outlet flow (4.5, 6 and 9 L/h), HRT (8, 6, 4 and 4 h), organic load concentration (COD = 500, 400 and 300 mg O_2/L), and phosphorus concentration (15, 12 and 10 mg/L) values were considered. Table 2 summarizes the operating conditions programmed at the pilot plant.

The media used in the modified Phoredox system are of Kaldnes K3 type. These media were employed in this study because they are very common and inexpensive, and their control and cleaning are easy. These media have been

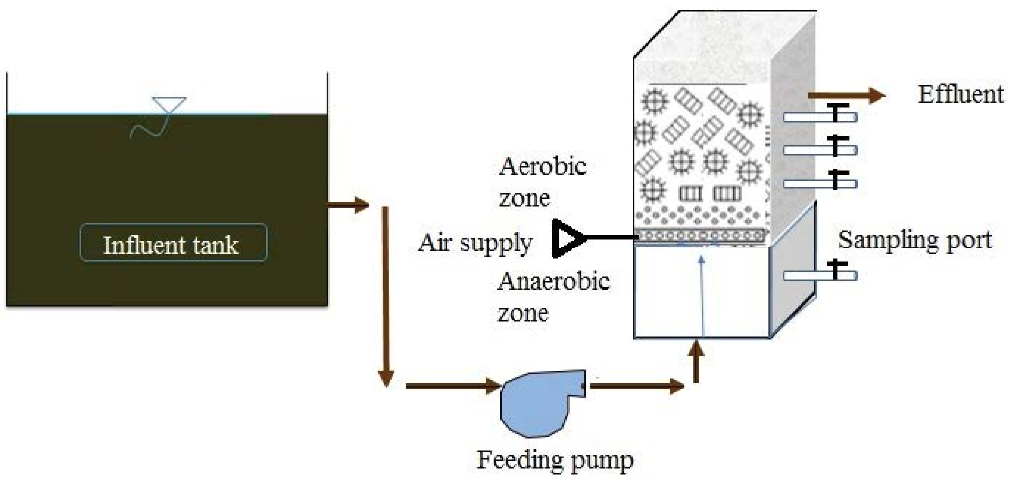

Fig. 1. Schematic representation of modified Phoredox process with emphasis on nutrient biological removal.

Table 2
Implementation schedule of the modified Phoredox system

$COD_{Initial}$ (g/L)	Phosphorus concentration (mg/L)			Outlet flow (L/h)			Hydraulic retention time (h)			
0.3	10	12	15	4.5	6	9	2	4	6	8
0.4	10	12	15	4.5	6	9	2	4	6	8
0.5	10	12	15	4.5	6	9	2	4	6	8

evaluated to be appropriate in many studies conducted in Iran. In Table 3, the characteristics of these media were represented.

2.2. Analytical methods

To determine orthophosphate (phosphorus), PhosVer 3 with the ascorbic acid method was applied (HACH Co. Test, United States). This method, which is approved by United States Environmental Protection Agency (USEPA), can determine TP in the appropriate laboratory conditions and hydrolysis of ascorbic acid by DR5000 spectrophotometer [7]. COD was measured using the test kits from Hach Lange (GmbH, Dusseldorf, Germany), and the DR5000 device was performed according to the standard method for the examination of water and wastewater [32]. All chemicals used in this study were supplied by Merck (Germany). Samples were analyzed for BOD, according to the Standard Methods for the Examination of Water and Wastewater [32].

3. Results and discussion

Fig. 2 shows that the modified Phoredox system was efficient in removing BOD_5 and COD from wastewater. The

Table 3
Characteristics of the media (Kaldnes K3 type) used in this study

Parameter	
Material of medias	HDPE*
Total surface area, m^2/m^3	584
Special conserved surface, m^2/m^3	500
Diameter, cm	2.5
Height, cm	1.0
Rate of nitrate formation (lab conditions), g/m^3 of media per day	560
Rate of COD removal (lab conditions), g/m^3 of media per day	1,200
Denitrification rate (lab conditions), g/m^3 of media per day	670

*High-density polyethylene.

present research attempted to consider the most optimized state obtained for COD parameter in three values of TP. As expected, COD and BOD_5 removal efficiency was increased by an increase in the HRT in each phase. The highest COD removal efficiency was 95.5% for initial concentration of 400 mg/L in HRT 8 h while BOD_5 removal efficiency was 94.9%. According to this figure, COD concentration at the outlet of system for HRT of 4, 6 and 8 h was <50 mg/L, complying with the USEPA effluent standard for wastewater treatment plants. The elongated HRT of the modified Phoredox reactor may provide longer contact time for the degradation of organics, leading to the improved COD and BOD_5 removal in this system [33,34].

Similar result was also reported by Zhang et al. [35] who observed the average COD removal of 84%–89% from a domestic wastewater, with CODs ranging from 232 to

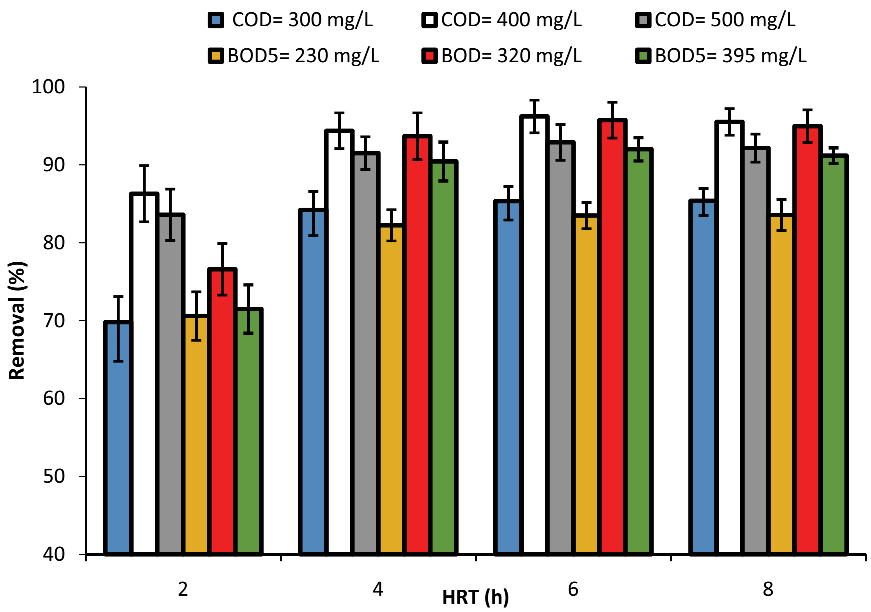

Fig. 2. Comparison of COD removal efficiency in optimized conditions obtained in different HRTs along the steering of modified Phoredox system in TP concentration of 10 mg/L.

331 mg/L, using an A2O-BAF system with a total HRT of 8 h, R of 3, anaerobic to aerobic bioreactors volume ratios of 2:5–6:1, and sludge retention time of 20 d.

3.1. Effect of HRT in phosphorous removal

Fig. 3 illuminates that modified Phoredox system had an appropriate efficiency in removing TP at the inlet organic loading rate of 500 mg/L. In this phase, three TP loads including 10, 12, and 15 mg/L were utilized. As observed, the highest removal efficiency of TP belonged to the HRT of 8 h in TP load of 15 mg/L. The results revealed that the highest removal efficiency obtained from TP in modified Phoredox system at HRTs of 2, 4, 6 and 8 h was 78.5%, 90.7%, 94.8% and 96.5%, respectively. Generally, biological phosphorus removal occurs under anaerobic conditions when volatile fatty acids are converted to degradable organic matters through fermentation and then stored in the cellular inner granulates such as PHBs by polyphosphate-accumulating organisms (PAOs). The energy required to store PHBs under anaerobic conditions is supplied by breaking down stored polyphosphate which leads to degradation of orthophosphates and increasing PHBs concentration in the liquid. Under aerobic conditions, PAOs consume the stored PHBs, and through this process, they achieve the energy needed to grow and absorb the orthophosphate from the liquid [36]. According to the biological principle of natural selection, by fast storage and consumption of substrate, microorganisms will gain a competitive advantage under feast–famine conditions, and the absorption of the substrate into storage material is the key to the formation of the competitive advantage [37]. Generally, the more COD was consumed, the more poly-beta-hydroxy-alkanoates was stored, meaning a stronger *P*-uptake potential for the subsequent aerobic phase [38].

Fig. 4 shows a meaningful relationship between the three parameters of HRT concerning the consumption of phosphorus and organic load (the inlet of 500 mg/L) in optimized conditions obtained in modified Phoredox system. As observed the consumption rate of COD was increased and decreased by increasing the retention time from 2 to 4, 4 to 6 and 6 to 8 h, respectively. However, the consumption rate of TP was increased, with a big difference, by increasing the retention time from 2 to 8 h. As shown in Fig. 4, the obvious positive correlations were observed between COD consumption and *P* removal during the various HRT.

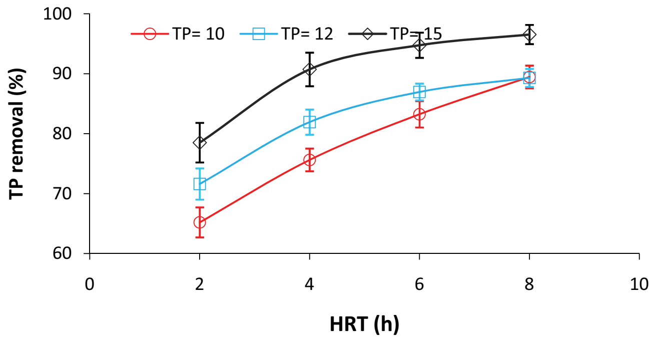

Fig. 3. Comparison of TP removal efficiency in organic load of 500 mg/L in optimized conditions obtained from different HRTs along the steering of modified Phoredox system.

In traditional BNR system, both denitrification and phosphorus removal require organic carbon sources. The removal efficiency of TP was often limited when the organic carbon in wastewater was insufficient. In this case, the soluble chemical oxygen demand available for phosphorus removal was sufficient and high phosphorus removal efficiency was achieved. In systems for simultaneous removal of nutrients, a large amount of COD is consumed by the denitrifiers and PAOs. The high COD removal in this reactor can be due to need for organic matters of phosphate accumulating bacteria and denitrifying bacteria's [39]. In addition, 10 mg COD is consumed per phosphate milligram, both of which can significantly reduce organic matters in the reactor [40].

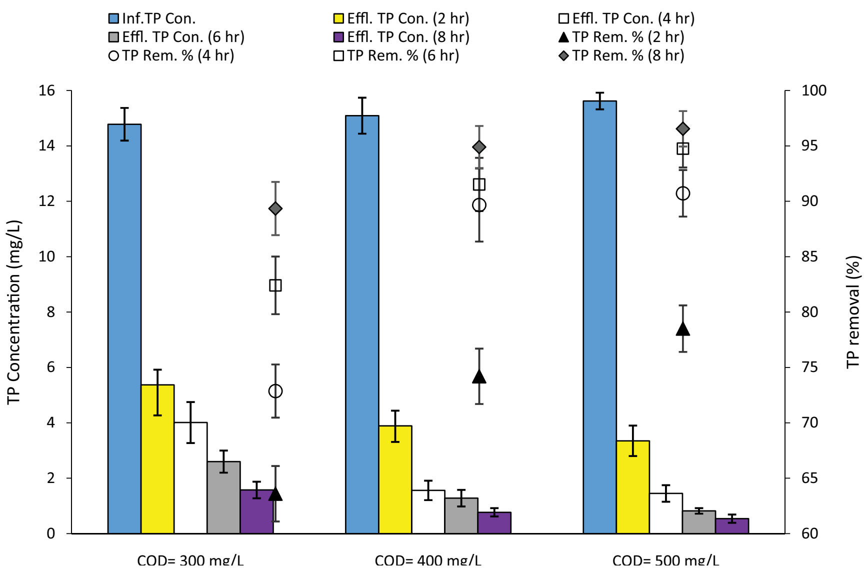

Fig. 4. Efficiency of modified Phoredox system in the relationship between phosphorus consumption and organic load (TP = 15 mg/L).

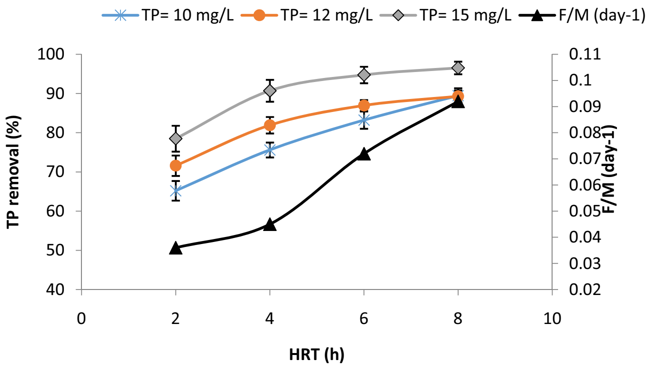

Fig. 5. Meaningful relationship between F/M ratio and TP consumption in loading the organic load (500 mg/L) in three variables of hydraulic retention time.

Similar result was also reported by Yang et al. [40] that studied a moving bed reactor for simultaneous removal of nutrients and COD, and concluded that in the anaerobic phase, the nutrients residue is eliminated, by using the influent COD as substrate, leading to reactor effective performance in removing organic matter in some cases. Zhang et al. [41] found that the average phosphate removal efficiency increased from 66.4% to 78.7% and then to 91.6% when HRT increased from 1.8 to 2.7 h and then to 3.5 h at influent phosphate concentrations ranging from 4 to 7 mg/L.

Fig. 5 shows a meaningful relationship between three parameters of HRT in terms of phosphorus consumption and food to microorganism Ratio (F/M) rate (the inlet organic loading rate of 500 mg/L) in optimized conditions obtained in modified Phoredox system. As observed, the consumption rate of TP has continuously increased by increasing the retention time from 2 to 8 h. However, the ratio of F/M at this stage of the study along the HRT has continuously increased, so that this ratio starts from 0.03 and ends at 0.09. The results suggested that under the appropriate.

Organic loading rate and F/M ratio, the bacteria could synthesize sufficient PHB, which could increase the phosphorus release and phosphorus removal capacity [42].

4. Conclusion

By investigating the data obtained in this research, it was found that the modified Phoredox system had the maximum COD removal efficiency (96.2%) at the organic loading rate of 400 mg/L, the HRT of 6 h, media filling rate of 60%, and the inlet phosphorus concentration of 10 mg/L. The residual COD in this optimized phase was 15.04 mg/L. Moreover, the maximum TP removal was 96.5% at the organic loading rate of 500 mg/L, the inlet TP concentration of 15 mg/L at the HRT of 8 h and media filling rate of 60%. The residual TP in this optimized phase was 0.54 mg/L, which was much lower than the standard limit specified by the Department of Environment to discharge sewage into the environment; in addition, this lower rate indicated the effective performance of the modified Phoredox system to achieve the environmental standards. The rate of F/M for the optimized consumption of COD and TP was 0.09 and 0.06, respectively, and it is recommended that the cellular retention time for this part of the operation should be 11 to 15 d.

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