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Scientific Article

Treatment and resource utilization for a non-biodegradable organophosphorus wastewater using micro-channel reactor

Tratamento e utilização de recursos para um efluente organofosforado não biodegradável usando reator de microcanal

Hongxia Liu[1,2], Zhiguo Wang[1,2]

ABSTRACT

This study aimed to develop a method to treat and reuse non-biodegradable organophosphorus industrial wastewater using the micro-channel reactor. As an important pharmaceutical and fine chemical intermediate, diethyl hydroxymethylphosphonate (DHP) produces large amounts of industrial wastewater, which poses a serious threat to natural environment and human health. It is of great value to find a treatment method of the DHP industrial wastewater with simple operation, good safety, low cost, and environment friendly. In this study, hydrogen peroxide (H_2O_2) and DHP industrial wastewater were reacted in the micro-channel reactor. Reaction conditions were optimized by adjusting reaction temperature, reaction time, reaction pressure, and sampling flow rate. The treated wastewater was further neutralized by sodium hydroxide (NaOH). After the oxidation and neutralization reaction of the DHP industrial wastewater, the removal rate of chemical oxygen demand (COD) in treatment wastewater can reach 97.3%. Moreover, after the treated solution being dried, the inorganic phosphate solid was obtained with the phosphorus content as high as 92.1%. It can realize the reuse of phosphorus resources for the DHP industrial wastewater.

Keywords: non-biodegradable organophosphorus industrial wastewater; micro-channel reactor; resource utilization; treatment of wastewater; diethyl (hydroxymethyl)phosphonate.

RESUMO

Este trabalho teve como objetivo desenvolver um método para tratar e reutilizar efluentes industriais organofosforados não biodegradáveis usando o reator de microcanal. Como um importante intermediário farmacêutico e químico fino, o dietil hidroximetilfosfonato (DHP) produz grandes quantidades de efluentes industriais, o que representa uma séria ameaça ao ambiente natural e à saúde humana. É de grande valia encontrar um método de tratamento de efluentes industriais DHP com operação simples, boa segurança, baixo custo e ecologicamente correto. Neste estudo, o peróxido de hidrogênio e o efluente industrial DHP foram reagidos no reator de microcanal. As condições de reação foram otimizadas ajustando-se a temperatura de reação, o tempo de reação, a pressão de reação e a taxa de fluxo de amostragem. O efluente tratado foi posteriormente neutralizado por hidróxido de sódio. Após a reação de oxidação e neutralização das águas residuais industriais DHP, a taxa de remoção da demanda química de oxigênio nas águas residuais de tratamento pode chegar a 97,3%. Além disso, depois da secagem da solução tratada, o fosfato inorgânico sólido foi obtido com teor de fósforo tão alto quanto 92,1%. Pode-se reutilizar recursos de fósforo para as águas residuais industriais DHP.

Palavras-chave: efluente industrial organofosforado não biodegradável; reator de microcanal; utilização de recursos; tratamento de águas residuais; dietil hidroximetilfosfonato.

INTRODUCTION

Generally, advanced oxidation was often used to treat the high concentration, non-biodegradable organic industrial wastewater. It can decompose or mineralize organics, which cannot be oxidized by ordinary oxidants, based on the high activity hydroxyl radical produced by light, sound, electrical, magnetic, and other physical and chemical processes. The publications (ANDREOZZI *et al.*, 1999; KLAVARIOTI; MANTZAVINOS; KASSINOS, 2009) have summarized the method of advanced oxidation into six types: chemical oxidation, chemical catalytic oxidation, wet oxidation, supercritical water oxidation, photochemical oxidation and catalysis, and electrochemical oxidation. Among these above methods, wet oxidation can decompose organics into CO_2, H2O, and other inorganics or other small organics with H_2O_2, O_3 or air as oxidants under high

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temperature and high pressure conditions. Significantly, this method requires much harsh reaction conditions, such as high temperature between 125 to 320 ºC and high pressure between 0.5 to 20 MPa. Zeng, Liu and Zhao (2017) and Wu (2022) have described the disadvantages of wet oxidation with high equipment cost and large investment cost.

As for the high concentration phosphorus wastewater, treatment mainly include precipitation, adsorption, and biological methods, as well as the newly developed electrolytic method, calcium method, Sequencing Batch Reactor (SBR) enhanced biological method, ceramic membrane coagulation reaction method, and chemical precipitation-coagulator method-activated carbon adsorption method. Publications (YEOMAN *et al.*, 1988; PRATT; PARSONS; SOARES, 2012; PEISHI; XIAORAN; YUNZHI, 2013) have concluded the following insufficiencies: high requirements for reaction equipment, large investment, and small treatment capacity. Furthermore, none of these methods can achieve the resource utilization of phosphorus.

In the early 1990s, sustainable and high-tech development needs promoted the research of microchemical technology. Shown in Figure 1A, a continuous flow microtubular reactor with characteristic size between 10 and 1,000 μm was manufactured by precision manufacturing technology. Therefore, chemical reactions can be carried out by pumping reagents into the microchannel reactor for mixture and controlling reaction temperature by the hot swap controller and reaction pressure by the back pressure valve. Having a maximum specific surface area (about hundreds of times or even thousands of times fold the specific surface area of the stirred tank), microreactor showed excellent heat and mass transfer ability, which can achieve instant uniform mixing of materials and efficient heat transfer, in addition to process strengthening by adjusting the reaction pressure to change the reaction kinetic process. Therefore, the microreactor can achieve high yield, high selectivity, and high safety of chemical reaction. Furthermore, the "micro" for microreactor indicated that the fluid channel was at the micron level but did not show that the micro reaction profile was small or that the product yield was small. As shown in Figure 1B, there can be millions of microchannels in the microreactors, so as to achieve high yields. Since the launch of the microchannel reactor, it has rapidly become a new development direction and research hotspot in the field of chemical industry, materials, and medicine, just as described in the publications by Doku *et al.* (2005), Roberge *et al.* (2005), Mason *et al.* (2007), Matsumoto (2015), and Talaiekhozani *et al.* (2020). At present, there is no literature reporting on the application of microchannel reactors in the field of environmental protection, especially in the study of enhancing the degradation reaction of organic matters.

Diethyl hydroxymethylphosphonate (DHP) is an important pharmaceutical and fine chemical intermediate, which is widely used in the synthesis of anti-HIV and anti-HBV drug tenofovir disoproxil fumarate (TDF), anti-HBV drug adefovir dipivoxil, and anti-CMV drug cidofovir. DHP can also be used in the synthesis of herbicides, fungicides, and organophosphorus flame retardants. At present, the main synthesis method is obtained through addition reaction followed by intramolecular rearrangement using diethyl phosphonate and paraformaldehyde or formaldehyde as raw materials. Thus, the DHP production process produces large amounts of industrial wastewater with high chemical oxygen demand (COD) (mg/L) ranged from tens of thousands to hundreds of thousands, and poor biodegradability by the low ratio value (0.1) of biochemical oxygen demand (BOD) to COD. It should be noted that the industrial wastewater is a kind of high concentration non-biodegradable organophosphorus wastewater with phosphorus content ranged from 100 to 3,000 mg/L. It is an important environmental problem in wastewater treatment, which poses a serious threat to natural environment and human health. Therefore, it is of great value to find a treatment method of DHP industrial wastewater with simple operation, good safety, low cost, and environment friendly.

Aimed at high concentration and hard-biodegraded DHP industrial wastewater, this study depicts a microchannel reaction first used to enhance the degradation process based on the advantages of rapid mixing, efficient heat and mass transfer, continuous sample injection and no amplification. A continuous treatment method for a kind of the high concentration and non-biodegradable organophosphorus industrial wastewater was constructed by heating hydrogen peroxide (H_2O_2) to produce a large number of free radicals, and then fast reacting it with organophosphorus under a certain temperature and pressure, so as to meet the level of purification in compliance with emission standards. Meanwhile, the treatment method can carry out resource utilization for organophosphorus using the microchannel reactor. The results of the study will

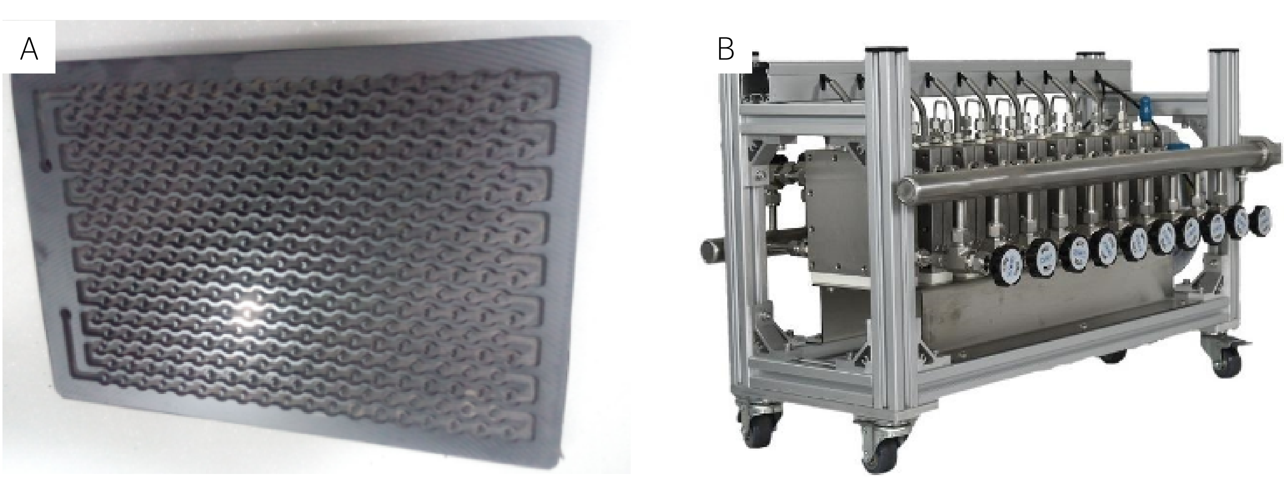


Figure 1 – The device of industrial micro-channel reactor: (A) Inner structure of the microchannel reactor; (B) The high-throughput micro-channel reactor.

achieve rapid, efficient, safe, easy to control, and quantifiable continuous degradation of phosphorus-containing organic wastewater and will also provide new ideas and technologies for the efficient degradation of other non-biodegradable organic pollutants.

MATERIALS AND METHODS

The designed microchannel reactor

The microchannel reactor was designed by oxidation reaction of the DHP industrial wastewater with H_2O_2 and neutralization reaction of the solution after oxidation reaction with NaOH. The specific experimental process schematic is shown in Figure 2. Micromixer 1 (P-713) was set up for mixing the raw materials with the two analytical liquid chromatography pumps 5 and 6 (NP7010C). Connected with micromixer 1, microreactor 2, which is a tubular reactor, was designed for oxidation reactions. Microreactor 2 was made of stainless steel with an inner diameter of 0.5~1 mm and a volume of 20 mL. Followed by microreactor 2, back pressure valve 7 (BP-10) was used to adjust the pressure of the reaction solution. Next, micromixer 3 (P-713) was set up to mix reaction materials with the analytical liquid chromatography pump 8 (NP7010C). Connected with micromixer 3, microreactor 4, which is a tubular reactor, was designed for neutralization reactions. Like microreactor 2, microreactor 4 was made of stainless steel with an inner diameter of 0.5~1 mm and a volume of 20 mL. Following microreactor 4, container 9 was used to collect the waste solution.

The treatment process

According to the process schematic shown in Figure 2, the DHP industrial wastewater and H_2O_2 were pumped by pump 5 and 6 and mixed with the volume ration of 1:1 in micromixer 1. Then, the oxidation reaction was run in microreactor 2 by adjusting reaction temperature, reaction time, reaction pressure, and sampling flow rate. After the oxidation reaction, in micromixer 3, the reaction solution was mixed with 0.1 mol/L sodium hydroxide (NaOH) pumped by pump 8 in a volume ratio of 1:1. The neutralization reaction was carried out in microreactor 4 at room temperature for about 1~5 min. The treated solution was collected by container 9 and distilled under reduced pressure. The distilled water determined the value of COD and NH_3-N, and the residual solid determined the total phosphorus (TP) content.

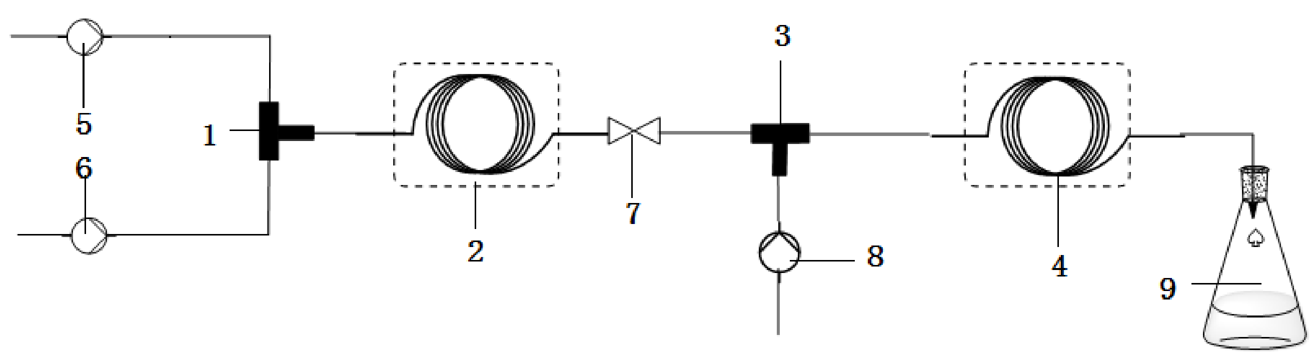
Materials and instruments

DHP industrial wastewater was originally collecting from Huangshi Fuertai Pharmaceutical Tech Co., Ltd., China, which is a leading producer and supplier of TDF intermediates and has been developing for over 10 years. In this study, the COD value of DHP production wastewater is 112,367 mg/L, the ammonia nitrogen (NH_3-N) value is 1,742 mg/L, the ratio of BOD to COD is 0.15, and the phosphorus content is 2,500 mg/L. The oxidant H_2O_2 (analytically reagent — AR) for oxidation reaction and the neutralizing reagent NaOH (AR) for neutralization reaction were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd, China. Chemicals of sulfuric acid (H_2SO_4) (AR), nitric acid (HNO_3) (AR), ammonium molybdate ($(NH_4)_2MoO_4$) (AR), ascorbic acid (AR), potassium antimonyl tartrate (AR), and perchloric acid ($HClO_4$) (guarantee reagent — GR), monopotassium phosphate (KH_2PO_4) (GR) for determination of TP were obtained from Sinopharm Chemical Reagent Co., Ltd., China.

The value of COD was determined by the detector (COD-203A) from Hach Water Quality Analytical Instruments (Shanghai) Co., Ltd., China. NH_3-N value was determined by the detector (HM-17A) from Shandong Hengmei Electronic Technology Co., Ltd., China. Phosphorus content was determined by a spectrophotometer (UV-2000) from Shanghai Precision Instuments Co., Ltd., China. As for the microchannel reactor, an analytical liquid chromatography pump (NP7010C) was obtained from Zhejiang Harbor Technology Co., Ltd., China. Electric heating high temperature reactor with double temperature zone (GC-2) was obtained from Shandong Jinde New Material Co., Ltd., China. Back pressure valve (BP-10) was obtained from Zaiput Flow Technologies, the United States. Micromixer (P-713) was obtained from IDEX Corporation, the United States.

Determination methods of total phosphorus

According to the Chinese standard GB 11893-89, TP content of DHP production wastewater before treatment and the residual solid after treatment were determined. The sample was digested with HNO_3 and $HClO_4$ in order to oxidize all phosphorus into orthophosphate. Then, the orthophosphate was reacted with $(NH_4)_2MoO_4$ in the presence of potassium antimony tartrate to form molybdophosphate heteropoly acid, which was immediately reduced by ascorbic acid to form the blue complex. The phosphorus content in the blue complex was determined by spectrophotometer (UV-2000). The standard curve of phosphorus content was shown in Figure 3.



1: micromixer; 2: microreactor; 3: micromixer; 4: microreactor; 5: feed pump; 6: feed pump; 7: back pressure valve; 8: feed pump; 9: container for waste solution.

Figure 2 – Process schematic of the treating DHP industrial wastewater using the microchannel reactor.

The correlation coefficient (R^2) between TP content (mg/L) and absorbance reached 0.999 5.

RESULTS AND DISCUSSIONS

Optimum conditions for the treatment method

In order to find the optimal reaction conditions to treat DHP industrial wastewater by the microchannel reactor, aimed at the oxidation reaction, a series of experiments were made by adjusting the reaction temperature (T), reaction time (t), reaction pressure (P), and sampling flow rate (F). The corresponding value of COD and NH_3-N were determined for each experiment. Detailed experimental data were listed in Table 1. The experimental results of DHP industrial wastewater treatment were illustrated in Figure 4.

Under constant reaction pressure (500 Pa), reaction temperature, reaction time, and sampling flow rate, an important effect on the value of COD and NH_3-N of the treated wastewater was observed. As for reaction temperature, with other conditions (reaction time and sampling flow rate) unchanged, both the COD and NH_3-N value increased significantly with the rising reaction temperature. The result indicated that the relatively lower temperature can achieve better degradation effect. At the lowest reaction temperature (140°C), the value of COD and NH_3-N was the lowest, with 3,000 and 83 mg/L, respectively. It can be speculated that higher temperature promotes the decomposition of H_2O_2, resulting in poor degradation effect of wastewater treatment. As for reaction time, with other conditions (reaction temperature and sampling flow rate) unchanged, both the COD and NH_3-N value decreased significantly with the increasing reaction temperature. The result showed that relatively longer reaction time (13.3 min) can get better degradation effect. As for sampling flow rate, with other conditions (reaction temperature and reaction time) unchanged, both the COD and NH_3-N value decreased significantly with the slowed flow rate. The result showed that the relatively slower sampling flow rate (1.5 mL/min) was conducive to the decomposition of wastewater.

Taken the influence of reaction temperature for example, the removal rate of NH_3-N and COD for the treatment DHP industrial wastewater using the microchannel reactor were shown in Figure 5. When the reaction temperature increased from 140 to 180°C, the removal rate of NH_3-N and COD decreased from 97.3 to 86.6% and from 95.2 to 90.2%, respectively. From the above analysis, the optimum conditions for treating DHP industrial wastewater using the microchannel reactor are as follows: lower

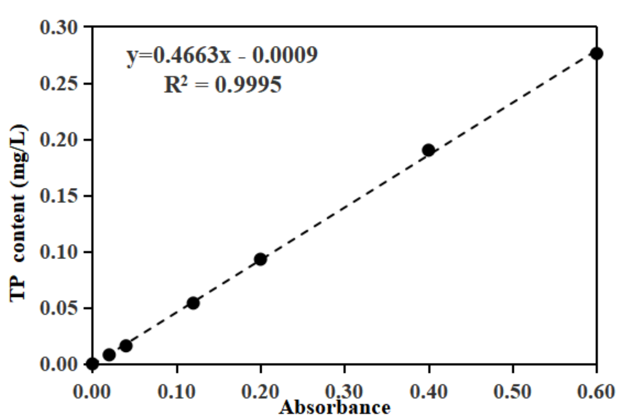


Figure 3 – The standard curve of determination of total phosphorus.

Table 1 – Experimental data.

No.	Reaction condition				Experimental result	
	T/°C	t/min	P/Pa	F/(mL/min)	COD/(mg/L)	NH_3-N/(mg/L)
1	140	10	500	2	6,100	120
2	140	13.3	500	1.5	3,000	83
3	150	10	500	2	8,600	116
4	150	13.3	500	1.5	6,600	92
5	160	10	500	2	17,740	180
6	160	13.3	500	1.5	14,360	170
7	180	10	500	2	25,040	160
8	180	13.3	500	1.5	15,040	140

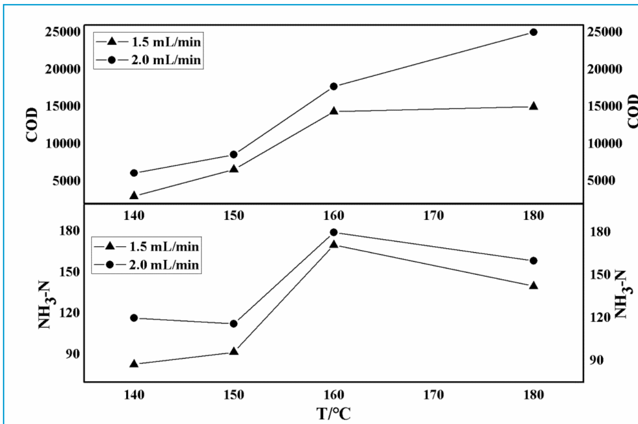


Figure 4 – Experimental results of DHP industrial wastewater treatment using the microchannel reactor.

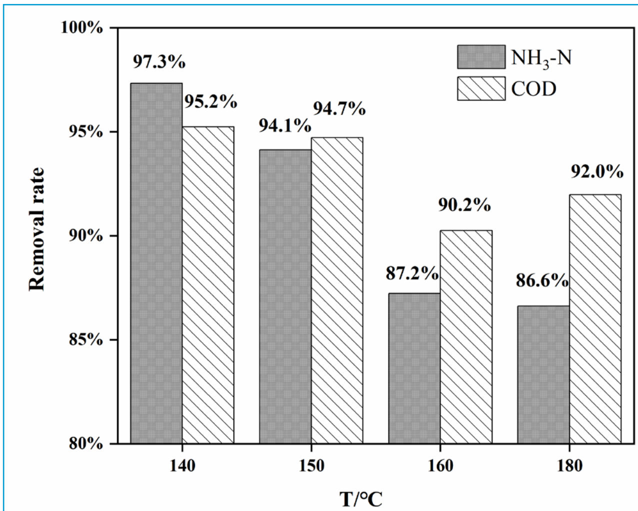


Figure 5 – Removal rate of NH_3-N and COD for DHP industrial wastewater treatment using the microchannel reactor.

temperature (140°C), longer reaction time (13.3 min), slower sampling flow rate (1.5 mL/min). Under the above optimum conditions, the better degradation effect can be achieved with the higher removal rate of NH_3-N (97.3%) and COD (95.2%).

Resource utilization for DHP industrial wastewater using the microchannel reactor

After the oxidation and neutralization reactions of DHP industrial wastewater treatment using the microchannel reactor, the treated solution with yellow color was obtained. Then, it was distilled to separate the water and get the solid with the yellow color. Under the above optimum conditions, a series of parallel experiments were performed and the corresponding yellow solids were obtained. The mass of the yellow solid was weighed. According to Chinese standard GB 11893-89, the TP content of the yellow solid was determined. Detailed information were listed in Table 2.

As seen in Table 2, under the same reaction conditions, the yellow solids obtained appeared almost the same mass ranged from 13.9 to 14.1 g. Similarly, the TP contents of the yellow solids presented the same mass ranged from 12.7 to 12.9 g. By calculation, the recovery rate of P from the yellow solid was ranged from 90.7 to 92.1%. The result showed that the treated DHP industrial wastewater by microchannel reactor can obtain the relatively stable and high P content of the yellow solid.

Table 2 – Information of the phosphorus recovery.

No.	Reaction condition				Experimental result		
	T/°C	t/min	P/Pa	F/(mL/min)	Mass of solid/g	TP/g	Recovery rate of P (%)
1	140	13.3	500	1.5	14.0	12.9	92.1
2	140	13.3	500	1.5	14.1	12.8	90.8
3	140	13.3	500	1.5	13.9	12.7	91.4
4	140	13.3	500	1.5	14.0	12.7	90.7

CONCLUSIONS

Based on the advantages of rapid mixing, efficient heat and mass transfer, continuous sample injection and no amplification, microchannel reactor was first used to treat the high concentration and hard-biodegraded DHP industrial wastewater. According to the oxidation reaction of the DHP wastewater with H_2O_2 and the neutralization reaction of the solution after oxidation reaction with NaOH, the DHP wastewater was treated with good degradation effect. Also, treated DHP wastewater can perform resource utilization with high P content.

- Optimal conditions for treating DHP industrial wastewater using microchannel reactor are as follows: lower temperature (140°C), longer reaction time (13.3 min), and slower sampling flow rate (1.5 mL/min);
- Under ideal conditions, good degradation effect for DHP industrial wastewater can be reached with the high removal rate of NH_3-N (97.3%) and COD (95.2%);
- Inorganic phosphate solid was obtained with P content as high as 92.1%, which can perform the reuse of phosphorus resources for the DHP industrial wastewater.

The treatment process using the microchannel reactor for the DHP industrial wastewater indicated the advantages of simple operation, good safety, controllable conditions. Also, it can be amplified in parallel without amplification effect, which is suitable for industrial application.

AUTHORS' CONTRIBUTIONS

Liu, H.: Funding acquisition, Data curation. Wang, Z.: Investigation, Formal analysis.

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