Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20338

76 (2017) 155–165
May

Research on the application of the modified aquatic mat pond and integrated vertical-flow constructed wetland coupling process based on luffa sponges for micro-polluted water treatment

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Received 8 April 2016; Accepted 31 October 2016

ABSTRACT

This paper presents a scientific performance study of the application of the modified aquatic mat pond (MAMP)-integrated vertical-flow constructed wetland (IVCW) coupling process for treating micro-polluted river water using luffa sponge material. In addition, the surface modifications of luffa sponge were investigated. The results showed that luffa sponge functioned well in a bench scale experiment and in a demonstration project, and the main effluent water indexes reached the class IV standard defined by the surface water quality standard of China (GB3838-2002). However, natural luffa sponge is easily hydrolyzed and should be replaced at regular intervals. A microwave-enhanced KH550 (Silane coupling agent γ-aminopropyltriethoxysilane) coupling method for modifying luffa sponges were performed to reduce the water absorption rate and prolong the engineering service time of the sponge. The results showed that the water absorption rate of the tested luffa sponge fibers was reduced to 22.39% after the fourth set of modifications, and an orthogonal test revealed that the priority order for the factors that affected the modification process was KH550 concentration > microwave reaction time > NAOH concentration > soaking time. The optimal set of modification conditions for luffa sponge fibers was 2% (w/w) NAOH, 1% (w/w) KH550, 30 min of soaking and 180 s of microwave treatment.

Keywords: Modified aquatic mat pond; Integrated vertical-flow constructed wetland; Surface modification; Luffa sponge

1. Introduction

Recently, the biological material "luffa sponge" has become increasingly attractive worldwide as an alternative environmental material for constructing man-made functional materials. Luffa sponges can be derived from the fruit of luffa cylindrica and are composed of luffa fibers. These fibers are interconnected with each other and form networks with micro-trusses that form vascular bundles and yield a multimodal hierarchical pore system [1]. Thus, luffa fiber has potential for using in a wide range of fields because of its merits like cheap and easy to get, has larger surface area and has three-dimensional and net-like structure [2–4].

Recent domestic and foreign studies have mainly focused on environmental protection [4–7] and can be

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divided into several areas of study, such as adsorption materials (e.g., adsorbed heavy metals, dyes); solid carbon sources and microbial carriers; mechanism analysis (e.g., elements, structure, properties and activities of enzymes); and cell immobilization for biotechnology [8–12]. Other studies have characterized luffa fibers for additional technical applications, such as the reinforcement of composite materials [13,14].

Current studies have shown that luffa sponge can be used in a wide range of water treatment applications; Few practical applications have been found due to a lack of experimental data. Furthermore, no scientific data have been found regarding the engineering applications of luffa sponge material to date [15]. Similar to most other natural polymer materials, luffa sponge is a type of plant fiber with surfaces rich in hydroxyls, which allows it to easily and quickly degrade in water [16]. This degradation leads to the limited lifetime of the material, which affects the stability and cost of the system and counteracts the benefits of engineering applications that use luffa sponge as a carrier in the field of wastewater treatment.

To obtain better use of luffa sponge, diverse surface modification methods are necessary to reduce the number of surface hydroxyls of the fiber surface, decrease the hydrophilic properties of the natural fibers, improve its resistance to microbial corrosion and finally prolong its service life.

Commonly used methods for material modification can be divided into physical and chemical methods. Physical modification methods include physical processing, blending modification, surface etching, and the use of alkaline reagents [17], while chemical modification methods include coating, interface coupling, and graft copolymerization [18,19]. Interface coupling is an important modification method that can alter the interface adhesion between different materials. The number of hydroxyl groups on the surface of natural fibers decreases after the fibers are modified by certain coupling agents, reducing the water absorption capacity of the fiber. Furthermore, treatment with coupling agents could form a cross-linked network between the fibers and polymers, thereby reducing the swelling effect of the fibers.

Reaction conditions also play a very important role in the material modification process. Microwave heating technology is a type of chemical reaction that is promoted by emerging technologies and has distinct advantages over traditional techniques [20–22]. Unlike water bath heating or other methods, microwave heating does not cause secondary pollution. Its unique advantages include the following: (1) it can quickly and efficiently undergo simultaneous internal and external heating; (2) it results in energy savings; (3) the heated material is not in direct contact with the heat source; (4) the material can be selectively heated (a polar material is easy to heat but a nonpolar material absorbs very little microwave heat); and (5) it is easy to control [23].

These advantages could greatly shorten the reaction time and improve production efficiency. Moreover, no temperature gradient is generated, which could inhibit byproduct formation during the reaction process.

Therefore, one purpose of this paper was to investigate the surface modification of luffa sponges produced by the silane coupling agent-microwave heating method. KH550 was used to reduce the water absorption of the material, prolong the period of luffa sponge use, and determine the optimal modification parameters for engineering uses in an orthogonal experiment.

In summary, this study was motivated by the fact that no quantitative study has examined the engineering behavior of luffa sponge. In this study, the behavior of luffa sponge as a solid carbon source and biofilm carrier in a bench scale experiment and in the "Qiantang River diversion denitrification demonstration project" (West Lake, Hangzhou) was investigated, and the effects of surface modifications of luffa sponges were studied.

2. Materials and methods

2.1. Set up of the bench scale experiment and the demonstration project

As shown in Fig. 1, The "Qiantang River diversion denitrification demonstration project" (Part of the second task of the National Eleven-Five Science and Technology Major Project for Water, No.2009ZX07106-002-02) was first proposed to resolve the problem of the transfer of water containing high concentrations of nitrate and low concentrations of carbon from the Qiantang River to the West Lake. Further measures were urgently needed to decrease the nitrate concentrations in the diversion of the Qiantang River. The total nitrogen content in the water from the Qiantang River flowing into West Lake was more than 2 mg/L, and the concentration remained at 1.5 mg/L after sedimentation. As shown in Table 1, nitrates accounted for more than 50% of total nitrogen, making the water quality worse than the national surface water class V level.

Therefore, a bench scale experiment was designed to study the performance of the luffa sponge as a carrier and solid carbon source for microorganisms that remove nitrogen and to accumulate experience and determine design parameters for the "Qiantang River diversion denitrification demonstration project".

Fig. 2(a) and 2(b) show the bench scale experiment and the denitrification demonstration project, respectively, which

Fig. 1. Roadmap of the diversion from Qiantang River to the West Lake in Hangzhou.

consisted of two units: modified aquatic mat pond (MAMP) and integrated vertical-flow constructed wetland (IVCW).

The influent of the bench scale experiment was artificial and simulated according to the water content of the diverted Qiantang River, and the effective volume of the collector well was 140 L. The MAMP unit was composed of organic glass, was 250 mm × 250 mm × 350 mm in size, and had an effective volume of 17.30 L. Luffa sponges were connected in series by ropes after they were cut into several cylindrical sections and were hung in the middle of the MAMP unit.

The prototype of the IVCW unit was first proposed during the "Ninth five-year plan" period under the international cooperation framework of the European Union by the Chinese Academy of Sciences, University of Cologne, Germany, and Vienna Kasetsart University of Austria [24].

Table 1
Surface water quality standard of China and Qiantang River water quality (mg/L)

Levels	TN	NO_3^--N	NH_4^+–N	COD_{Cr}	TP
I	0.20	–	0.15	15	0.02
II	0.50	–	0.50	15	0.10
III	1.00	–	1.00	20	0.20
IV	1.50	–	1.50	30	0.30
V	2.00	–	2.00	40	0.40
Qiantang	3.00	2.20	0.48	19	0.12

The IVCW system in the bench scale experiment consisted of two units (CW1#, CW2#), and each unit had dimensions of 50 cm × 50 cm × 100 cm. CW1# and CW2# were made of PVC material and had particle sizes ranging from 8 cm to 4 cm from the bottom to the top. CW1# was planted with *Canna indica* in the downstream chamber and *Acorus calamus* in the upstream chamber, and the CW2# unit was planted with Napier Grass (*Pennisetum purpureum*) in both chambers. CW1# and CW2# consisted of a downstream chamber and an upstream chamber, and the two chambers were connected by a middle wall with a perforated tracery located at the bottom to conduct water. The substrate layer of the downstream chamber was designed to be 1–20 cm higher than that of the upstream chamber. IVCW technology has been applied in more than 21 cities or provinces in China.

The coupling system of the demonstration project had a disposal flux of 1500 t/d. The MAMP system, which acted as a biological denitrification reactor, was built of concrete and had regular dimensions of 16.0 m × 4.0 m × 2.0 m. Natural luffa sponge was chosen as the core material for the modified aquatic mat filler. The diameter of a luffa sponge material used in this engineering is about 100 mm, and the length of it is about 60 mm to 100 mm, which is surrounded by a hollow plastic ball outside. The distance of each plastic ball is about 200 mm. The distance between each rope is 300 mm. Luffa sponge has the advantages of a larger specific surface area and faster biofilm culturing speed. The specific surface area of the luffa sponge in this study is 1185 m^2/g, while the conventional parameters are 300–500 m^2/m^3 for elastic packing and 380–800 m^2/m^3 for suspended filler. In

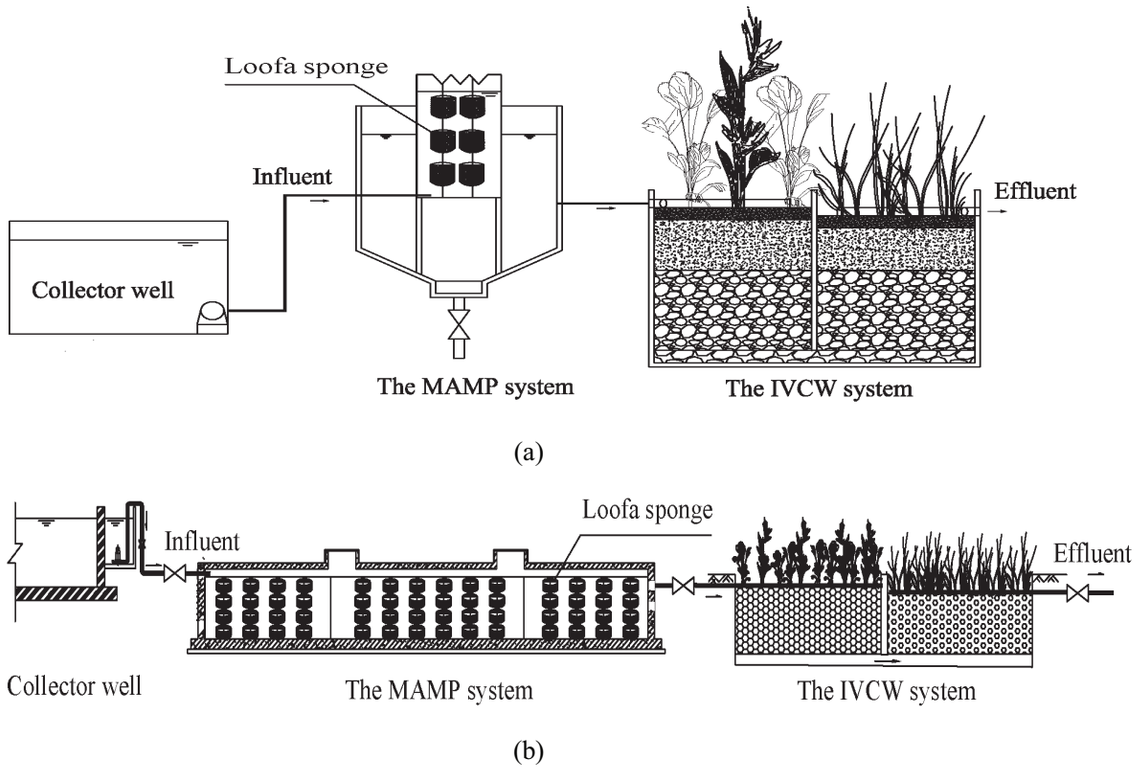

Fig. 2. (a) Schematic diagram of the bench scale experiment. (b) Schematic diagram of the denitrification demonstration project.

addition, luffa sponge could provide the biological degradation system and carbon source required for the denitrification process. A combination of physical settlement, storage, interception and biological purification was used to remove pollutants in the MAMP unit.

In this demonstration project, *Couldna, calamus,* barracuda grass, *Lythrum salicaria,* and *Arundo donax* were selected as wetland plants, and vermiculite, zeolite, scraping meter gravel, and ceramic particles were used as wetland substrates to adsorb contaminants and load microbial.

2.2. Methods

2.2.1. Operation parameters and methods used in the bench scale experiment and demonstration project

2.2.1.1. Operation parameters of the bench scale experiment and the demonstration project.

In the bench scale experiment, the nitrogen and phosphorus concentrations and COD_{Cr} in the water of the diverted Qian Tang River were simulated, and four different C/N ratios were used. The experiment was divided into four stages, the first stage (I) was performed during days 1–15, the second stage (II) was performed during days 18–32, the third stage (III) was performed during days 35–49, and the fourth stage (IV) was performed during days 52–66. The demonstration project was operated using settling conditions, and the influent water quality is shown in Table 2.

The operation parameters of the bench scale experiment and demonstration project are shown in Table 3.

2.2.1.2. Methods used for the bench scale experiment and demonstration project

The measured parameters and methods included the following: COD_{Cr} (Cr stands for the use of potassium dichromate ($K_2Cr_2O_7$) as the oxidant of the determination of chemical oxygen consumption.), microwave digestion titration (It uses sulfuric acid dichromate digestion system, and the reaction liquid can function in microwave of 2450 MHz. The high-speed friction between molecules lead to the rapid increase of temperature. With the addition of Ag^+ as catalyst, the oxidation of organic matter in water can be in a relatively short time. In addition, the use of intelligent sensing control technology makes COD measurement simple and easy); NH_4^+–N, Nessler's reagent colorimetric method (GB 7479-1987); TN, alkaline potassium persulfate digestion and UV spectrophotometry (GB 11894-1989); NO_3^-–N, ultraviolet spectrophotometry (HJ/T 346-2007); NO_2^-–N, spectrophotometry (GB 7493-1987); and TP, ammonium molybdate and spectrophotometry (GB11893-1989). SPSS 20.0 was used for data analysis.

Table 2
Influent quality indicators

Operation phase		ρ/(mg/L)						C/N
		TN	NO_3^-–N	NO_2^-–N	NH_4^+–N	TP	COD_{Cr}	
Bench	I	3.81	3.08	0.06	0.48	0.12	7.90	2.5
	II	2.93	2.61	0.02	0.43	0.11	23.80	8.9
	III	3.83	3.06	0.03	0. 47	0.11	23.60	7.7
	IV	3.83	3.11	0.03	0.47	0.11	15.20	4.9
Demonstration		2.47	1.89	–	–	0.04	11.70	4.7

Table 3
Operation parameters of the modified aquatic mat pond-integrated vertical-flow constructed wetland system

Phase		Unit	Operation method	HRT/h	Hydraulic load[1]	Volume load kg COD/(m^3·d)
Bench	I	MAMP	Continuously	2.00	0.14	0.10
		IVCW	Intermittently(12 h)	32.90	204	–
	II	MAMP	Continuously	2.00	0.14	0.29
		IVCW	Intermittently(12 h)	32.90	204	–
	III	MAMP	Continuously	2.00	0.14	0.28
		IVCW	Intermittently(12 h)	32.90	204	–
	IV	MAMP	Continuously	2.00	0.14	0.18
		IVCW	Intermittently(12 h)	32.90	204	–
Demonstration		MAMP	Continuously	0.77	0.97	0.01
		IVCW	Intermittently	8.57	379	–

[1]The units used for hydraulic load were $m^3/(m^2·h)$ for the MAMP system and mm/d for the IVCW system.

2.2.2. Experimental modification of luffa sponge fiber material

2.2.2.1. Methods and procedures

1) Alkali treatment

Several rectangular strips (10 mm × 10 mm × 10 mm) of luffa sponges were soaked in NaOH solutions with different concentrations (1%, 2% and 3%) and rinsed with deionized water to neutralize them after 2 h of alkali treatment at room temperatures.

2) Preparation of the silane coupling agent KH550 and the ethanol solution

First, 95% ethanol (or isopropanol) and 5% water were mixed to form an alcohol-water solution. Acetic acid was added to the alcohol-water solution to maintain a pH range of 4.5–5.5 (solution A). Then, the silane coupling agent KH550 was added to solution A while stirring to form three solutions (solution B) with different concentrations (1%, 3% and 5%). The solutions were stirred for another 5–10 min to fully dissolve the coupling agent.

3) Preparation for modifying luffa sponges by using the interface coupling method

Alkali-treated luffa sponges were soaked in the three solution B mixtures prepared above for different times according to the orthogonal experimental design. The sponges were subsequently removed after soaking, washed to neutralize them, placed in a microwave oven for different amounts of time, placed in a desiccator at 85°C until a constant weight was achieved, and then stored in a dryer until further analysis.

2.2.2.2. Experimental design for the microwave method.

Four factors and three levels were selected in this experiment, as shown in Table 4. An orthogonal test table was designed as shown in Table 5.

2.2.2.3. Materials, equipment and methods for the material test.

The materials included: (1) Methyl orange indicator (99% pure AR for analysis from Tianjin); (2) Luffa sponges (dried from the market); (3) KH550 (From Nanjing Downing Chemical Co. Ltd. Group).

Methods for the material test included: (1) FTIR (Nexus Fourier Transform Infrared Spectrometer, Thermo Nicolet Co, USA); (2) SEM (Field Emission Scanning Electron Microscope S-4800, Hitachi Co, Japan).

The weight method was used to measure the water absorption properties of the materials and treated fibers with a constant weight were placed in a controlled box (The equipment is HBY-40B cement concrete curing box with constant temperature and humidity which produced by shanghai gold instrument and Equipment Co., Ltd) at 20°C and a relative humidity of 80% (constant temperature and humidity). When the temperature is lower than the set temperature control of the lower limit, the equipment instrument output the heating control signal; while when the temperature is higher than the set temperature control range, the instrument output refrigeration control signal; and when the temperature comes to the window area setting control value, the instrument will stop heating or cooling, making the temperature into a temperature constant stage. When the humidity is lower than the set humidity control value, the instrument output humidity signal, while when the humidity is higher than the lower limit of the set humidity control value, the humidification will stop.

Table 4
Experimental design parameters for the microwave method

Factors	Levels		
Microwave reaction time (s)	60	180	300
Soaking time in NaOH (min)	30	60	90
Concentration of KH550 (wt%)	1	3	5
Concentration of NaOH (wt%)	1	2	3

Table 5
Orthogonal experimental design for the microwave method

Card	NaOH (wt%)	KH550 (wt%)	Soaking time in NaOH (min)	Microwave reaction time (s)
1	1	5	90	180
2	3	5	30	300
3	2	1	90	300
4	2	5	60	60
5	3	3	90	60
6	1	1	30	60
7	1	3	60	300
8	2	3	30	180
9	3	1	60	180

Then, an analytical balance was used to accurately measure the weight of the luffa sponges at specified times. The weights of unmodified fibers and a variety of modified fibers were calculated in this manner to determine their water absorption rates. The calculation method for water absorption (A_w) is given by the following equation:

$$A_w(\%) = (W_1 - W_0)/W_0 \times 100\% \quad (1)$$

where W_0 and W_1 are the weights of the original luffa sponge and the weight after water absorption, respectively.

3. Results and discussion

3.1. Effect of the modified aquatic mat pond-integrated vertical-flow constructed wetland coupled system

3.1.1. Performance of the bench scale system

Fig. 3 shows the performance of the bench scale system and indicates that this system had a range of TN removal of 61.90%–91.40%. The C/N ratio had a significant effect on the removal of TN in the bench scale system, and the proper C/N ratio in the MAMP unit was 4.90 [16].

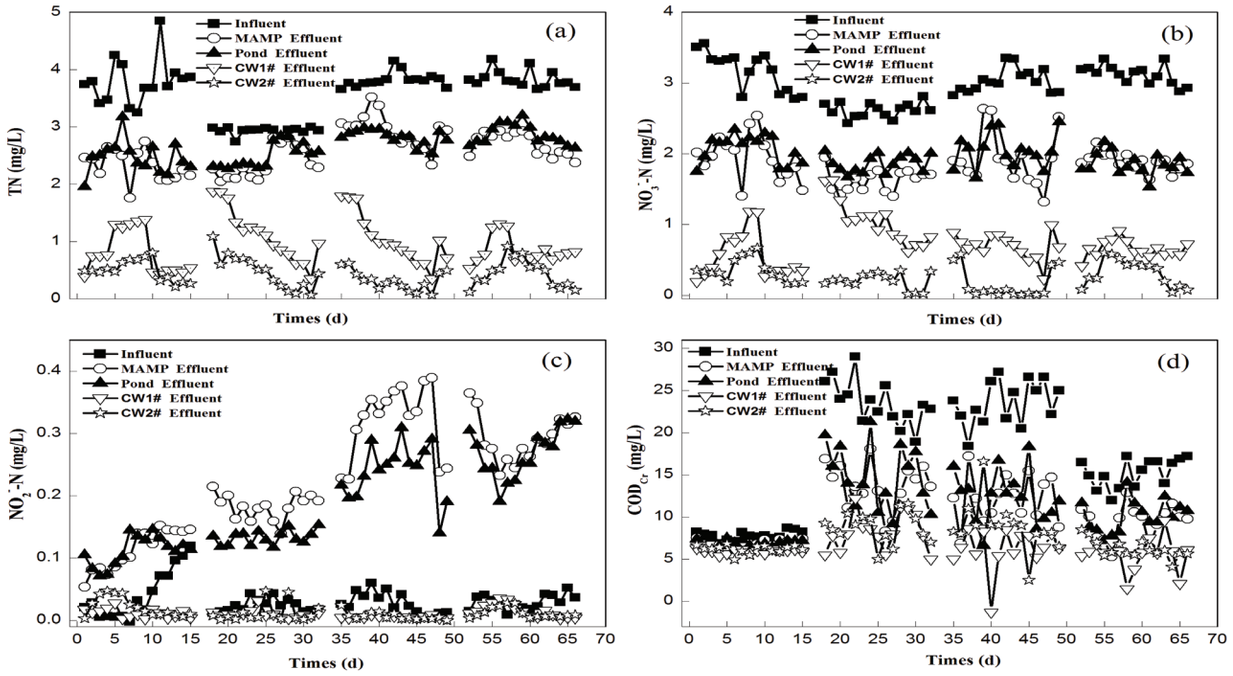

Fig. 3. Variation of TN, NO_3^-–N, NO_2^-–N and COD_{Cr} in the coupled system in the bench scale experiment.

As described above, units CW1# and CW2# stand for the two different IVCW system (with different plant types) in the bench scale experiment, respectively. The average concentration of TN in the effluent of CW2# was less than that of CW1#, and the effluent of CW2# reached the IV level defined by the Surface Water Quality Standards (GB3838-2002). The average removal rate of effluent NO_3^-–N by the MAMP unit was 38.20% when the concentration of influent NO_3^-–N in phase I and II fluctuated from 2.43–3.56 mg/L. The performance of CW2# was more stable than that of CW1#, and the average value of effluent NO_3^-–N in CW2# was 0.28 mg/L. NO_2^-–N accumulated in the effluent of the MAMP unit. CW1# and, especially, CW2#, which had a NO_2^-–N removal rate of 92.40%, resulted in good NO_2^-–N removal.

The bench scale system did not function well at low influent COD_{Cr}; however, the removal rate of COD_{Cr} by CW1# reached more than 61.80% as the influent COD_{Cr} increased. CW2# demonstrated a less efficient performance than CW1#.

3.1.2. Performance of the demonstration project

Fig. 4 shows the removal of COD_{Cr}, TN, NO_3^-–N and TP by each unit in the demonstration project. The C/N ratio during the entire run of the coupling system was maintained at 3.78–6.42, with an average value of 4.77, which was slightly lower than that of the bench scale experiment described above.

Table 6 provides a list of the pollution removal rates for the demonstration project. The MAMP unit worked well for removing TN and NO_3^-–N in the initial stages; however, the TN removal rate decreased gradually as the temperature decreased. Table 5 shows that the average removal rates of TN and NO_3^-–N for the full period were only 30.53% and 30.18%, respectively. Xie et al. [25] studied the performance of luffa sponges loaded in a denitrification reactor and found that the TN removal rate increased from 26.83% to 80.77% and that the average COD removal rate of the entire system was 91.22%. These results seem much more efficient than those of the present denitrification demonstration project. The difference between these results mainly occurred because the previous experiment lasted one month (from 18 June to 18 July), while the project presented in this paper lasted four months and included a low temperature period. These findings showed the large influence of microbial activity and its indirect effects on the performance of the biological treatment unit [24]. Shen et al. observed that the nitrate removal efficiency at 15°C was only 55.06% of that at 25°C [4], and other researchers [26] have argued that nitrate removal rates at 14°C are approximately one-third of the removal rates observed at 32°C. Furthermore, HRT was conducted from 3 h to 12 h in previous experiments in this study, but only for 2 h, which could account for the lower observed TN removal rates.

The figure in Table 5 also shows that the MAMP unit was not effective for TP removal. Instead, the MAMP unit increased the effluent TP concentration and resulted in a negative TP removal rate of 70.90%. Explanations for this phenomenon are presented below.

1) Due to the complexity of the dissolved oxygen conditions in the MAMP unit, many different micro-environments existed, which formed alternating aerobic/anoxia/anaerobic regions and indirectly accelerated the performance of phosphorus accumulating bacteria for the release and absorption of phosphorus.

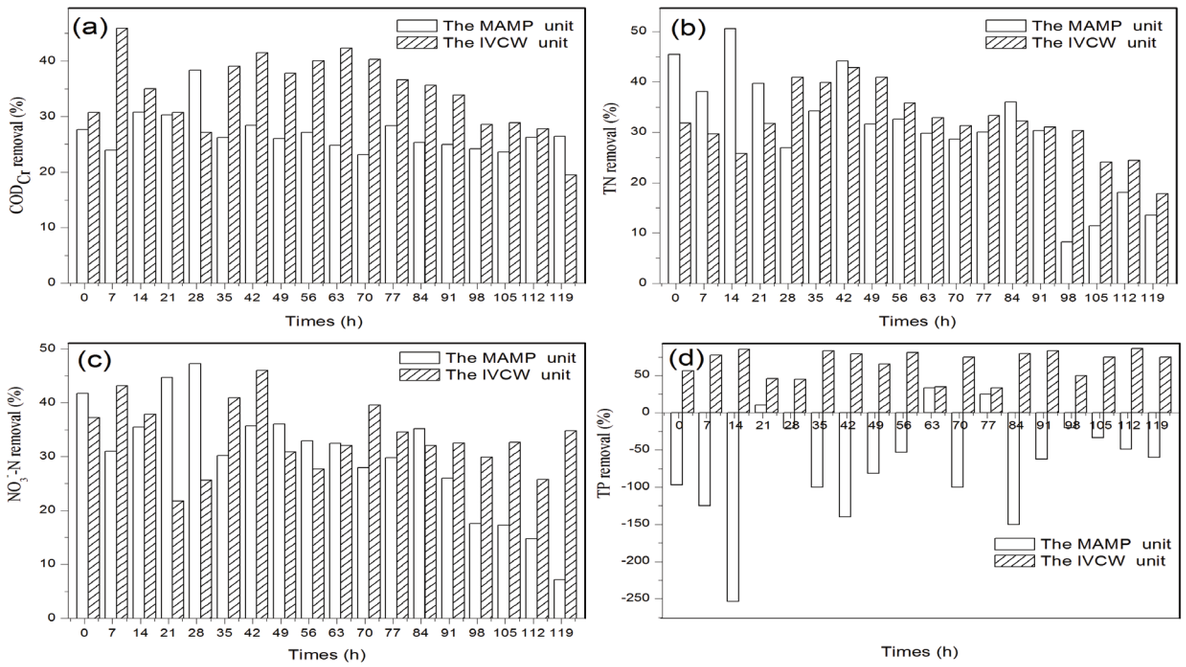

Fig. 4. Variations of COD_{Cr}, TN, NO_3^-–N and TP in the coupled system in the demonstration project.

Table 6
Removal of COD_{Cr}, TN, NO_3^-–N and TP by each unit and the coupled system

Item	MAMP unit (%)	IVCW unit (%)	Coupled system (%)
COD_{Cr}	27.01	34.53	52.27
TN	30.53	32.05	52.49
NO_3^-–N	30.18	33.61	53.69
TP	–70.90	67.39	52.79

2) The activities of worms could have caused this phenomenon. Worm bloom can cause the release of nitrogen and phosphorus into the effluent [27]. In studies of biofilm reactors filled with luffa sponges, researchers have shown that effluent TP concentrations increase significantly after worms appear in a bioreactor; furthermore, the TP concentrations return to their original levels after the worms disappear [28]. However, the mechanisms by which worms increase the TP concentrations in effluents have not been explained in detail. Previous studies have shown that luffa sponges contain an abundant amount of phosphorus, reaching up to 518.94 μgP/g luffa sponge [29]. Therefore, the appearance and growth of worms could reduce the biofilm on the surface of the luffa sponge, inhibit the degradation process, and release the phosphorus contained in the sponge to the body of water.

The IVCW unit obtained a stable pollutant removal efficiency, especially for TP (removal rate, 67.39%), and gradually increased. In the four-month period, the two units performed as a single organic entity, producing complementary advantages and guaranteeing the effluent quality of the demonstration project. The main water quality indexes of the "Qiantang River diversion denitrification demonstration project" reached class IV of the Surface Water Quality Standards (GB3838-2002).

3.2. The degradation of luffa sponges in the denitrification demonstration project

Natural luffa sponge, which consists of a fibrous network, is obtained from the mature dried fruit of the cylindrical luffa plant. Luffa sponge has a highly complex macroscopic architecture template and is an inexpensive and sustainable resource [30]. Luffa sponge is chemically composed of 60% cellulose, 30% hemicelluloses and 10% lignin and consists of an open network of random lattices of small cross-sections and very high porosity (79–93%) [31], resulting in a density of approximately 0.78 g/cm^3 [32]. However, because natural luffa sponge can be easily hydrolyzed, it is not stable and it is not economically feasible to use luffa sponge as a filter when treating sewage.

Fig. 5 shows SEM (under 180× magnification) images of natural fiber materials before and after engineering applications (after 202 days of operation). Unlike the smooth structured luffa sponge in Fig. 5(a), the surface of a used luffa sponge is covered with a layer of ash powder, which could be an intermediate degradation product, such as cellobiose, monosaccharides, and glucose. These intermediate degradation products mainly result from the long degradation time of cellulose and semi-cellulose via the synergistic functions of cellulase, enzymes, exonuclease and glycosidase.

Furthermore, the small holes observed in Fig. 5b could result from metabolic gases, such as carbon dioxide, that

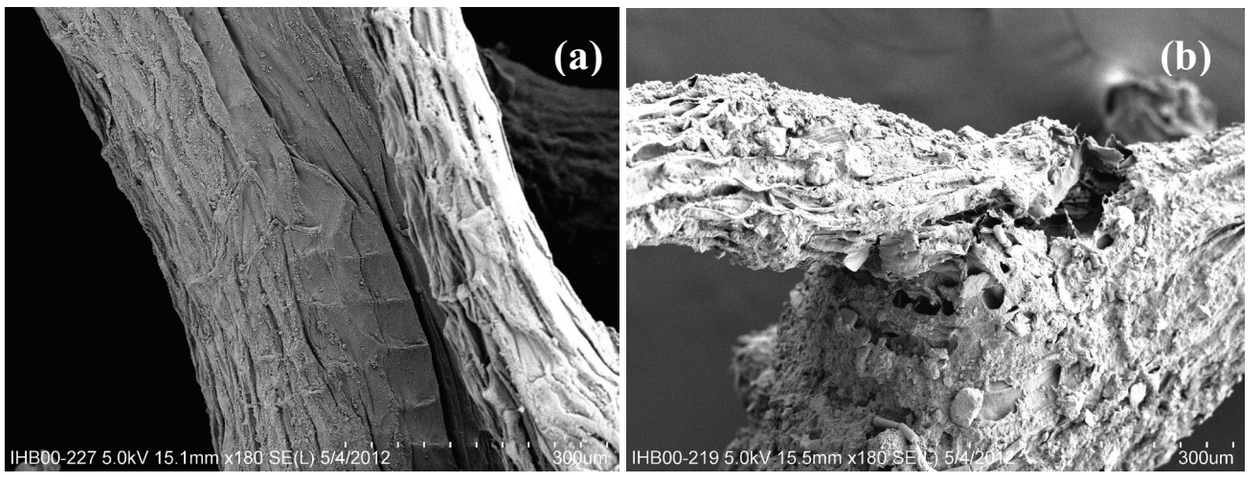

Fig. 5. SEM images of an original luffa sponge (a) and a used luffa sponge (b) after 202 d of use in the project.

are generated during the degradation of the material, as well as the activity of micro metazoa. However, Fig. 5b shows that the surface of the test sample has been destroyed, indicating that the carbon frame structure of the tested luffa sponge was changed and that the luffa sponge became increasingly fragile due to microbial degradation.

3.3. The surface modification of luffa sponges

Surface pretreatment was necessary to maximize the potential use of luffa sponges. The aim of this study was to prolong the service life of luffa sponge as an engineering carrier and solid carbon source. Thus, the alkali modification process was adopted as a pretreatment method to improve the ability of the sponge to contact other materials and alter the surface properties for the next modification process.

The principle of microwave heating is closely related to the effects of microwave treatment on the structure of the material. A group of experimental conditions was selected for the modified materials to test and analyze specific mechanisms. This group of experimental conditions consisted of 2% (w/w) NaOH, 3% (w/w) KH550, 30 min of soaking and 60 s of microwave heating. Luffa sponge fiber samples from the luffa sponge were examined using SEM and Fourier Transform Infrared Spectroscopy (FTIR) to explore its structural changes.

3.3.1. SEM analysis of the modifications of luffa sponge

Fig. 6(a) and 6(b) show the SEM images of luffa sponges before and after the alkali modification process. The treatment involved soaking the fibers in 2% (w/w) NaOH to dissolve or remove low molecular weight impurities; reduce the microfibril angle of rotation of the fiber material, making the surface rough and forming many cavities; and increase the activities of sites on the fiber surface, improving the ability of the fiber to react with other modification reagents. In addition, alkali modification caused fibrillation of the fibers, which decreased the size of the fiber bundle, increased the length to diameter ratio, and effectively enlarged the contact area with the modifier.

The alkali pretreatment dissolved some of the amorphous concomitant materials, such as hemicellulose, lignin and pectin, which were embedded in the crystalline region during the growth period, resulting in imperfect crystallization of the fiber materials and changes in the characteristics of the surface topography [2]. After pretreatment, the fibers expanded in the alkali solution, resulting in a weaker interfacial interaction between the fibrils, and the intermediate cavity and fiber wall thickness increased. However, the surfaces of the fibers became smooth, and some channels appeared after treatment. The alkali-treated fibers had an irregular surface because a larger amount of the surface material was removed [33], which reduced the weight of the material by approximately 6% in another study [34].

As observed in Fig. 6c, the surface of the fibrous material before modification was scattered, rough, and exhibited irregular channels, debris, and impurities. Due to the heating effect of the microwave, a chemical reaction occurred that accounted for the increase in roughness of the fiber surface after it was soaked in KH550 (Fig. 6d). However, based on the emergence of an unreacted region at the corner, the microwave process did not have a complete effect on the surface modification. This result could be related to the monomer concentration, microwave processing time, or immersion time.

3.3.2. FTIR analysis of material modifications

Due to microwave treatment, the surface of the luffa sponge fibers became rough, and the specific surface area increased. However, the specific changes in the surface also had a direct influence on the moisture absorption properties of the materials. However, infrared spectrum analysis was needed to study the reaction mechanisms and changes in the surface groups of fiber materials with KH550 treatment and microwave heating.

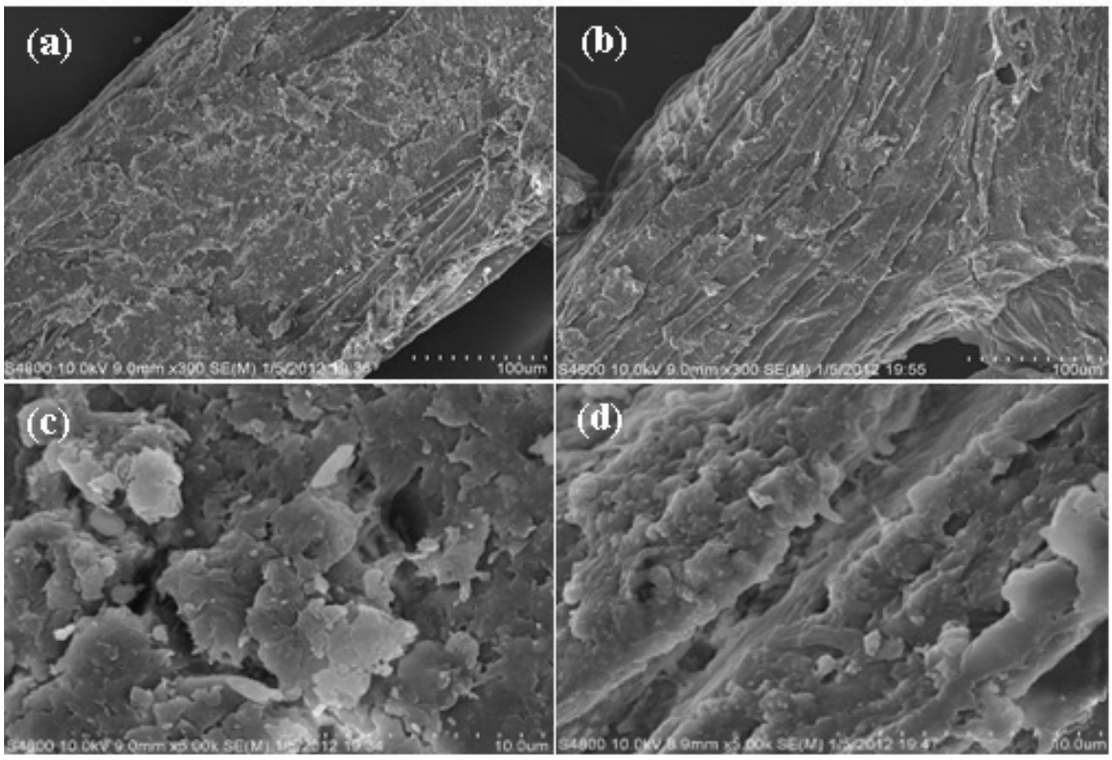

Fig. 6. SEM images of luffa sponge fibers before and after the modification process. (a) before alkali modification; (b) after alkali modification; (c) before alkali modification and microwave modification; (d) after alkali modification and microwave modification.

Fig. 7 shows the infrared spectrum of the fiber materials before and after microwave treatment. As observed in the graph, the appearance of an absorption peak at 3425 cm^{-1} indicates the occurrence of O–H bond stretching vibrations, which account for the occurrence of changes in the intramolecular hydrogen bonds of the sample and the KH550 reagent after microwave treatment. The emergence of a strong absorption peak at 2922 cm^{-1} explains the flexural vibration of the C–H bond. The absorption peak at 1050 cm^{-1} indicates the strong Si–O–C bond stretching vibration of cellulose. However, some of the characteristic peaks of the fiber material disappeared or became weaker between 901 cm^{-1} and 471 cm^{-1}, and the emergence of new absorption peaks at 471 cm^{-1} demonstrated the bending vibrations of the Si–O bond. Changes in the peaks listed above proved that KH550 had been coupled and covered the surface of the luffa sponge material after the microwave treatment.

The reaction mechanism occurred as follows: KH550 ($NH_2(CH_2)_3Si(OC_2H_5)_3$) was first hydrolyzed to silanol and then adsorbed onto the surface of the fibrous material. Hydrogen bonds were formed during the polycondensation reaction between the silanol formed by the hydrolysis of KH550 and the hydroxyl groups on the fiber surface. Subsequently, the silicon functional groups of KH550 were connected to the surface of the luffa sponge fibers using microwave heating and dehydration, thereby coating the surface of the luffa sponge fibers with KH550, which seemed to change the surface roughness and hydrophilic properties of the material.

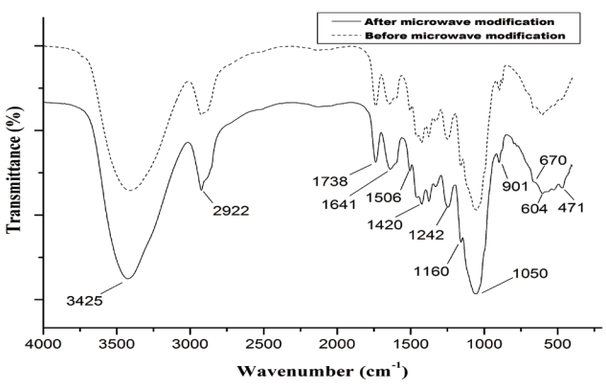

Fig. 7. FTIR graph of the luffa sponge fibers before and after microwave treatment.

3.3.3. Variations of water absorption by the tested luffa sponge fibers

The modification experiment was conducted considering four factors: a three level orthogonal table (Table 4) in which the concentration of the silane coupling agent, reaction time of the microwave treatment, soaking time of the tested fiber, and concentration of alkali pretreatment were chosen as experimental parameters. The water absorption values for each group of microwave treated fiber material at 30 min and 120 min are shown in Table 7, where "0" rep-

resents the original luffa sponge fiber and "1, 2, 3, etc." indicate the different test groups.

Heat generated directly by the microwave originated from the internal area of the heated object and was simultaneously transferred along the thickness of the object. The luffa sponge fibers and the silane coupling agent reacted in a high frequency electric field, and the intramolecular and intermolecular hydrogen bonding changed, producing a low surface energy KH550 coating on the luffa sponge fibers and a membrane layer. Table 6 also shows that the water absorption rate of fibers subjected to the fourth group of modification conditions decreased to approximately 22.39% of that of the original sample, demonstrating a significant modification. This set of conditions, consisting of 2% (w/w) NaOH, 5% (w/w) KH550, 60 min of soaking, and a microwave reaction time of 60 s, produced a relatively high KH550 value and a suitable soaking time for the hydrolysis of KH550.

3.3.4. Results of the orthogonal test and optimization of the modification conditions

By combining the water absorption values of luffa sponge fibers obtained in the orthogonal test, the effects of inter-subjectivity for each factor were tested and analyzed, and the results are shown in Table 8.

Table 7
Water absorption of the luffa sponge fibers after microwave treatment

Item	30 min water absorption rate(%)	1200 min water absorption rate(%)
0	7.31	15.45
1	6.64	13.94
2	5.90	12.28
3	7.75	12.24
4	5.24	11.99
5	8.36	14.11
6	6.23	13.75
7	5.56	12.88
8	7.00	13.69
9	5.65	12.56

According to Table 8, the microwave reaction time and KH550 concentration significantly affected the modification of the luffa sponge ($P < 0.01$). By comparing the *F*-values, the order of importance of the factors responsible for modifying the material was KH550 concentration > microwave reaction time > NaOH concentration > soaking time.

To optimize the modification conditions, a comparative analysis of the mean values for each factor was conducted. The results show that high KH550 concentrations can cause many KH550 molecules to adhere to the surface of luffa sponge fibers, leading to uneven heating and causing severe gelatinization in the microwave heating process. However, the use of an appropriate concentration of KH550 can prevent this problem. The low-concentration alkali treatments resulted in less modification. A long soaking reaction time increased hydrolysis and the generation of silanol for KH550 but also allowed self-polymerization, thus affecting the modification efficiency. A short microwave heating time resulted in incomplete surface treatment; however, a long treatment time may cause material gelatinization from the inside out.

Therefore, the optimal set of conditions for luffa sponge fiber modification in this orthogonal test was 2% (w/w) NAOH, 1% (w/w) KH550, a soaking time of 30 min and a microwave treatment time of 180 s.

4. Conclusions

The bench scale experiment and the demonstration project system were both stable, and main water effluent indexes met class IV of the Surface Water Quality Standard (GB3838-2002). The microwave-enhanced silane coupling agent modification method was used for luffa sponges, and after modification, the water absorption rate was reduced to as little as 22.43% of the original value. The priority order for the factors that affected sponge modification was KH550 concentration > microwave reaction time > NaOH concentration > soaking time. The optimal conditions were 2% (w/w) NaOH, 1% (w/w) KH550, a soaking time of 30 min and a microwave treatment time of 180 s.

Table 8
Main effects of the inter-subjectivity of microwave treatment

Item	III type of squares	d_f	Mean square	F	Significance
Correction model	0.008[1]	8	0.001	5.810	0.008
Intercept	0.830	1	0.830	4.968	0.000
(w/w) NaOH %	0.001	2	0.000	1.621	0.251
(w/w) KH550 %	0.004	2	0.002	10.67	0.004
Soaking time	0.000	2	0.000	0.681	0.531
Microwave time	0.003	2	0.002	10.27	0.005
Error	0.002	9	0.000		
Sum	0.839	18			
Sum of correction	0.009	17			

[1]$R^2 = 0.838$ (Adjustment $R^2 = 0.694$).

Acknowledgements

This work was supported by Major Science and Technology Program for Water Pollution Control and Treatment of China 12th Five-Year Plan (No. 2012ZX07101007-005). We thank Profs. Yongyuan Zhang, Baoyuan Liu, Drs. Shenghua Hu, Biyun Liu, Junmei Wu, and Ms. Faming Huang, Dandan Kou, Peng Xu, Liping Zhang for their assistance with the experimental design and in preparing the paper, and we thank other laboratory colleagues for their assistance.

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