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Eutrophic lake water treatment using a diatomite porous ceramic membrane

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ABSTRACT

A porous ceramic membrane was prepared to remove algae in eutrophic lake water. Effects of preparation parameters, including starch content, granulation mesh size, and molding pressure on water quality index removal were also investigated in detail. The results showed that starch content, granulation mesh size, molding pressure influence water flux, removal of Chl-a, and turbidity. The optimized preparation conditions of the ceramic membrane were starch content of 15%, granulation mesh size of 40 mesh and molding pressure of 30 MPa. Under the treatment conditions of trans-membrane pressure 0.09 MPa, filter time 30 min by the prepared membrane, the removal percentages of Chl-a, turbidity, COD_{Mn}, TN, and TP were up to 99.62, 99.04, 33.89, 19.61, and 61.37%, respectively. The porous ceramic membrane can be effectively used to treat eutrophic lake water with high flux, outstanding efficiency, and excellent stability.

Keywords: Porous ceramic membrane; Eutrophic lake water; Algae removal

1. Introduction

In recent years, with the booming social and economic development, algae bloom caused by eutrophication has become a serious threat to drinking water safety. Color, odor, algal toxins, and other harmful substances are produced during the metabolic process of algae [1]. Several processes, including enhanced coagulation, ozone oxidation, flotation, filtration, and other counter-current flotation are often used to remove algae in production [2,3]. But the conventional processes, particularly the chemical methods, will facilitate the release of organic matter from algal cells into water, thus reducing water security, and increasing the difficulty of subsequent processing [4]. Therefore, due to the difficulty in removing algal cells, secondary pollution problems brought by the conventional process, it is urgent to develop efficient algaal removal technology and equipment.

Inorganic membranes were first produced in the late 1970s while industrial inorganic microfiltration and ultrafiltration membranes appeared till the 1980s. Inorganic membranes have tremendous advantages in many aspects such as chemical stability, mechanical resistance, anti-microbial ability, narrow pore size distribution, and high separation efficiency compared to polymer membranes [5,6]. The traditional water treatment processes are usually used to remove turbidity, color, and sterilizatioin from raw water in most areas

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of China. However, the conventional water treatment processes are limited, especially for micro-polluted water treatment. To improve the safety of drinking water supply, the development of the ceramic membrane technology offers the possibility to solve this problem. Bottino [7] and other researchers found that ceramic membranes can effectively remove algal cells from water. The water flux of the ceramic membrane was 0.8 $m^3/(m^2 h)$ under the operating conditions of 0.45 MPa. However, its flux is too small to limit the practical application. In recent years, many researchers have carried out applications of ceramic membranes in water treatment. Li [8] found that hybrid coagulation combined with the ceramic membrane process can remove DOC and UV_{254} efficiently. Li [9] used coagulation–microfiltration combined with four different ceramic membranes to treat lake water, and obtained high removal of turbidity, UV_{254}, and TOC. However, less research is focused on the application of ceramic membranes to algal cells' and TP removal.

Ceramic membranes can be made from alumina, mullite, cordierite, silica, spinel, zirconia, and other refractory oxides [10–12]. This research examines the effects of different starch contents, mesh granulation, and molding pressure on the flux and turbidity of the ceramic membrane, and then optimizes the preparation conditions of the ceramic membrane. What's more, the prepared ceramic membrane was used to treat eutrophic lake water, and the removal of Chl-a, COD_{Mn}, turbidity, TN and TP was also investigated.

2. Materials and methods

2.1. Raw water quality

Raw water was taken from Taihu Lake, Jiangsu in May, 2011. The raw water quality index is as follows: temperature was 22.7–33.5℃, pH was 6.80–8.16, Chl-a content was 59.17–77.23 ug/L, turbidity was 23–41 NTU, COD_{Mn} was 27.23–34.43 mg/L,TN was 1.903–2.135 mg/L and TP was 0.131–0.202 mg/L. The climate in May was hot and rainless, which can easily lead to eutrophication in lakes. What's more the proliferation of algae caused waters in the Taihu Lake to appear dark green and smelly.

2.2. The experiment system

The experimental device is shown in Fig. 1. The membrane module is an organic glass cylindrical container with a flat membrane inside it. The height of the device is 25 cm, with the diameter of 15 cm and an effective filtration area of 6.16 cm^2. The trans-membrane pressure (TMP) was provided by N_2 bottle. Water samples were passed through the ceramic membrane to the water tank under TMP.

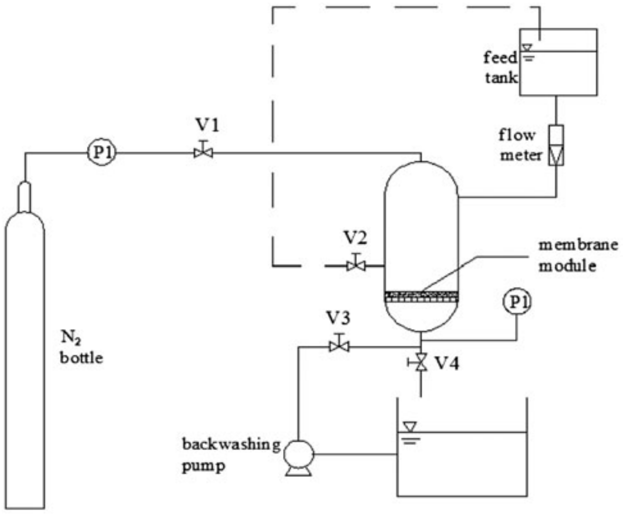

Fig. 1. Schematic diagram of the experimental system.

2.3. Analytical items and methods

Water quality indexes, including TP, TN, and chemical oxygen demand (COD_{Mn}), were determined according to the Standard Test Method [13]. Acidic potassium permanganate titration method was used to measure COD_{Mn}. Ammonium molybdate spectrophotometric method was used to measure TP, Alkaline potassium persulfate digestion-UV spectrophotometric method was used to measure TN. Spectrophotometry method was used to measure Chl-a. Turbidimeter was used to measure turbidity. The membrane permeate flux was calculated by Eq. (1):

$$J = \frac{V}{T \times A} \tag{1}$$

where J is the membrane permeate flux, V is the sampling volume, A is the the membrane area, and T is the sampling time.

2.4. Membrane preparation

In this research, diatomite was used as the main material for the production of ceramic membranes. The compositions of the diatomite and natural zeolite are shown in Table 1. Starch (analysis pure) was utilized as a pore-former agent. Natural zeolite was added as sintering aids.

Raw powder consisted of a mixture of diatomite and natural zeolite (1 wt.%), and different contents of

Table 1
The chemical composition of diatomite and natural zeolite

Component	Contents (%)	
	Diatomite	Natural zeolite
SiO_2	73.83	74.78
Al_2O_3	13.82	10.15
Fe_2O_3	8.15	6.41
K_2O	2.58	3.47
Ti_2O	2.05	—
CaO	0.33	2.59
Na_2O	—	0.68

starch were added as pore-former with 10–30 wt.%.The mixed raw powder were wet grinded by Planet-Ball-Grinding machine (NJU, ND7–4L) for 8 h. The mixed raw powders were granulated to 20–100 mesh at different sizes, and then the granular raw material was shaped in the mold under the pressures of 20, 30, 40, 50, and 60 MPa. The ceramic body was taken into the drying oven and dried at 80℃ for 24 h so that the moisture could be removed. Finally, the green densities were placed in a muffle furnace for sintering and heated to 400℃ in air for 3 h using a heating rate of 3℃/min to burn out the starch, and then heated to 1,100℃ in the air for 3 h using a heating rate of 6℃/min which was set as the line of best sintering. The ceramic body in the muffle furnace was cooled down to room temperature, and finally we could get a porous ceramic microfiltration membrane with a flat shape.

2.5. *Characterization of the ceramic membrane*

The structural characterization of the porous ceramic membranes was realized using Archimedes drainage method to determinate the porosity of the membranes, and water flux was measured by a ceramic membrane module, which is shown in Fig. 1. Morphology of the porous ceramic membrane was observed by enhanced scanning electronic microscopy (JEOL, JSM-6360LA). The ceramic substrate materials' crystalline phase structures were detected using X-ray diffraction device (Rigaku, D/max 2500 PC) with Cu Kα target.

2.6. *The experimental process*

The prepared ceramic membrane was put into the system of the ceramic membrane module. This system used filtrated deionized water under 0.09 MPa TMP. The water flux of the ceramic membranes that were prepared under different conditions was measured in the membrane module system. The TMP was constantly kept under 0.09 MPa, and ceramic membranes were chosen in different preparation conditions to treat eutrophic lake water. The Chl-a content and turbidity of the effluent water were measured, which were used to select the optimum preparation conditions of the ceramic membrane. The optimum ceramic membrane was used to treat the eutrophic lake water sample and was analyzed at regular intervals.

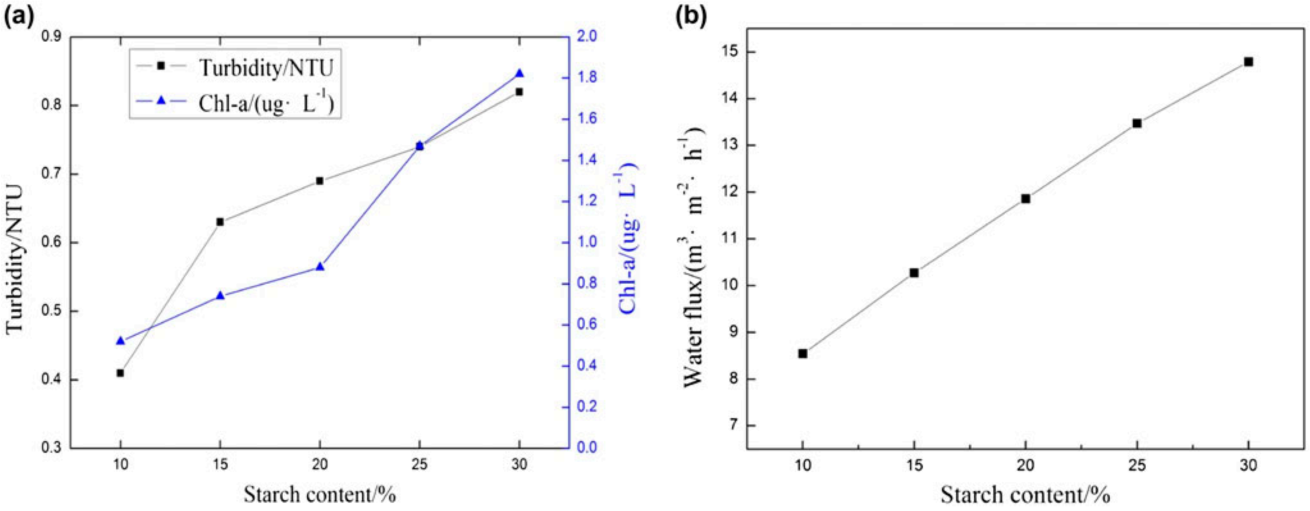

Fig. 2. Effects of starch content on water flux and the performance of the porous ceramic membrane for the eutrophic lake water treatment (TMP 0.09 MPa, temperature 28℃).

3. Results and discussion

3.1. Effect of starch content

The effects of 10, 15, 20, 25, and 30 wt.% starch content on Chl-a content, turbidity, and water flux were investigated and compared. The 40 mesh granulation mesh size, 30 MPa molding pressure, and TMP 0.09 MPa were kept constantly, and then the ceramic membranes with different starch contents were replaced. The experimental results are shown in Fig. 2.

As shown in Fig. 2(a), as the dosage of pore-former agent (starch) increased, Chl-a content and turbidity were gradually increased. When the amount of the pore-former agent increased from 10 to 35%, the turbidity increased from 0.41 to 0.82 NTU, while Chl-a content increased from 0.52 to 1.82 ug/L. There is excessive starch outside the diatomite particles, which play a significant role in making pores and makes the combination between the particles relatively loose. It makes the holes between the particles to become larger and the porosity also will be larger.

As shown in Fig. 2(b), when the dosage of the pore-former agent (starch) increases, the porous ceramic membrane water flux was close to the linear increase, the amount of the pore-former agent increased from 10 to 35%, the water flux increased from 8.54 to 14.89 $m^3/(m^2 h)$. The increase of the water flux can be explained by the increasing porosity, which leads to the decrease in filtration resistance, therefore the water flux increases. However, it will leave too many microholes at high temperature sintering when the dosage of the pore-former agent is excessive. These holes could lead to greatly reducing the mechanical strength of the green body, or even result in the failure of forming. Considering the requirements of algae removal in water and water flux, 15% was selected as the optimum starch content.

3.2. Effect of granulation mesh size

The effects of 20, 40, 60, 80, and 100 mesh on Chl-a content, turbidity, and water flux were investigated and compared. The operation parameters were 15 wt.% starch content, 30 MPa molding pressure, and a TMP of 0.09 MPa, and the ceramic membranes with different granulation mesh sizes were replaced. The experimental results are shown in Fig. 3.

As shown in Fig. 3(a), with a decrease of the granulation mesh size, the water turbidity and Chl-a content were gradually decreased. With the granulation mesh size increasing from 20 to 100 mesh, turbidity reduced from 1.69 to 0.41 NTU, Chl-a content reduced from 1.45 to 0.45 ug/L. The porous ceramic membrane water flux gradually reduced with the decrease of the granulation mesh size from 16.77 to 9.54 $m^3/(m^2 h)$.

In the dry forming, the flowability of raw powders with high specific surface was poor. Therefore powders cannot fully fill the mold and easily lead to voids while reducing the volume in mold. So it is critical that the granulation process should be added.

When the granulation particle size was 40 mesh, the water flux was 10.27 $m^3/(m^2 h)$. It represents a large flux, and can ensure the removal of most of the algal cells. Therefore, 40 mesh was selected as the best granulation mesh size.

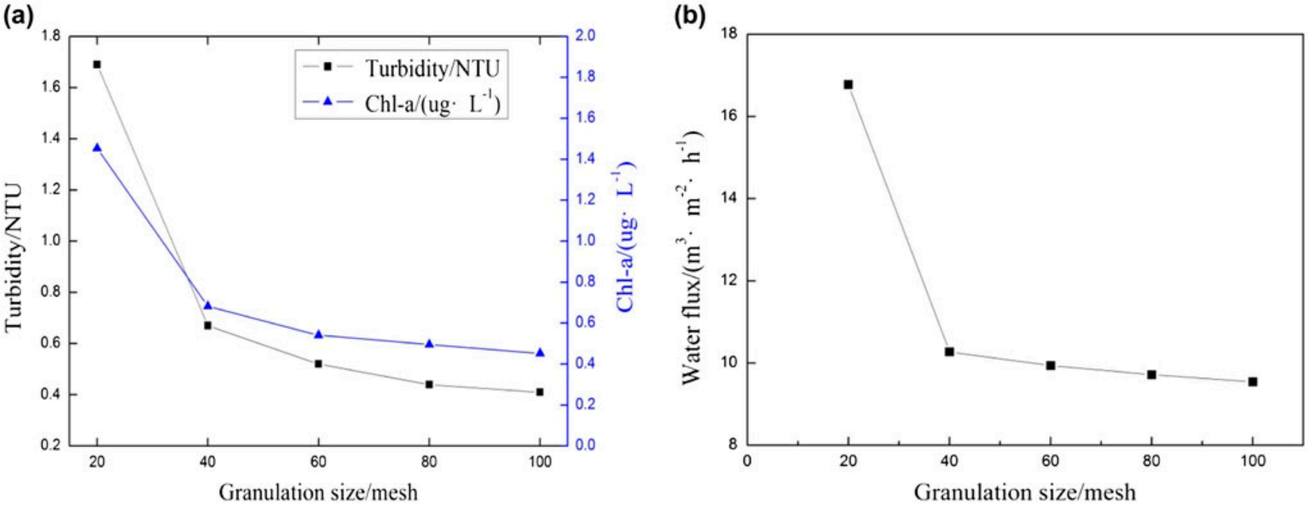

Fig. 3. Effects of granulation mesh size on water flux and the performance of the porous ceramic membrane for the eutrophic lake water treatment (TMP 0.09 MPa, temperature 28℃).

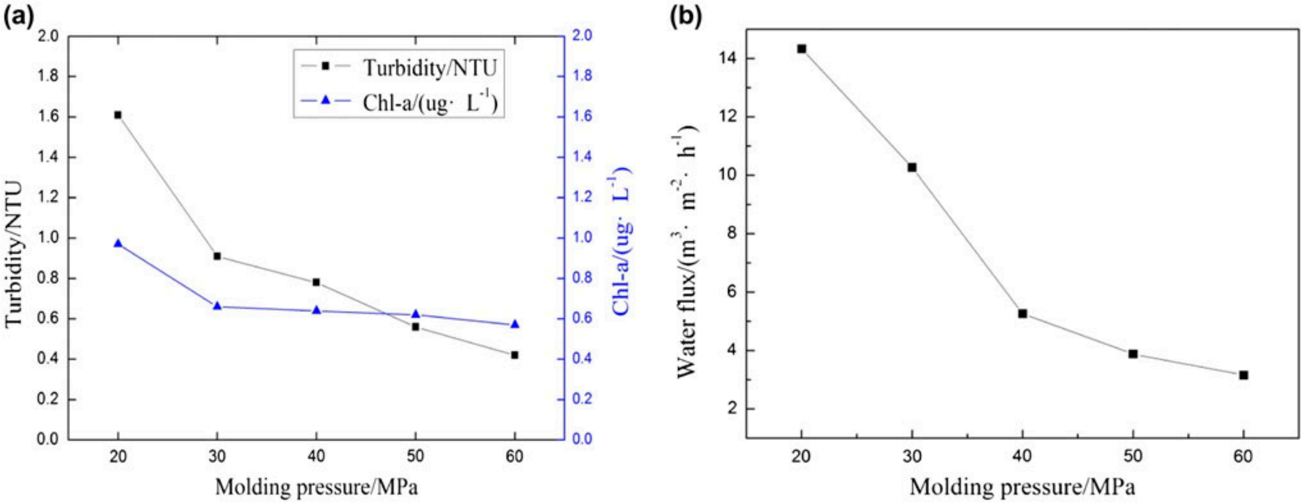

Fig. 4. Effects of molding pressure on water flux and the performance of the porous ceramic membrane for the eutrophic lake water treatment (TMP 0.09 MPa, temperature 28℃).

3.3. Effect of molding pressure

The effects of molding pressure on the turbidity and water flux were investigated and compared. The operation parameters were 15 wt.% starch content, 40 granulation mesh size and 0.09 MPa TMP. The experimental results are shown in Fig. 4.

As shown in Fig. 4(a), the molding pressure has a greater impact on the performance of porous ceramics, with an increase in molding pressure, water turbidity and the Chl-a content gradually reduced. The molding pressure increased from 20 to 60 MPa, the turbidity reduced from 1.61 to 0.42 NTU, and the Chl-a content reduced from 0.97 to 0.57 ug/L. As shown in Fig. 4(b), with the molding pressure increase, the porous ceramic membrane water flux declined quickly from 20 to 40 MPa and declined slower from 40 to 60 MPa. The molding pressure increased from 20 to 60 MPa, water flux reduced from 14.34 to 3.16 $m^3/(m^2 h)$.

The results of water flux variation were interpreted as follows. With the increase of the molding pressure, the internal pores reduce, and the porosity of the membrane after sintering would correspondingly decrease, which results in increasing the membrane resistance to water, thereby reducing the water flux. The reason for the removal of Chl-a and turbidity could be due to the increase of the molding pressure. It can lead to a greater degree of compaction of the ceramic green body, and result in the internal diameter becoming smaller and the overall porosity becoming lower. The downward trend of the water flux appeared to be leveling off after 40 MPa due to internal particles compacted to a certain degree, while leading to the reduction of quantity and size of pores inside the ceramic briquette.

If the molding pressure is too high, it can get a higher mechanical strength of the ceramic matrix, with usually with low porosity, low water flux which cannot reach the requirements. While the molding pressure of the porous ceramic membranes decreases, even though the water flux increases, the removal of the turbidity and Chl-a will decrease. Therefore, we need to get a balance between the mechanical resistance and capability. In this paper, 30 MPa was selected as the optimal molding pressure.

3.4. Apparent morphology and crystalline structure

Fig. 5 is the photograph of the two membranes, one which is after filtration and the other was before

Fig. 5. Diatomite porous ceramic membrane (a) after filtration and (b) before filtration.

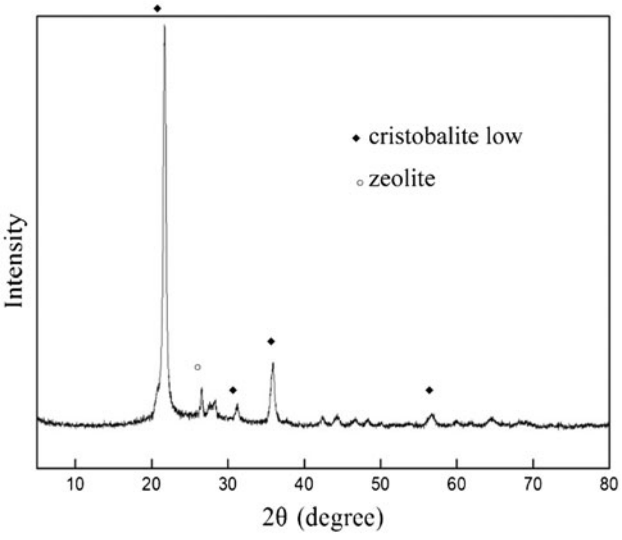

Fig. 6. XRD pattern of porous ceramic membrane.

the filtration. It can be observed that there is a green cake layer on the ceramic membrane after filtration. The green cake layer is mainly composed of algal cells in the eutrophic lake water. The dimensions of the porous ceramic membrane were 2.5 mm thick and 38 mm diameter.

Fig. 6 shows the XRD spectra of the porous ceramic membrane with 15 wt.% starch. It can be observed that the two phases exist simultaneously. The primary phase is the cristobalite low phase and other phase is the zeolite phase. It should be noted that diatomite used in this work and the starch added in were non-crystalline or amorphous. So the formation of the SiO_2 crystalline phase can be considered as formed in the process of sintering.

The surface and cross-section morphology of the membrane were observed by enhanced scanning electron microscopy (SEM). Fig. 7 shows the scanning electron microscope picture of cross-section of a porous ceramic membrane. It can be seen that it is relatively narrow with an average pore size of about 1 μm and it can also be seen that the ceramic membrane system is asymmetric. The asymmetric character of the membrane system is a very important parameter for the energetic efficiency of the process [14,15].

In this research, water samples were taken from the Taihu lake, Jiangsu Province, China, which has a high algal density. These algae are mainly composed of phytoplankton, cyanobacteria, green algae, diatoms with the size of 2–200 μm. Water samples were observed under the optical microscope. It can be observed that the dominant species were microcystis aeruginosa which was the major cause of algal blooms and nearly 3–7 μm-diameter spherical cells. As scanning electron micrographs show, the pore diameter of the ceramic membrane used in this paper was between 0.5 and 1 μm. Screening and the closure principle with certain TMPs can effectively remove algal cells in waters.

3.5. Continuous operation effect of the ceramic membrane device

In the pretest, the removal of turbidity and Chl-a and optimal water flux was used as the standard to measure optimized preparation conditions. 15 wt.% of starch content, 40 mesh of granulation mesh size, 30 MPa of molding pressure were selected as the optimized preparation conditions. After installing such a

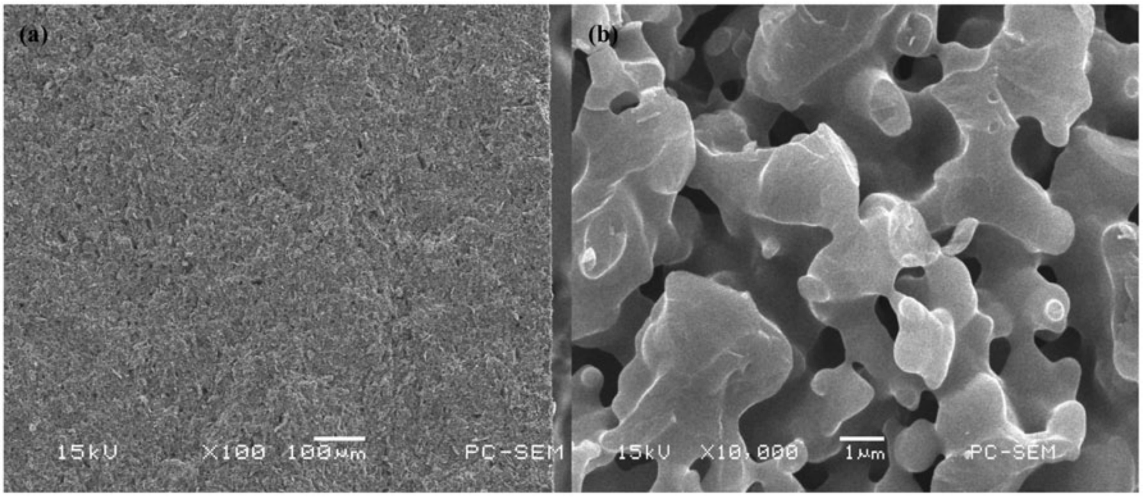

Fig. 7. SEM micrograph of the porous ceramic membrane (a): surface 100× and (b): cross-section view 10,000×.

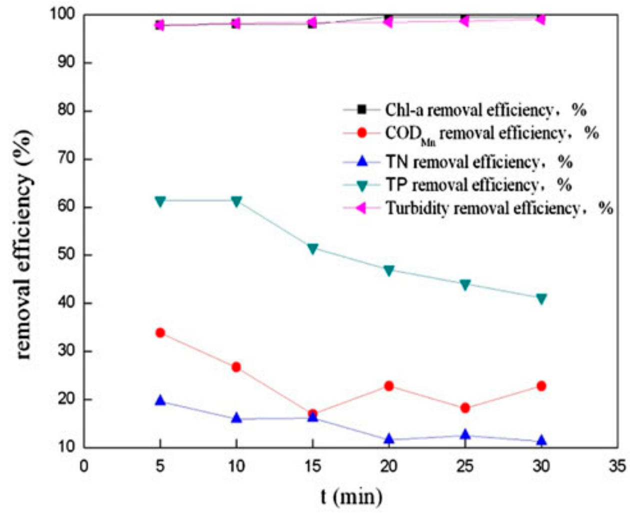

Fig. 8. Continuous operation effect of the ceramic membrane device.

kind of a ceramic membrane in the membrane module, it was run 30 min continuously and the water samples were analyzed every 5 min. The ceramic membrane devices for Chl-a, COD_{Mn}, TN, TP, and turbidity removal in eutrophic lake water were examined. The results are shown in Fig. 8.

As shown in Fig. 8, removal of Chl-a and turbidity were stable during 30 min on the process. The maximum removal rate reached 99.62 and 99.04% respectively, the removal rate was stabilized after 5 min. The removal efficiencies of COD_{Mn}, TN, and TP slightly decreased, the maximum removal rates were 33.89, 19.61, and 61.37%, respectively, but the removal rate leveled off after 20 min.

4. Conclusions

According to the turbidity and water flux in the study, the best ceramic membrane preparation conditions for the starch content of 10 wt.%, granulation mesh size of 40 mesh, and molding pressure of 30 MPa were selected. When the TMP was 0.09 MPa, the flux of treating the eutrophic lake water reached $10.27\,m^3/(m^2\,h)$, the Chl-a content reached 0.45 ug/L, and turbidity reached 0.41 NTU.

Diatomite was used as the main raw material for the preparation of porous ceramics. As the dosage of the pore-forming agent increases, the granulation mesh size decreases and the molding pressure reduces. All can increase the water flux of the ceramic membrane. The dosage of both the pore-forming agent and molding pressure can affect water flux. When the pore-forming dosage increased, this resulted in the increase in granulation mesh size and reduction of molding pressure which can have an impact on the filtration efficiency of lake water.

The porous ceramic membrane can be effectively used to treat eutrophic lake water with high flux, outstanding efficiency, and excellent stability.

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