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Photocatalytic membrane reactor (PMR) for virus removal in water: Performance and mechanisms

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HIGHLIGHTS

- Photocatalytic membrane reactor (PMR) is a promising technology for virus removal.
- Optimum operating condition was intermittent suction mode with 40 L/(m^2 h) or above.
- F2 was mainly inactivated by photocatalysis process, membrane served as a barrier.
- Among the reactive oxygen species (ROS), ·OH was important for f2 inactivation.
- Electron (e^-) showed a stronger inactivation effect to phage f2 than vacancy (h^+).

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ABSTRACT

The microbiological safety of drinking water is an important public health matter. Even if the content of viruses in drinking water is very low, it can pose a threat to human health. The photocatalytic membrane reactor (PMR) is a hybrid reactor in which photocatalysis is coupled with a membrane process, and is a promising technology to inactivate viruses and other microorganisms. In this study, the virus removal efficiency and mechanism in an integrated PMR system was evaluated. Bacteriophage f2 (mean size of 25 ± 1 nm), which is similar in size to the human enteric virus, was used as the model virus. The influences of filtration flux and permeation mode were tested with a continuous flow. The optimum operating conditions of PMR were determined to be intermittent suction mode with 40 L/(m^2 h) or greater of the filtration flux. PMR removed more than 5 log of phage f2 on average after 24 h of continuous operation (f2 in feed tank was 5.22 log). The f2 was primarily inactivated during the photocatalysis process, and the membrane served mainly as a barrier. The mechanism of f2 inactivation during photocatalysis process was investigated. Among the three kinds of reactive oxygen species (ROS), the hydroxyl radicals (·OH) was important for the inactivation of f2, which was collected through the reaction of electron vacancy – "hole" (h^+) and H_2O. Compared with h^+, electron (e^-) showed a stronger inactivation effect of f2.

1. Introduction

In recent years, several kinds of viruses have been detected from the drinking water sources in some countries. Even the presence of a few viral particles in a large volume of drinking water poses a threat to public health based on the statistics data of the World Health Organization. The risk is higher without effective treatment, since viruses are very difficult to be completely removed, especially in considering their small size and high resistance to traditional disinfection technologies [1]. The standards for virus removal in America has been improved to 4 log (99.99%), which poses a challenge to the drinking water treatment processes, especially disinfection. Although traditional chlorine disinfection is highly effective for virus inactivation with large doses, harmful disinfection by-products (DBPs) are generated at the same time [2]. According to the *Ultraviolet Disinfection Guidelines for Drinking Water and Water Reuse (3rd edition)*, UV fluence requirements for 4 log removal of viruses has been increased from 40 mJ/cm^2 to 186 mJ/cm^2, which significantly increases the energy demand and leads to a higher treatment cost. Moreover, the photoreactivation could be another hidden trouble for UV disinfection [3,4]. The employment of photocatalysis could potentially enable as effective virus inactivation in drinking water as chlorine, while limiting the formation of DBPs and requiring less energy compared to UV disinfection [5].

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Photocatalysis, one of the Advanced Oxidation Processes (AOPs), had demonstrated its efficiency in inactivating both bacteria, such as Salmonella, *Pseudomonas aeruginosa*, *Escherichia coli*, and some model viruses, including MS2, ΦX174 [6–8]. However, the low efficiency of photocatalyst and instability of effluent quality have limited its application [9,10]. The photocatalytic membrane reactor has been found to be a very promising method for solving problems concerning separation of the photocatalyst as well as products and by-products of photodecomposition from the reaction mixture. MF and UF have been most widely used in the hybrid systems coupled with photocatalysis for removing organic pollutants, including pharmaceuticals, humic, nitrophenol and dyes [11,12]. However, the virus removal effect in the PMR has been barely investigated.

In order to gain high effluent quality, researchers had investigated the influence of different operating variables on PMRs including water feeding pattern, permeation mode, and hydraulic retention time [13,14]. Continuous flow, though less efficient than batch flow, is more promising due to its high throughput potential. Intermittent methods, as well as aeration techniques, are used with the PMR system in order to minimize membrane fouling [15]. The application of intermittent permeation could be beneficial if the intermittence frequency was low enough as reported [16,17].

In this paper, the removal of virus in integrated PMR was investigated with continuous flow under both intermittent and continuous permeation. The mechanism of virus inactivation is also discussed.

2. Materials and methods

2.1. Model virus

Bacteriophage f2 was used as a model representing human enteric virus, since it has similar biological properties as poliovirus, coxsackie virus, IKE virus, Norwalk and hepatitis A viruses. It has strong survival ability, but little negative effects on human health.

Bacteriophage f2 and its host bacteria (*E. coli* 285) were purchased from the Institute of Hygiene and Environmental Medicine, Academy of Military Medical Sciences (Beijing, China). The culture medium for *E. coli* 285 was as follows: peptone 10 g/L, beef extract 3 g/L, sodium chloride 5 g/L, and pH value 7.3. The agar in the top layer and the bottom layer was 0.8% and 1.2–1.5%, respectively. The medium was autoclaved at 121 °C for 20 min before use.

The preparation for phage concentrate was as follows: a loop of bacteriophage f2 was seeded in a flask containing a culture medium of *E. coli* 285 which had been incubated at 37 °C for 12 h to ensure growth of the bacterium. The flask was then continuously shaken at 37 °C for another few hours to complete cell lysis. Thereafter, the flask was supplied with some culture medium that had incubated for 6 h to obtain young *E. coli* 285 cells so as to enhance the titer of the phage, and was then shaken until another complete lysis was completed. The lysate was collected and centrifuged at 4000 rpm for 10 min, then filtered with 0.22 μm membrane. The filtrate was bacteriophage f2 concentrate.

2.2. Experiments

2.2.1. Optimization of operating conditions for photocatalysis treatment

The effects of TiO_2, ranging in concentration from 0 to 100 mg/L, on the virus removal were assessed during photocatalysis treatments to determine the optimum photocatalysis dosage. In the reactor shown in Fig. 1 (without the membrane module), viruses were diluted to 10^7 pfu/mL using tap water to simulate surface water. The TiO_2 suspension was dispersed by ultrasonication before adding to the reactor. Samples were taken after 0.5, 1, 2, 3 and 4 h of UV irradiation from the reactor.

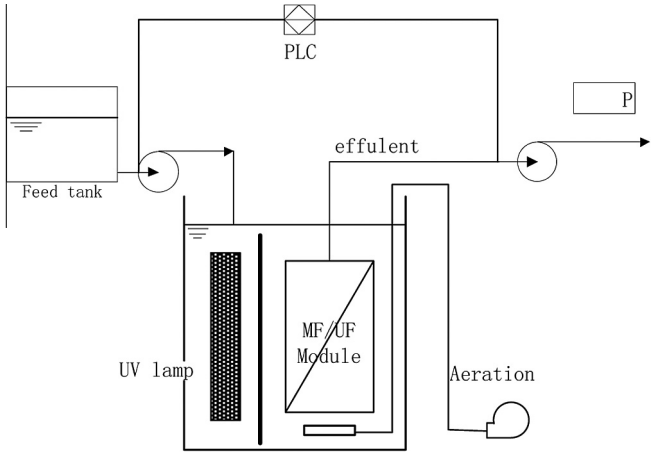

Fig. 1. Diagram of PMR system.

2.2.2. Model virus removal in PMR

As shown in Fig. 1, the experiments were conducted in the reactor with the available volume of 12.75 L (0.17 × 0.25 × 0.3 m), which was fitted with a 4 W UV-C (254 nm) lamp. The average UV intensity was 0.16 mW/cm^2 at the top surface of the water. The reactor was separated into two connected parts by a baffle which is opaque to UV radiation. A flat-sheet PVDF membrane (provided by Tongji University of China, pore size of 0.15 μm, membrane area of 0.03 m^2) was assembled in the larger part of the reactor. The surface morphology and cross section was characterized with Scanning Electron Microscope (SEM). And the SEM images were shown in Supporting Materials (Fig. S2). Aeration rate provided to the reactor tank was 10 L/min, with the aerator under the membrane module.

The nano-TiO_2 P25 was used as the photocatalyst, which was provided by school of Material Science and Engineering, University of Science and Technology Beijing. The specific surface area of P25-TiO_2 was 50 ± 15 m^2/g, and the average particle size was 21 nm. A quantity of P25-TiO_2 (25 mg/L) was added into the reactor and stirred to form well dispersed suspension.

The system was operated under constant flux, and the feed temperature maintained at 20–25 °C. To investigate the influence of flux, three different fluxes (20 LMH, 40 LMH, 60 LMH) was set in the study. Virus concentration in the feed tank was set to be approximately 10^3 pfu/mL and 10^5 pfu/mL, respectively, to simulate seriously biologically polluted surface water. The attenuation of phage f2 was less than 0.3 log in the feed tank after 24 h. Virus inactivation was tested in PMR under different permeation operations: the continuous mode (referred as "Con"), and the intermittent mode (referred as "Int"), which was controlled by the PLC system with the interval of 10 min in 70 min cycle.

Water samples in the feed tank, reactor and membrane effluent were taken every 2–3 h during 24 h running. Samples were stored at 4 °C in dark and analyzed within 24 h. The samples were gradient diluted with 0.03 mol/L PBS buffer solution and double layer agar method was used for virus determination. The injected Petri dishes were incubated at 37 °C for 4–6 h, and then the plaque forming units (PFU) of each dish were calculated. The data in this experiment was analyzed by One Way ANOVA.