

Article

# Photocatalytic Membrane Reactor (PMR) for Virus Removal in Drinking Water: Effect of Humic Acid

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**Abstract:** In the actual water environment, the health risk of waterborne viruses is evaluated to be  $10^1$ – $10^4$  times higher at a similar level of exposure compared with bacteria and has aroused strong concern in many countries in the world. Photocatalytic membrane reactor (PMR), a new process for virus inactivation in water, has gradually become one of the main tools to inactivate pathogenic organisms in water. However, there is relatively little attention to the effect of natural organic matters (NOMs) on the PMR system, which actually exists in the water environment. In this paper, the  $\text{TiO}_2$ -P25, a common type in sales and marketing, was selected as the photocatalyst, and humic acid was regarded as the representative substance of NOMs for investigating thoroughly the influence of humic acid on virus removal by the PMR system. It was found that competitive adsorption between the virus and humic acid occurred, which markedly reduced the amount of virus adsorbed on the surface of the photocatalyst. Moreover, with humic acid, the direct contact behavior between the virus and the photocatalyst was blocked to some extent, and the disinfection of phage f2 by the active free radicals produced by photocatalysis was furthermore badly affected. Meanwhile, the special structure of humic acid, which made humic acid be able to absorb light of 270–500 nm, led to the reduction of photocatalytic efficiency. Further experiments showed that when there was a certain concentration of humic acid in water, intermittent operation mode or higher membrane flux ( $>40 \text{ L}/(\text{m}^2 \cdot \text{h})$ ) was selected to partly alleviate the adverse effects of humic acid.

**Keywords:** PMR; NOMs; humic acid; virus; photocatalysis; adsorption; active radicals

## 1. Introduction

Pathogens causing waterborne diseases usually include bacteria, viruses, protozoans, and parasitic worms. The microbiological safety of drinking water is closely related to the citizens [1]. In the actual water environment, there are noxious bacteria and viruses, even though the number of virus or bacteria in drinking water is generally low, they can also pose tremendous risks to human health [2,3]. Especially in the developing countries, the supplies of drinking water are extremely scarce, resulting in a higher risk of waterborne-disease transmission [4]. The health risk of waterborne viruses, in particular, is evaluated to be  $10^1$ – $10^4$  times higher at a similar level of exposure compared with bacteria and has aroused strong concern in many countries around the world [5].

The current disinfection processes, such as chlorination, ozone, and ultraviolet disinfection, can be used to remove virus to a certain extent in drinking water, but harmful disinfection by-products of chlorination, including three trihalomethanes, haloacetic acid, bromate, and strong carcinogens

were produced [6]. Although ultraviolet disinfection has good disinfection effect, its demand for ultraviolet intensity resulted in a high cost and energy consumption [7,8]. Therefore, a feasible, environmental-friendly technology without secondary pollution and high cost is eagerly needed at present.

In recent decades, as an emerging oxidation technology, TiO<sub>2</sub> photocatalytic oxidation (TPO), one of the main advanced oxidation processes (AOPs), has proved to be efficient in degrading a wide range of pollutants [9,10], and inactivating both bacteria, such as *Pseudomonas aeruginosa*, *Salmonella*, *Escherichia coli*, and some model viruses, including MS2, ΦX174 [2,3,11–14]. While in many types of photocatalytic reactors, the photocatalytic membrane reactor (PMR), a hybrid reactor in which photocatalysis is coupled with a membrane process, is regarded as a most promising technology to disinfect viruses and other microorganisms due to its high removal efficiency and the mild temperature and pressure conditions [15,16]. Furthermore, the recycling from treated water and aggregation of photocatalysts are effectively achieved by PMR [17]. Most studies of virus removal by PMR taking the influence of pH value, initial concentration of virus, feeding pattern, and the presence of common anions such as phosphate and bicarbonate into account, while relatively few considering the effect mechanism of natural organic matter on virus removal.

When using PMR system as the advanced treatment in drinking water or disinfection technology, whether the change of the concentration of natural organic matter in water will have an influence on the treatment effect is still unknown, owing to photocatalytic degradation of natural organic matter. In the photocatalytic membrane reactor system, the competition relationships are established between the natural organic matter and viruses, which indicated that humic acid has an unknown effect on the photocatalytic disinfection of virus. For example, the humic acid is one of the common organic compounds in water. Humic substances in natural waters accounted for more than 50% of total organic matters in water. In the presence of humic acid, some special influence may happen during photocatalytic reactions [18,19]. For instance, the widespread presence of ·OH scavengers in aqueous medium was regarded as the main short board of the application of AOPs. The major scavenger was reported as organic substances e.g. humic acid, fulvic acids, and so on. Meanwhile, the anionic functional groups, primarily carboxylic, and phenolic groups of humic substances introduce negative charges and have a strong affinity for positively charged mineral surfaces or metal cations (e.g. Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and so on) [20]. Therefore, the effect of humic acid on the PMR system should be explored thoroughly.

In this paper, a batch of experiments was designed to make a thorough study the effect of humic acid on the PMR system, and the influence mechanism was discussed. The phage f2 has been used as a surrogate for human enteric viruses.

The main objectives of this study were to evaluate the effects of humic acid on individual units of PMR system, including catalyst adsorption, ultraviolet (UV) effects, and photocatalysis process. At the same time, the effects of humic acid on the efficiency of photocatalytic disinfection were explored under the conditions of different operation modes and membrane flux for clarifying the effect of humic acid in the PMR system and providing the data support for the application of PMR system in the near future.

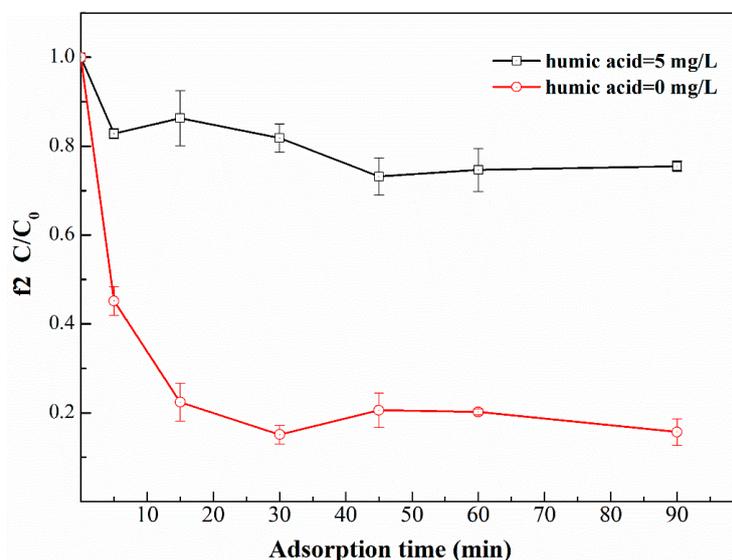
## 2. Results and Discussion

### 2.1. Influence of Humic Acid on Individual Units of PMR System

#### 2.1.1. Effect on Adsorption Unit

The adsorption process is usually related to the photocatalysts and happens firstly after the pollutants entering the PMR system. Then batch experiments were designed to explore the effects of humic acid on the adsorption of phage f2 by TiO<sub>2</sub>-P25 in the dark. The initial concentration of phage f2 and TiO<sub>2</sub>-P25 is set as 5–6 log and 100 mg/L, respectively. The pH value of simulated water was adjusted to 7.0–7.3 by 0.1 M hydrochloric acid or sodium hydroxide solution.

As shown in Figure 1, in the presence of humic acid, the maximum adsorption efficiency of TiO<sub>2</sub>-P25 on phage f2 decreased from 90% to 36.1%. The corresponding adsorption capacity dropped from  $1.56 \times 10^6$  plaque-forming units (PFU)/mg to  $3.95 \times 10^5$  PFU/mg, an order of magnitude lower.

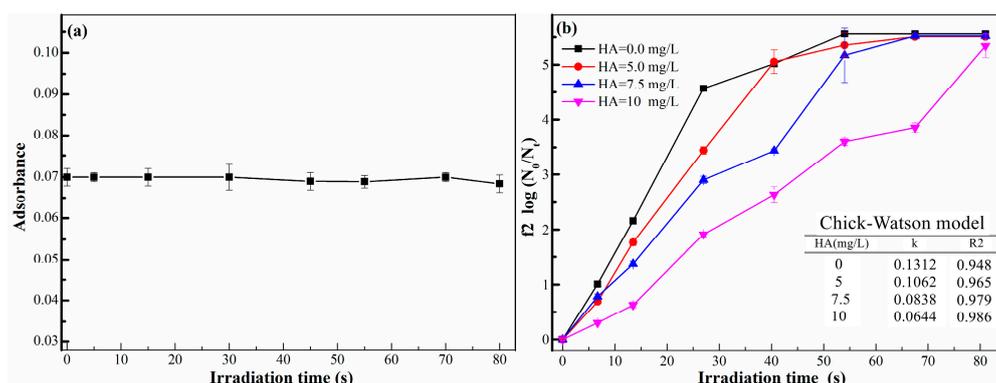


**Figure 1.** The effect of humic acid on the adsorption of phage f2 by TiO<sub>2</sub>-P25 in the dark.

In our previous work [21], the adsorption process of TiO<sub>2</sub>-P25 for phage f2 is in accordance with the quasi-second-order adsorption kinetic model, which follows the mechanism of chemisorption, and the diffusion in particles is an important rate control step in the adsorption process. In addition, related research reported that when humic acid was present in water, it interacted with TiO<sub>2</sub> by electrostatic attraction, hydrogen bond interaction, Ti-O bonds, and condensation reaction [22]. In this study, the humic acid is negatively charged and the TiO<sub>2</sub>-P25 surface (zero point charge = 6.3) is also negatively charged, resulting in an electrostatic repulsion [23]. However, competitive adsorption with humic acid and phage f2 on the surface of the TiO<sub>2</sub>-P25 still exists, which indicates that there are other types of interactions between humic acid and TiO<sub>2</sub>-P25 such as hydrogen bonds, Ti-O bonds, and condensation [24]. Hence, the surface adsorption sites of TiO<sub>2</sub>-P25 particles were occupied by humic acid, with the presence of humic acid.

### 2.1.2. Effect on UV Disinfection

The initial concentration of the phage f2 was diluted to 5.49 log, and the concentration of humic acid was set to 0, 5, 7.5, 10 mg/L respectively in water. It can be seen from Figure 2a that the concentration of humic acid in water remained basically unchanged, with an increase in irradiation time, indicating that UV has no degradation effect on humic acid under this reaction condition. However, from Figure 2b, we can clearly see that the phage f2 was completely inactivated within about 54 s; when the humic acid concentration was 5–10.0 mg/L, disinfection of phage f2 will need about 67 s, 67 s, and 85 s, respectively. This means that with the increase of humic acid concentration, UV disinfection efficiency of phage f2 gradually decreased.

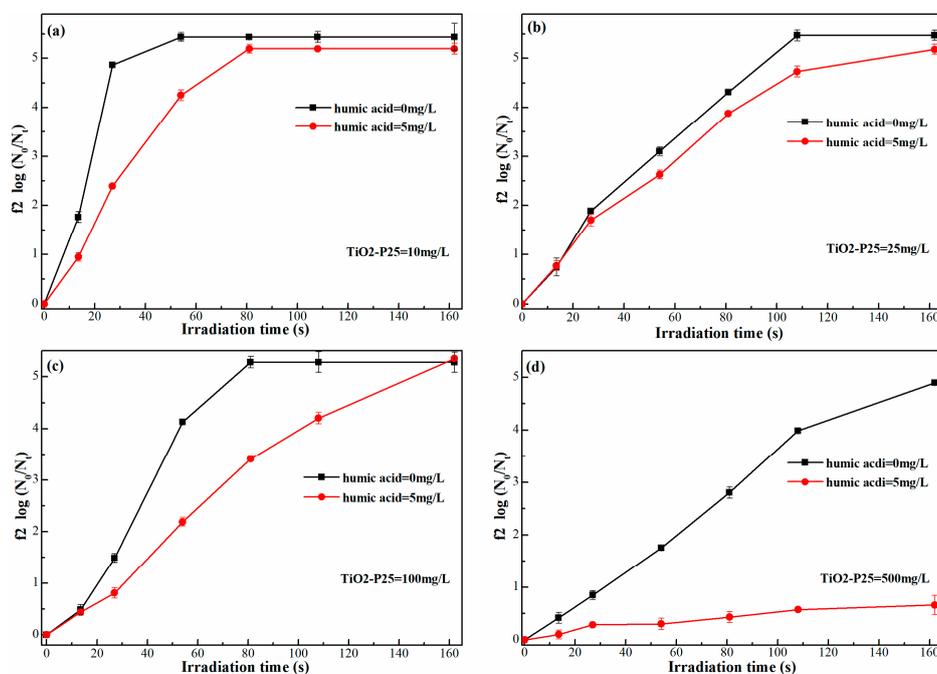


**Figure 2.** Degradation trend diagram of humic acid by ultraviolet (UV) (a) and disinfection efficiency of phage f2 with different concentration of humic acid under UV irradiation (b).

The Chick-Watson model (insert table in Figure 2b) was used to fitting the experimental data [25]. The results obviously showed that with an increase in the concentration of humic acid, the constant  $k$  value gradually decreased from 0.13 to 0.06, which indicated a gradual decrease in the corresponding reaction rate. It was reported that the structure of benzene ring in humic acid molecule can absorb ultraviolet light with the wavelength of 254 nm, so that the effective UV content was reduced in the reaction system [26]. It is worth pointing out that the existence of humic acid has no effect on the kinetics type of UV disinfection, but the rate of UV disinfection by UV light irradiation.

### 2.1.3. Effect on Photocatalysis

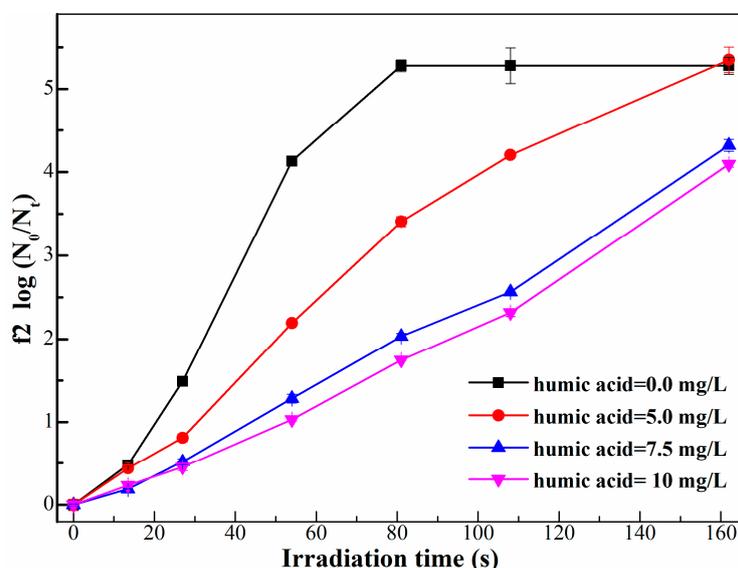
The effects of humic acid on the photocatalytic disinfection of phage f2 were investigated with different concentrations of  $TiO_2$ -P25. The initial concentration of phage f2 in the four groups of experiments was 5.18–5.46 log. The results were shown in Figure 3.



**Figure 3.** The effect of humic acid on photocatalytic disinfection efficiency of  $TiO_2$ -P25 with different concentrations (a: 10 mg/L; b: 25 mg/L; c: 100 mg/L; d: 500 mg/L).

From Figure 3, we could clearly see that the higher the concentration of TiO<sub>2</sub>-P25, the more obvious the negative effect of humic acid on photocatalytic disinfection efficiency. The reason was that the influence of humic acid mainly included the process of adsorption of catalyst on phage f2, and photocatalysis of catalyst on phage f2. On the one hand, with the increase of the concentration of TiO<sub>2</sub>-P25, the UV transmittance of the solution gradually decreased, and the humic acid absorbed UV light to a certain extent, and the effective UV dose in the system decreased significantly, which resulted in the decrease of photocatalytic efficiency and disinfection efficiency [18]. On the other hand, in the presence of humic acid, TiO<sub>2</sub>-P25 had little adsorption on the phage f2, which reduced the disinfection efficiency of phage f2.

In order to further investigate the influence mechanism of different concentrations of humic acid on photocatalysis, 100 mg/L of TiO<sub>2</sub>-P25 was set to achieve UV transmittance of zero under this condition, which effectively avoided the disinfection effect of UV on the phage f2. The result is shown in Figure 4.



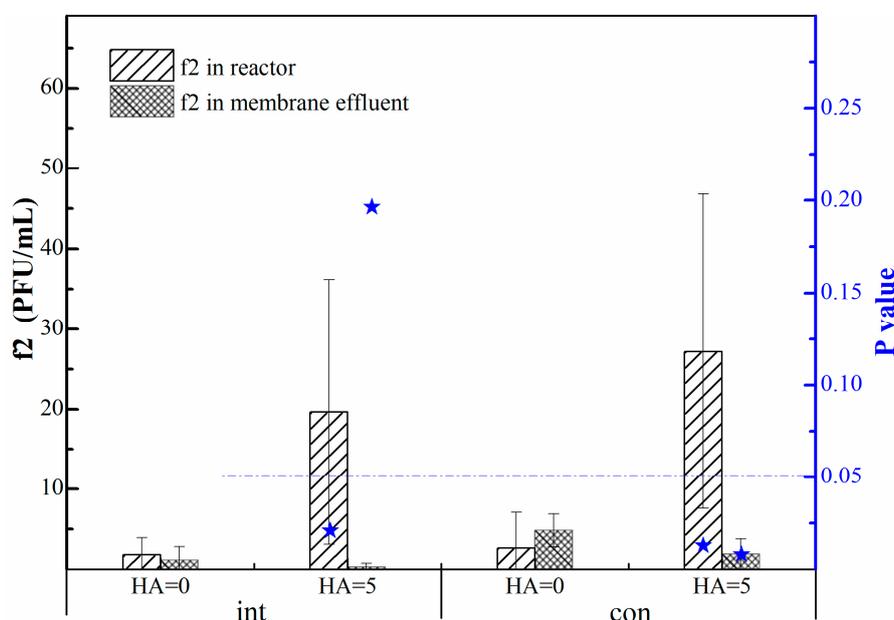
**Figure 4.** The effect of different concentrations of humic acid on photocatalytic disinfection of phage f2 by TiO<sub>2</sub>-P25.

When the concentration of humic acid changed from 0 to 7.5 mg/L, the photocatalytic disinfection efficiency of phage f2 by TiO<sub>2</sub>-P25 reached 5.4 log, 3.51 log, and 2.17 log, respectively after 80 s of UV light irradiation. However, with the higher concentration (7.5 to 10 mg/L) of humic acid, the obvious change had not taken place (4 log after 160 s). According to previous studies [16,27], the photocatalytic disinfection of phage f2 involved several active radicals, while hydroxyl radicals proved to be the most important role. With the participation of humic acid in photocatalytic process, the competitive relationship between the phage f2 and humic acid was established, which led to a significant decrease in the photocatalytic disinfection of phage f2 [27]. On the other hand, the photocatalytic disinfection reaction is based on the surface complexation reactions rather than the reactions taking place in aqueous medium [27]. As previously described and mentioned (Figure 1), the addition of humic acid greatly reduced the adsorption ability of the TiO<sub>2</sub>-P25 photocatalysts to the phage f2, and further wakened the corresponding efficiency of photocatalytic disinfection. So the photocatalytic disinfection efficiency of phage f2 was significantly reduced with the presence of humic acid [28]. Naturally, when the concentration of humic acid increased to 7.5 or 10 mg/L, the hydroxyl radicals produced in photocatalytic process was completely captured by humic acid (enough), and the photocatalytic disinfection of phage f2 attributed to other active particles (h<sup>+</sup>, e<sup>-</sup>, ·O<sub>2</sub><sup>-</sup>, and so on). Then, the disinfection rate of the phage f2 did not decrease with increasing humic acid concentration.

## 2.2. Influence of Humic Acid on PMR under Different Parameters

### 2.2.1. Operation Mode

Under two ways of continuous suction (con) and intermittent suction mode (int), the effects of humic acid on the photocatalytic disinfection of phage f2 were investigated, as shown in Figure 5.



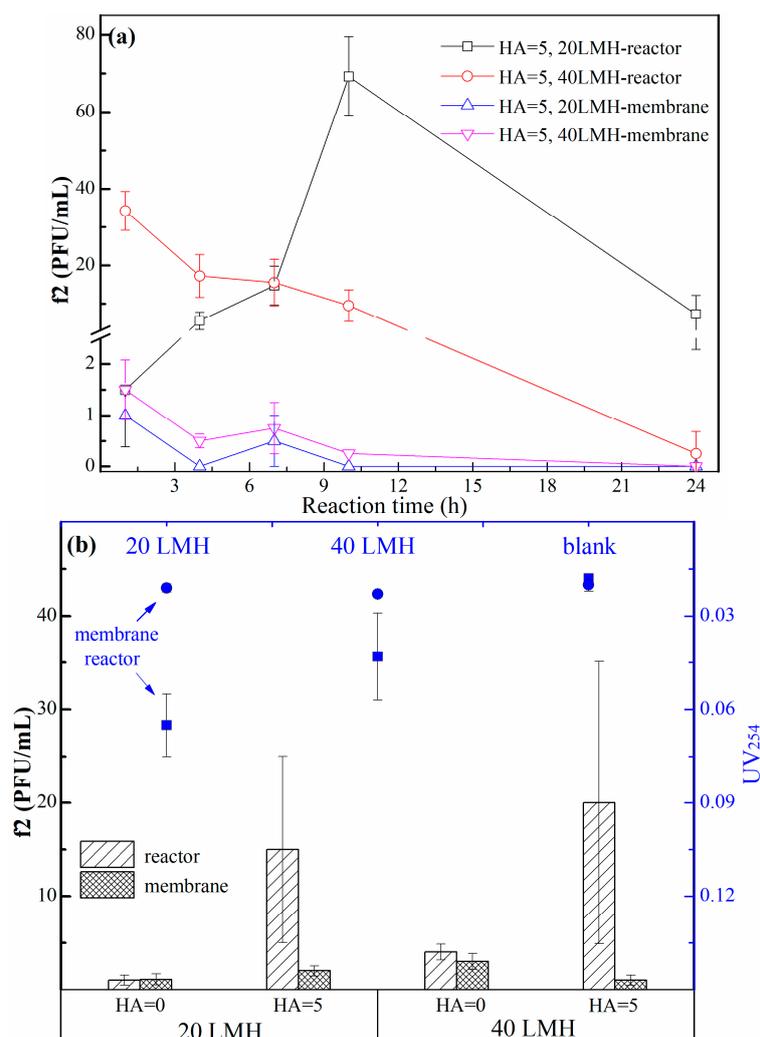
**Figure 5.** Influence of humic acid on disinfection of Photocatalytic Membrane Reactor (PMR) under different operation mode.

In the presence of humic acid, the average concentration of phage f2 in the membrane effluent almost remained unchanged, which was less than 5 PFU/mL. However, with the existence of humic acid in photocatalytic system, the concentration of phage f2 in the reactor increased significantly in both operation modes. And the concentration of phage f2 in the reactor in con mode was higher than that in the int mode.

Through statistical analysis of one-way Analysis of Variance (ANOVA) (Figure 5), the blue star chart showed that humic acid only has no significant effect on concentration of phage f2 in membrane effluent, but significant effect on concentration of phage f2 in reactor under int mode, which means that int mode could adapt to the existence of humic acid in water. However, humic acid has a significant effect on the concentration of f2 in both membrane effluent and reactor under con mode. It showed that humic acid had a significant effect on the removal process of the virus by the photocatalytic system under two operating modes.

### 2.2.2. Membrane Flux

Membrane flux is a critical parameter for photocatalytic membrane reactors. Furthermore, after the humic acid being added, the concentration of phage f2 in the reactor has been remarkably improved compared to the original water without humic acid as shown in Figure 6b. In addition, we also found that with the membrane effluent changing to 40 L/(m<sup>2</sup>·h) (LMH), the UV<sub>254</sub> value in membrane effluent slightly changed, while the UV<sub>254</sub> in the reactor changed significantly, which also confirmed the influence of humic acid on photocatalytic process, resulting in the weakness of phage f2 removal.



**Figure 6.** The changes of phage f2 in different reaction time (a) and effect of humic acid on photocatalytic disinfection and changes of UV<sub>254</sub> under different L/(m<sup>2</sup>·h) (LMH) condition in water (b).

In the presence of humic acid, for 40 LMH, the removal of phage f2 in the reactor was affected to some extent. From Figure 6a, we can see that with the increase of reaction time, the influence of humic acid was gradually counteracted and reached the same level after 24 h for 40 LMH in reactor. While 20 LMH in reactor, the change was not regular, relatively speaking. The possible reason was that with the increase of LMH value, the flow rate was remarkably accelerated, which led to the more uniform mixing of TiO<sub>2</sub>-P25 and the faster reaction speed. It was also confirmed from the results in Figure 6, in which the UV<sub>254</sub> value was obviously reduced when the membrane flux changed from 20 LMH to 40 LMH.

Hence, when a certain amount of humic acid exists in the water environment, the effect of humic acid on the PMR system can be partly alleviated by selecting the intermittent mode (int) and increasing the flux of the membrane (>40 L/(m<sup>2</sup>·h)).

### 3. Materials and Methods

#### 3.1. Model Virus and Chemicals

In this study, bacteriophage f2 was used as the model virus of whole enteric viruses of human due to its extremely similar biological characteristics with other causative virus (Coxsackie virus, hepatitis A virus, poliovirus, and so on). Furthermore, bacteriophage f2 does a little negative harm

to human health and could be used to investigate the mechanism of water treatment. Phage f2 and its host bacteria, *E. coli* 285, in this experiment, were purchased from the Institute of Hygiene and Environmental Medicine (IHEM, Berlin, Germany), Academy of Military Medical Sciences. The culture medium for *E. coli* 285 was as follows: the ratio (g/L) of peptone, beef extract, and sodium chloride was 10: 3: 5, and the pH value of solution was adjusted to 7.3. Then the double layer culture method was used for the counting of phage f2. The agar content in upper layer and the bottom layer was 0.8% and 1.2–1.5%, respectively. The most important thing is that the prepared medium, clean test tube, and plastic gun head must be sterilized by autoclave at 120 °C for 30 min before further use. In addition, preparation for phage f2 with different concentrations was as follows: a loop of phage 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 12 h to achieve the complete cell lysis. Then, the flask was supplied with some culture medium that had incubated for 6 h to obtain newborn *E. coli* 285 cells so as to enhance the number of the phages and was then shaken until another complete cell lysis was completed. The lysate solution was collected and centrifuged at 4000 rpm for 10 min or so, followed by filtering with a 0.22 µm membrane. The obtained filter liquor was used as a reserve solution for a certain period of time. Different concentrations of virus were achieved by dilution of tap water.

Humic acid was purchased from Fluka Company (Sigma-Aldrich, St. Louis, MO, USA) and chosen as a representative substance of natural organic matter, as it is one of the most important dissolved and suspended organic substances, which widely exists in the water environment [29]. A total of 1 g/L stock solution of humic acid was prepared by dissolving 0.5 g humic acid into 250 mL 0.01 M sodium hydroxide (NaOH) solution until the mixture is dissolved and then transferred to a brown bottle for further use. The stock solution was diluted to the desired concentrations.

TiO<sub>2</sub>-P25 was friendly provided by the School of Materials Science and Engineering of University of Science and Technology Beijing (USTB, Beijing, China). Furthermore, the specific surface area, average particle size, and pHpzc (the pH value at the point of zero charge) in NaCl solution of TiO<sub>2</sub>-P25 is 50 ± 15 m<sup>2</sup>/g, 21 nm, and 6.2, respectively. Before experiment, a quantity of TiO<sub>2</sub>-P25 photocatalysts were added into the reactor and stirred well.

All used chemical stock solutions in this study were prepared using ultrapure water from a millipore system (Master-S30 UVF). Hydrochloric acid (HCl, 36–38% purity) and sodium hydrate (NaOH, ≥99% purity) were both purchased from Beijing Chemical Works (BCW, Beijing, China).

### 3.2. Experiment Setup

The PMR system is illustrated in Figure 7. The phage f2 was diluted to 5–6 log PFU/mL using tap water as a substitute for surface water. The TiO<sub>2</sub>-P25 particles were evenly dispersed by ultra-sonication before being added to the feed tank of PMR system. The experiments were carried out in the reactor with the effective volume of 12.75 L (17 cm × 25 cm × 30 cm), which was equipped with a 4W UV-C (λ = 254 nm) lamp (JEBO, Guangdong ZhenHua Electric Appliance Co., Ltd., Zhongshan, China). The reactor consisted of two connected parts separated by a non-transparent baffle. A falt-sheet 0.15 µm polyvinylidene fluoride membrane (Tongji University of China, Shanghai, China, membrane area of 0.03 square meters) was assembled in the larger part of the reactor. In addition, the aeration unit was installed at the bottom of the membrane module with a flow rate of 10 L/min, as shown in Figure 7. The programmable logic controller (PLC) (XinLing Electrical Co., Ltd., Zhongshan, China) was assembled to detect the intermittent suction operation mode by controlling the operation and stopping time of the inlet/outlet pumps.

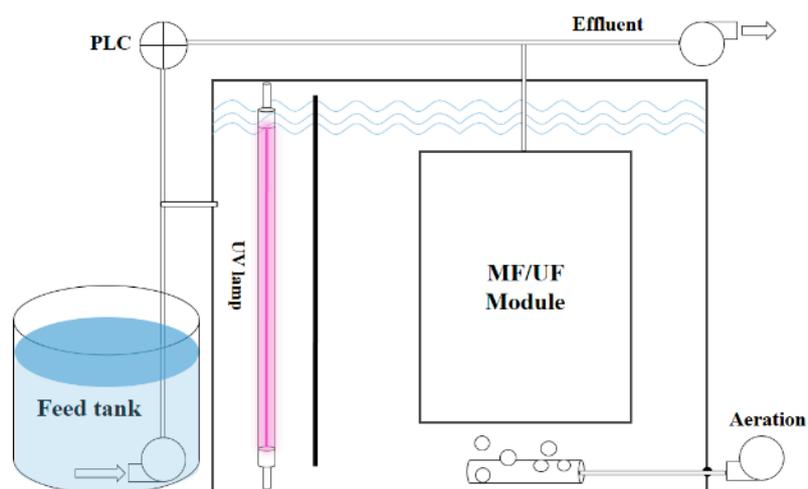


Figure 7. Experimental set-up diagram of photocatalytic membrane reactor.

In addition, the system was operated with two constant filtration fluxes (20, and 40 L/(m<sup>2</sup>·h)) (LMH), and the feed temperature maintained at 20–25 °C. The concentration of phage f2 and humic acid in the feed tank was adjusted to around 5–6 log PFU/mL and 5 mg/L to simulate biologically polluted surface water. The attenuation values of phage f2 was less than 0.3 log in the feed tank within 24 hr. Meanwhile, photocatalytic disinfection of phage f2 was tested in PMR under different operation modes: the continuous suction mode (represented by con), and the intermittent suction mode (represented by int), which was implemented by the PLC system with the interval of 10 min in 70 min cycles. Samples were taken after 0.5, 1, 2, 3, and 4 h of UV irradiation from the reactor, respectively.

### 3.3. Methods of Data Analysis and Virus Culture

The amount of phage f2 was determined by a double agar culture method, a relatively accurate and universal method of counting [30]. Moreover, in order to ensure the accuracy of the experimental data, we chose the number of 30–300 as the valid value. Water samples in the feed tank, reactor, and membrane effluent were taken every 2–3 h during the whole 24 h running process. The obtained samples were stored at 4 °C in dark and analyzed in time within 24 h. The experiment was carried out twice for obtaining the average value.

The photocatalytic disinfection efficiency of phage f2 was accurately calculated with the following Equation (1):

$$Re = \log_{10}N_0 - \log_{10}N_t = \log_{10}(N_0/N_t) \quad (1)$$

where Re represents the disinfection efficiency of virus (f2), t represents the reaction time (seconds), N<sub>0</sub> and N<sub>t</sub> is the concentration of virus at the initial time and t time, respectively.

UV<sub>254</sub> reflects the total number of the NOMs and aromatic compounds containing C=C double bonds and C=O double bonds in the water. In this experiment, the UV<sub>254</sub> of water at a given time was determined by UV-9600 spectrophotometer in Beifen-Ruili Analytical Instrument Company (BRAIC, Beijing, China). One of the most fundamental and simple models to analyze the principle of disinfection kinetics is the Chick-Watson model, which is usually used to compare the experimental results obtained under different experimental conditions [25,31],  $\log(N_0/N) = kct$ , which assumes that the rate of disinfection of the microorganisms by the disinfectants is primarily affected by the combination of the concentration of the disinfectants (c) and the contact time (t) (c × t, which is expressed as the ct value), as shown in Equations (2) and (3):

$$\log \frac{N_0}{N} = 0 \text{ if } ct \leq ct_{lag} = \frac{1}{k} \log \left( \frac{N}{N_0} \right) \quad (2)$$

$$\log \frac{N_0}{N} = kct + kct_{lag} \text{ if } ct \geq ct_{lag} = \frac{1}{k} \log \left( \frac{N}{N_0} \right) \quad (3)$$

where  $N_0$  is the initial amount of phage f2 (PFU/mL),  $N$  is the amount of phage f2 at time  $t$  (PFU/mL),  $c$  is the disinfectant concentration (mg/L),  $t$  is the reaction time (seconds),  $k$  is the disinfection-by-disinfectant rate constant (L/(mg·min)), and  $ct_{lag}$  is the intercept of the disinfection curve on the  $x$  axis.

#### 4. Conclusions

In this paper, the influences of humic acid on each unit of PMR and the whole PMR system were discussed:

- (1) The adsorption efficiency of TiO<sub>2</sub>-P25 on phage f2 decreased in the presence of humic acid, possibly due to the competition of adsorption sites between humic acid and phage f2 in the PMR system in the dark.
- (2) The benzene ring structure of humic acid molecules, which could adsorb ultraviolet with the wavelength of 254 nm, reduced the effective dose of UV in the reaction system, indirectly weakening the photocatalytic disinfection efficiency of phage f2.
- (3) When humic acid exists in the actual water environment, in addition to the influence of humic acid on UV disinfection, the effect of humic acid on photocatalytic disinfection mainly involves two parts: the adsorption of phage f2 by TiO<sub>2</sub>-P25 is relatively blocked, which further reduces the photocatalytic disinfection efficiency of phage f2; On the other side, the hydroxyl radicals produced by TiO<sub>2</sub>-P25 in UV light are consumed by humic acid, resulting in the decrease of photocatalytic disinfection efficiency of phage f2.
- (4) In the intermittent operation mode, humic acid had no significant effect on the concentration of phage f2 in membrane effluent, which was less than 2 PFU/mL. While the concentration of phage f2 in the reactor was significantly affected by humic acid, which was more than 20 PFU/mL.
- (5) When there is a certain amount of humic acid in the water environment, intermittent operation mode or higher membrane flux (40 L/(m<sup>2</sup>·h)) was selected to partly alleviate the adverse effects of humic acid.

**Author Contributions:** Data curation, Q.W. and S.X.; Formal analysis, X.Z. and W.L.; Investigation, Q.W. and S.X.; Methodology, X.Z. and W.L.; Writing – original draft, R.C., L.S. and L.S.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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