



## Removal of sulfamethoxazole and tetracycline in water using polyvinylidene fluoride membrane modified with polyethyleneimine

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Received 28 December 2022; Accepted 24 June 2023

### ABSTRACT

With the increasing impact of antibiotics on the environment, membrane separation technology has been widely used to treat antibiotics in water environment. The poor hydrophilicity of polyvinylidene fluoride (PVDF) membrane leads to the problems of low water flux and easy surface pollution during membrane separation. In this study, the surface of PVDF base film was modified by polyethyleneimine (PEI). The influence of modified membrane on the retention capacity, anti-fouling property and operation characteristics of sulfamethoxazole (SMX) and tetracycline (TC) was investigated. The effect of PEI concentration on the comprehensive performance of pure water flux and antibiotic rejection was investigated by changing the molecular weight of PEI. The results showed that the comprehensive performance was relatively best when the molecular weight of PEI was 10,000 Da (P-10K). It could remove 57.5% and 30% of SMX and TC from the simulated water samples, and 88.2% and 62.4% of SMX and TC from the actual river water samples. However, it is also accompanied by a large degree of membrane fouling, resulting in a decrease in membrane separation performance. After the rotation test of single factor variables, it was found that the cation strength and humic acid concentration had the greatest influence on the flux and antibiotic retention of the modified membrane through the steric hindrance effect. In the anti-fouling performance test, the membrane flux can be restored to 85% and 92.3% of the initial flux after acid washing and alkali washing, indicating that the anti-fouling performance of the PVDF membrane after surface cross-linking modification is improved.

*Keywords:* Membrane treatment; Modified membrane; Sulfamethoxazole; Membrane fouling; Polyethyleneimine

### 1. Introduction

The extensive use of antibiotics in China has made the pollution of antibiotics in water increasingly serious. Excessive use of antibiotics poses a huge risk to aquatic ecosystems and organisms. In addition, antibiotics cannot be fully absorbed and utilized by the body. Most of them

are discharged through urine and feces. During the use of antibiotics, a large amount of antibiotic wastewater is excessively discharged into the water environment from hospitals, farms and sewage treatment plants, which will damage the normal water balance and pose a serious threat to human health. In recent years, the results of detection of rivers and drinking water sources in various parts of China

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have shown that different concentrations of antibiotics have been detected in water bodies, among which broad-spectrum antibiotics sulfonamides and tetracycline antibiotics account for a relatively high proportion [1]. Tetracyclines and sulfonamides are the main antibiotics in the Yangtze River Estuary [2], and sulfonamide residues were found in the Pearl River Delta and the Yangtze River Delta, with a concentration of up to 500 µg/L [3].

Various purification methods have been developed to effectively treat antibiotic wastewater, including adsorption, electrolysis, advanced oxidation and photocatalysis. The traditional treatment steps generally first go through physical and chemical pretreatment, then anaerobic and aerobic treatment, and finally discharge to the water environment after post-treatment. However, due to the current complex anaerobic and aerobic treatment operations, the larger project area and more types and quantities of chemicals, the conductivity of the water body is greatly increased, and the operation cost is increased. In addition, problems such as long treatment period and weak continuity of treatment process limit the large-scale application of the project to a certain extent, and the effluent is difficult to meet the reclaimed water reuse standard [4].

As a new separation technology, membrane separation technology is widely used in chemical wastewater treatment, pharmaceutical wastewater treatment, food wastewater treatment and many other aspects. It realizes the separation, purification or concentration of mixture by utilizing the selective permeation of each component in the solution in the membrane. Antibiotics in membrane treatment can be controlled by adsorption. In this adsorption process, antibiotics with hydrophobicity or strong hydrogen bond characteristics are easy to be adsorbed on the membrane at the initial stage of filtration. However, some of them can be removed by steady-state repulsion due to the space effect of uncharged solutes or the combination of space effect of charged solutes and electrostatic effect. These mechanisms depend on the physicochemical properties of compounds, solution properties, membrane properties, etc [5,6]. Compared with traditional water treatment technology, membrane technology has certain advantages in wastewater treatment. On the one hand, the small floor area makes it suitable for sewage treatment of any scale, which can realize indirect or continuous water inflow at room temperature, and the process is simple. On the other hand, this is a physical treatment process, without adding chemical reagents, and the treated substance can participate in the water circulation process; In addition, it has good selective permeability and high quality of filtered water. Sanguanpak et al. [7] used a porous geopolymer composite membrane (PGCM) containing TiO<sub>2</sub> to remove amoxicillin, ciprofloxacin, norfloxacin, sulfamethoxazole, tetracycline and trimethoprim from real hospital wastewater. Among them, PGCM containing 10% TiO<sub>2</sub> achieved the highest antibiotic removal efficiency, and the adsorption of target antibiotics was 38%–75%. Nasrollahi et al. [8] used nanofiltration membrane (NF) membrane to separate 20 different drug compounds and found that, in addition to the molecular weight of the container, the charge of the compound plays an important role in the repulsion of organic compounds. However, membrane fouling is very serious and comes from a wide range

of sources. The properties of membrane materials and operating conditions may lead to membrane fouling. Therefore, in order to effectively alleviate the problem of membrane contamination and control operating costs, it is necessary to prepare membranes with high water flux, good hydrophilicity and high anti-fouling property. Polyvinylidene fluoride (PVDF) is an ideal membrane material. At present, because of its excellent chemical and thermodynamic stability, good toughness, acid and alkali resistance and strong permeability, it is more popular in the field of membrane preparation. Although PVDF membrane has many advantages in membrane treatment, its hydrophobic surface seriously damages its separation performance and service life, which is a challenge to be solved urgently. However, these performance problems can be improved through modification [9]. Lin et al. [10] modified PVDF membrane with polyhexamethylene guanidine (PHMG) and tannic acid (TA), and found that the surface modification of PHMG and TA made PVDF microporous membrane have excellent anti-fouling and antibacterial properties. Polyethyleneimine (PEI) is a water-soluble macromolecule, which contains a large number of primary and secondary amine groups. In addition, it has high cation charge density, and is a good candidate for heavy metal ion scavengers [11]. At present, PEI modified polymers, membranes and nanoparticles have been widely used to remove heavy metal ions [12]. Polyvinyl pyrrolidone (PVP) is a synthetic water-soluble polymer compound with excellent film forming ability, biocompatibility, chemical stability, and low toxicity. It can change the hydrophilicity and permeability of membranes by controlling their pore structure and is often used as a pore forming agent [13]. In addition, the addition of PVP can reduce the surface tension of the solution and further improve the film forming performance [14].

This study explored the removal effect of surface modified PVDF membrane on two kinds of sulfamethoxazole (SMX) and tetracycline (TC) and the influence of different operating conditions on the interception effect of the modified membrane. Before PVDF membrane was modified, the best raw material ratio was selected through gradient test to prepare PVDF base membrane. On this basis, PEI was used as the modified material to prepare the surface modified PVDF film, and the removal effect of the modified film on SMX and TC was tested. Then, the simulation test was conducted to explore the influence of operating conditions (operating pressure, cycle times) and water quality conditions (initial feed concentration, pH, humus, ionic strength) on the membrane separation effect. Finally, the modified membrane is used to intercept the pollutants in the river water, and the practical application effect and anti-fouling property of the prepared modified membrane are explored.

## 2. Materials and methods

### 2.1. Materials

The chemical polyvinylidene fluoride (Mn = 80,000 Da) used to prepare modified PVDF film was purchased from Shanghai Sanaifu Co., Ltd.; PVP, N-N-dimethylacetamide (DMAc) and PEI (Mn = 600, 1,800, 10,000 Da) were obtained from Sinopharm Chemical Reagent Co., Ltd. The bovine serum albumin (Mw = 10,000 Da), ethanol (C<sub>2</sub>H<sub>5</sub>OH),

hydrochloric acid (concentration 36.0%–38.0%), sodium hydroxide (NaOH), sodium bisulfite (NaHSO<sub>3</sub>), acetone (HPLC grade), methanol (HPLC grade), dichloromethane (HPLC grade), formic acid (LC-MS grade) and acetonitrile (LC-MS grade) used in the test were purchased from Sinopharm Chemical Reagent Co., Ltd. The purity of three antibiotics (SMX, TC and D4) used in this test is more than 95%, which were obtained from Dr. Ehrenstorfer, Augsburg, Germany.

## 2.2. Preparation of PVDF membrane

### 2.2.1. Preparation of PVDF base film

The basic properties and microstructure of PVDF membranes are closely related to the concentration of PVDF and PVP. Therefore, in order to prepare the most satisfactory base membrane, different gradient tests were set up for PVDF aggregate and PVP. In the gradient test of PVDF, the proportion concentration of PVP is 3%, and the proportion of PVDF is 12%, 14%, 16%, 18% and 20%, respectively; When testing the influence of PVP concentration on the base membrane, set the proportion of PVDF to 20%, and make the proportion of PVP to be 1%, 3%, and 5%, respectively.

PVDF base film was prepared by immersion precipitation phase inversion method. Firstly, obtain PVDF, PVP and DMAc according to a certain mass ratio, and they were mixed evenly and stirred in a 65°C water bath for 12 h to form a homogeneous film casting solution. Then stop stirring and let it stand at 65°C for 12 h. After defoaming, pour a proper amount of casting solution onto the smooth glass plate and scrape it with a film scraper immediately. The film scraping speed is maintained at 1–1.5 cm/s and the film thickness is 200 μm. After that, the solvent is initially evaporated after standing in the air for 30 s, and then the glass plate is slowly immersed in deionized water at 25°C. When the membrane is formed, it is separated from the glass plate, and then the membrane is fished out and soaked in deionized water for full phase transformation, finally obtaining PVDF base membrane. The formed base film can be used only after being immersed in deionized water for 1 d. If the base membrane is not used for a long time, soak it in 1 wt.% NaHSO<sub>3</sub> aqueous solution to avoid affecting the membrane flux after dehydration. Soak it in deionized water for 4–5 h before use and fully rinse it.

### 2.2.2. Preparation of PEI modified PVDF ultrafiltration membrane

In this study, PVDF base film was modified by surface cross-linking method. PEI contain many amino groups, which makes it have strong cationic, high adsorption and high reactivity. As shown in Fig. S1, after PEI modification, the amino group of PEI is transferred to the surface of the base membrane or the structure of the base membrane is changed, so that the base membrane obtains the hydrophilicity and high reaction strength of the amino group, thereby improving the membrane separation treatment effect. The base membrane with the raw material ratio of PVDF: PVP:DMAc = 20:3:77 was selected for modification test. Three kinds of polyethyleneimines with different

molecular weights (Mw = 600, 1,800, 10,000 Da) were used to cross link the PVDF base films prepared in the same batch at 50°C and 70°C, and the best modification temperature and molecular weight were explored. According to the different molecular weight of PEI, the modified membranes were named P-600, P-1800, P-10K, respectively, and the blank group was named P-0. First, weight 0.5 g PEI and dissolve it in 500 mL ultrapure water, heat it to 70°C, stir it at constant temperature for 4 h, and control the solution temperature at 50°C–55°C before use. Then cut the appropriate size base membrane diaphragm according to the size of the ultrafiltration cup, soak it in a PEI aqueous solution of 50°C–55°C, and shake it in a thermostatic shaker for 4–5 h, and the shaker parameters are set to 55°C, 120 rpm. After the completion of oscillation, take out the diaphragm, fully flush it with deionized water, and store it in pure water for standby. Through the surface cross-linking modification at 50°C, the surface of PEI and PVDF film are closely combined to achieve the goal of hydrophilic modification of PVDF film.

## 2.3. Basic performance test of membrane

### 2.3.1. Pure water flux and BSA retention rate

Millipore UFSC20001 cup type ultrafiltration device from Millipore, Germany, was used to measure the membrane pure water flux, bovine serum albumin (BSA) rejection rate and subsequent filtration performance. The test condition is about 25°C at room temperature, and the regulating pressure is 0.10 MPa.

At room temperature of 25°C, first fix the selected PVDF membrane with smooth surface and no obvious defects in the ultrafiltration cup, so that the effective area of the membrane is 31.95 cm<sup>2</sup>. Add 200 mL of pure water and pressurize it to 0.10 MPa. The pure water flux was measured after the membrane flux was stabilized for 1 h; Then, under this condition, test the time *t* for *V* = 10 mL effluent, and calculate the pure water flux *J*<sub>0</sub> according to Eq. (1); Finally, prepare 0.5 g/L BSA bovine serum albumin solution (*C*<sub>0</sub>), keep the above conditions unchanged, filter the BSA aqueous solution, test the time taken for *V* = 10 mL effluent, and calculate the osmotic flux *J*<sub>*p*</sub> of BSA aqueous solution according to the pure water flux formula. The BSA permeate solution is retained, and the absorbance of the permeate solution is tested at the wavelength of 284.3 nm with a UV spectrophotometer. The BSA concentration *C*<sub>*p*</sub> of the permeate solution is calculated by the BSA standard curve drawn in advance, and then the rejection ratio *R* of PVDF membrane to BSA is calculated.

The calculation formula of pure water flux and BSA retention rate is given as:

$$J = \frac{V}{At} \quad (1)$$

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \quad (2)$$

where *J* is pure water flux, L/(m<sup>2</sup>·h); *V* is the sampling volume, L; *A* is the effective area of the membrane, m<sup>2</sup>; *T* is the

sampling time, h;  $R$  is the BSA interception rate;  $C_0$  and  $C_p$  are the initial concentration of BSA and the concentration of osmotic solution, g/L.

### 2.3.2. Flux recovery rate

The anti-fouling performance and continuous filtration capability of the membrane can be characterized by the pure water flux recovery rate (FRR). After testing the pure water flux  $J_0$  and BSA retention rate of the membrane, continue to filter BSA for 1 h, then take out the membrane, wash it with deionized water and gently scrub the membrane surface with hands, and then retest the pure water flux  $J'_0$  of the membrane according to the pure water flux test method, that is, recover the flux.

The calculation formula of pure water flux recovery rate is as follows:

$$\text{FRR} = \frac{J'_0}{J_0} \times 100\% \quad (3)$$

where  $J_0$  and  $J'_0$  are the initial pure water flux and recovery flux of the membrane, respectively  $\text{L}/(\text{m}^2\cdot\text{h})$ .

The higher the recovery rate of pure water flux, the better the anti-fouling performance and continuous filtration capacity of the membrane.

### 2.3.3. Aperture

The pore size of the base membrane and the selected modified membrane was measured by capillary pore size analyzer. Capillary pore size analysis is an analytical instrument based on the principle of gas-liquid displacement technology. The sample is completely wetted with a non-toxic wetting liquid. After the pores in the sample are completely filled with the wetting liquid, the gas that does not react with the wetting liquid and the sample is used to squeeze the wetting liquid in the sample channel. Controlling other pressures to slowly increase, when the liquid in the maximum pore is emptied, that is, when the bubble point pressure is reached, the pore diameter is the maximum pore diameter of the sample; when the pressure is continuously increased until all the liquid in all the channels is emptied, the pore diameter is the smallest. The test pressure is inversely proportional to the pore size. Through the complete test process, the maximum, minimum pore size, average pore size and the distribution ratio of each pore size can be obtained.

### 2.3.4. Surface morphology

ZEISS GEMINI 300 scanning electron microscope (SEM) was used to observe the surface morphology and cross-sectional morphology of the prepared PVDF base membrane and modified membrane, focusing on the uniformity of pore size distribution on the membrane surface and the pore structure inside the membrane. The membrane samples were dried using a freeze dryer before characterization. The characterization of the cross-sectional morphology needs to be quenched by liquid nitrogen to maintain a good cross-sectional structure for electron microscopy

observation. Before the test, the membrane sample was fixed on the sample stage with conductive adhesive and sprayed with gold to improve the conductivity.

## 2.4. Test method

### 2.4.1. Factors affecting the removal of antibiotics by modified PVDF membrane

In this test, simulated water samples were used to determine the relative optimal range of each factor by exploring the influence of operating conditions (transmembrane pressure, number of cycles) and environmental factors (initial feed concentration, pH, humic acid, ionic strength) on the interception effect of modified PVDF membrane to guide the subsequent river water sample antibiotic removal test. The gradient of operating conditions is set as 0.05 MPa/5 times, 0.10 MPa/5 times, 0.15 MPa/5 times. For the initial feed concentration of antibiotics, three concentrations are set, namely 50, 100 and 500  $\mu\text{g}/\text{L}$ . Five gradients are set from pH 1–9, and the concentration span is 2. Humic acid concentration is 5, 10 and 20 mg/L. The ionic strength gradient is similar to that of humic acid, namely 0, 5, 10 and 20 mmol/L.

Next, five groups of experiments were set up according to the single factor variable rotation method.

#### 2.4.1.1. Transmembrane pressure and number of cycles

Prepare an aqueous solution of target antibiotics of 100  $\mu\text{g}/\text{L}$ , adjust the pH to approximately 7.0, and no more inorganic salts and humic acids are added. Use the ultra-filtration cup to filter the simulated water sample. The transmembrane pressure is set to 0.05, 0.10 and 0.15 MPa, respectively. Each group is subject to five cycles of filtration. The membrane flux is tested every 5 min. At the end of each filtration, 10 mL of penetrant is retained for subsequent testing. The best transmembrane pressure and cycle times were determined according to the interception effect.

#### 2.4.1.2. Initial feed concentration

Prepare 50, 100, and 500  $\mu\text{g}/\text{L}$  target antibiotic aqueous solution, adjust the pH to about 7.0. The membrane filtration test shall be carried out under the optimal pressure and cycle times determined by the above test. The membrane flux shall be tested every 5 min. At the end of each filtration, 10 mL of penetrant shall be retained for subsequent testing. The relatively optimal initial feed concentration is determined according to the interception effect.

#### 2.4.1.3. pH

Under the optimal operating conditions and initial feed concentration determined by the above tests, respectively adjust the pH of the solution to be filtered to 1, 3, 5, 7 and 9, and then conduct the membrane filtration test. In order to make the difference of retention test results more obvious, the solution to be filtered at different pH shall be contacted with the modified PVDF membrane for 30 min before pressurized filtration. The flux measurement and the retention of the permeate water sample follow the previous example.

#### 2.4.1.5. Anion and cation strength

According to relevant literature, the anions and cations involved in the river water body include  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ , etc. Therefore, after the preparation of the solution to be filtered,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$  (6:5:3:1:1) are added to the simulated water sample according to the ion concentration and proportion of the Huangpu River system to adjust the cation concentration; Add  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$  (1:1:1) to adjust the anion concentration. The ion concentration gradient is set to 5, 10 and 20 mmol/L.

#### 2.4.1.6. Humic acid

As above, respectively prepare solutions to be filtered with humic acid concentration of 5, 10 and 20 mg/L for test.

In addition, in order to ensure the accuracy of test results as much as possible, PVDF modified membranes used in each group of tests were prepared in the same batch, and new membranes were used in each test. Before formally filtering the simulated water sample, it is necessary to pre-press the membrane for 1 h, that is, use PVDF membrane to pressurize and filter the pure water, and conduct the formal test after the effluent flux is stable. During the periodic filtration test, sample 10 mL at the end of each cycle, sample 5 times in 5 cycles of transmembrane pressure and cycles test, and sample 3 times in 3 cycles of other cycles test.

#### 2.4.2. Test of modified membrane filtration of actual water

After the experiment of influencing factors on the removal of antibiotics by the modified membrane was completed, the removal effect of the modified membrane on antibiotics in actual water samples was explored. The actual water sample is taken from the Fuxing Island Canal in Shanghai, where the concentration of  $\text{NH}_4^+-\text{N}$  is 0.230 mg/L, TP is 0.194 mg/L, and chemical oxygen demand (COD) is 38.4 mg/L. Add an appropriate amount of antibiotic stock solution into the water sample to adjust the initial antibiotic concentration of the water sample to 20  $\mu\text{g/L}$ . Other operating parameters shall be adjusted according to the simulation test results. The membrane filtration test is in the form of circulating filtration. The membrane flux is tested every 5 min in each cycle. After each cycle, 10 mL is sampled for testing. The membrane used for filtering the actual water sample and the membrane used for the simulation test are made in the same batch or have similar performance. The membrane is pre-pressed for 1 h before filtration, and the follow-up test is carried out after the effluent is stabilized.

### 2.5. Sample analysis and data processing

#### 2.5.1. Pretreatment of water sample

##### 2.5.1.1. Simulate water sample

Take the cryopreserved water sample and place it at room temperature, take 1 mL of water, add 20  $\mu\text{L}$  of the internal standard sulfamethoxazole-D4 dropwise to it, then filter using a 0.22  $\mu\text{m}$  polyethersulfone needle filter and transfer to a 1.5 mL brown injection flask for testing.

#### 2.5.1.2. Actual water sample

First, dilute 50 mL of water sample to 200 mL, and add 0.15 g  $\text{EDTA-Na}_2$  to react for 20 min (the purpose is to remove metals in water by complexing, so as to avoid interference to the subsequent solid phase extraction and quantitative detection process). Then use the vacuum suction filter (inner cushion 0.45  $\mu\text{m}$  glass fiber filter membrane) to filter the water sample in order to remove large, suspended particles or other solid impurities in the water sample. Next, use  $\text{HCl}$  and  $\text{NaOH}$  solutions to adjust the pH of the water sample to 7.0 ( $\pm 0.1$ ), and then realize the solid phase extraction of the water sample by activating the solid phase extraction column, loading the sample for extraction and enrichment, rinsing, vacuum drying, and elution. Then use the nitrogen blowing instrument to slowly blow dry the eluent. During the drying process, make the target to be measured precipitate and adhere to the inner wall of the container. Then carry out re dissolution: add 1 mL methanol into the drying container to fully shake and ultrasonic, so that the target to be measured can be fully dissolved.

Finally, add 20  $\mu\text{L}$  of the internal standard sulfamethoxazole-D4 to 1 mL complex solution and filter with a 0.22  $\mu\text{m}$  polyethersulfone needle filter, and transfer to a brown injection bottle for cryogenic storage for testing.

#### 2.5.2. Analysis and detection methods

Quantitative detection of the antibiotic of interest was performed using Thermo Fisher's Ultra High Performance Liquid Chromatography-Tandem Mass Spectrometry (UHPLC-MS/MS). The target antibiotic is separated by chromatographic column. During sample injection, the chromatographic column temperature is set to 25°C, and the sample injection volume is guaranteed to be 5  $\mu\text{L}$ . In addition, the mobile phase A and B are 0.3 v/v% formic acid aqueous solution and acetonitrile, respectively. The initial mobile phase ratio is set as A:B = 95:5, and the mobile phase flow rate is 0.25 mL/min. Gradient elution was used to separate the two target antibiotics step by step during detection.

The target to be tested is separated by the chromatographic column and then scanned by the mass spectrometer for quantification. The two target antibiotics are quantitatively detected at the same time. The detection parameters of the mass spectrometer are set as follows: detection mode-positive ion mode, ion source-thermoelectric spray ionization source (HESI), spray voltage 4,000 V, evaporation temperature 40°C, sheath gas pressure 35 bar, auxiliary gas pressure 3 bar, capillary temperature 350°C. Scanning mode-SRM, scanning time-0.1 s, scanning width-1.0 m/z. Before the formal quantitative test, the mass spectrometry operating conditions of the internal standard and the target antibiotic should be optimized to ensure the detection sensitivity in the detection process. The linear range of detection of two target antibiotics is set as 5–500  $\mu\text{g/L}$ , the internal standard method is used for concentration calculation.

Since the concentration of antibiotics belongs to the micro level, the gradient solution of standard samples in the corresponding range prepared in advance will be injected together for detection each time, and the standard curve will be updated in real time to ensure that the

measurement results are relatively accurate. In addition, the quantitative limit and detection limit of target antibiotics in the measurement process should also be determined: use antibiotic standard to prepare concentration gradient solution and find the corresponding solution concentration when the signal-to-noise ratio is  $RS/N = 3$  and  $RS/N = 10$  in the measurement process, that is, the detection limit and quantitative limit of each antibiotic. The detection effect of liquid quality is judged by the spiking recovery rate: take two identical samples, add a certain amount of standard to be tested to one of them, use the same analytical method to analyze and test the two samples, take the ratio of the difference value to the added physical theoretical value as the spiking recovery rate of the substance, repeat for five times, and get the spiking recovery rate range of the target antibiotic. The evaluation parameters of each antibiotic detection method are shown in supplementary Table S1. Refer to the previous literature of our research group for specific testing procedures [15].

COD is measured by Hash digestion analyzer (China Kehuai Instrument Co., Ltd., DRB200); total phosphorus (TP) was determined by ammonium molybdate spectrophotometry; ammonia nitrogen ( $NH_3-N$ ) is determined by Nessler's reagent colorimetry.

### 2.5.3. Data processing

Excel was used to record and analyze, Origin was used to draw charts, PPT and PS were used to draw mechanism diagrams, and SPSS was used to conduct correlation analysis.

## 3. Results and discussion

### 3.1. Selection of PEI modified PVDF film

As shown in supplementary Fig. S2, when the molecular weight of PEI is the same and the modification temperature is different, the membrane flux at the modification temperature of  $70^\circ C$  is higher than that at  $50^\circ C$ , the membrane flux in Group B is higher than  $400 L/(m^2 \cdot h)$ , and the highest P-600 is  $536.5 L/(m^2 \cdot h)$ . Such a high flux membrane may not be effective in the application of retaining trace pollutants. When the molecular weight of PEI is different, and the modification temperature is the same, the higher the molecular weight of PEI is, the lower the modified membrane flux is. There are two main reasons for the above phenomenon. On the one hand, the expansion of membrane pores under low temperature modification is more uniform, which makes up for the influence of molecular weight on membrane pores to a certain extent. Therefore, the flux increase is smaller when the molecular weight is larger, and the higher modification temperature will cause the uneven expansion of the pore size of the PVDF base membrane. The relatively long high temperature environment makes this expansion solidified, which eventually leads to the permanent expansion of the flux. On the other hand, PEI is a hydrophilic amphoteric polymer material. After being grafted onto the surface of PVDF membrane, it will improve the hydrophilicity of the membrane, reduce the membrane resistance, and increase the membrane flux. However, higher molecular

weight PEI may enter the membrane pores during the modification process, resulting in the actual reduction of the membrane aperture. Therefore, the flux of PVDF membrane modified by higher molecular weight PEI will decrease.

Furthermore, the PEI modified PVDF membrane prepared at  $50^\circ C$  was used for the preliminary test of removing antibiotics from simulated water samples, and the test results are shown in Fig. 1. SMX was not detected in P-1800 and P-10K penetrants after three cycles, indicating that the PEI surface cross-linked PVDF membrane has significant removal effect on SMX, but it does not greatly improve the removal effect on TC. The best performance was P-10K, and the TC removal rate reached 37.5%, while the final removal rate of TC by P-600 and P-1800 was less than 10%. This may be related to the solubility of TC and SMX. The smaller the solubility of the adsorbate, the easier it is to escape the solvent and adsorb on the adsorbent [16]. However, the removal rate of the second cycle was higher than that of the third

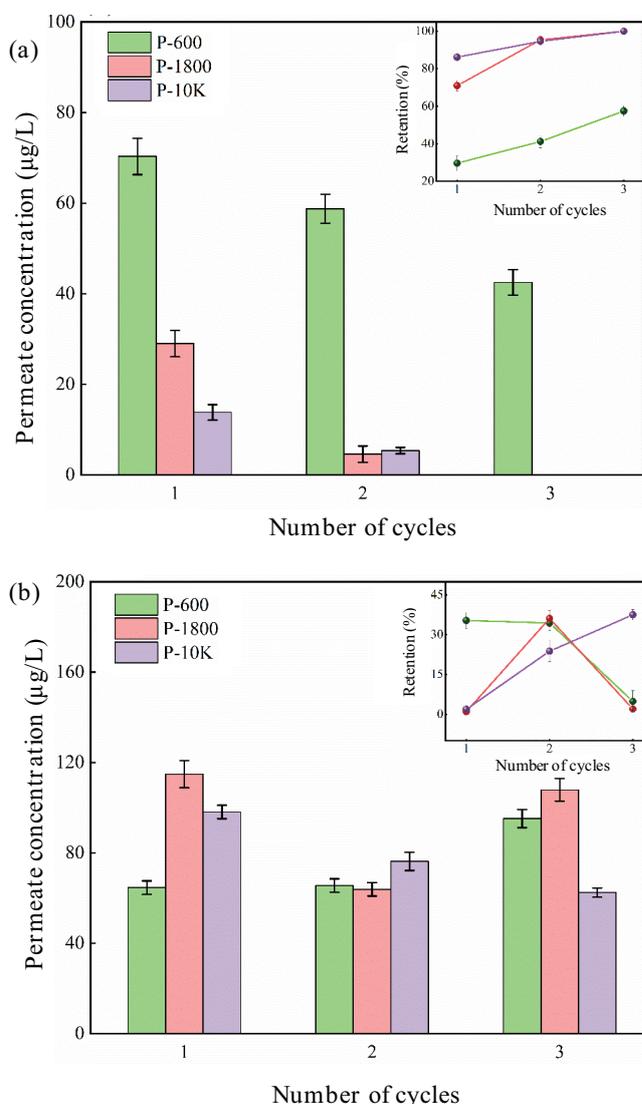


Fig. 1. Rejection of (a) SMX and (b) TC by surface cross-linked modified PVDF membranes at  $50^\circ C$  ( $0.10 MPa$ ,  $C_o = 100 \mu g/L$ ).

cycle, reaching more than 30%. This shows that the removal effect of PEI modified PVDF membrane on TC can reach more than 30%, and the subsequent filtration effect becomes worse, which may be due to the target antibiotic trapped in the membrane flowing out with the permeate again due to the circulating filtration.

To sum up, the base film with PVDF:PVP:DMAc = 20:3:77 was prepared by surface cross-linking modification of PEI (10,000 molecular weight) at 50°C.

### 3.2. Physical characterization of PVDF modified membranes

The scanning electron microscope and optical images before and after membrane modification are shown in Fig. 2. Before modification, the PVDF substrate membrane is white and translucent, and the membrane is slightly tough and slightly elastic after water bath phase transformation. After soaking in polyethyleneimine solution at 50°C for 4 h, the color of the membrane surface changed from light pink to dark pink. From the macroscopic results, polyethyleneimine was successfully attached to the surface of PVDF membrane by surface modification, which was consistent with other literature [17]. In addition, during the whole experimental study, the soaking time and soaking temperature were compared. The results showed that the surface color of the modified membrane was proportional to the soaking time and soaking temperature. When the soaking time exceeded 5 h or the soaking temperature reached 70°C, the surface color of the modified membrane was brown, and the filtration performance of the membrane decreased.

Fig. 2a and b are the surface microtopography of PVDF membrane before and after surface modification. By comparison, it can be seen that there are many pores on the surface of PVDF membrane before modification and the microscopic surface is bark-like. After the surface modification of polyethyleneimine, the small pores on the membrane surface decreased, the surface was flatter than before, and the bark-like crack morphology became smoother and neater. This indicates that polyethyleneimine successfully accumulates on the surface of PVDF membrane, which is consistent with the color change shown in optical photos. The rejection performance of the membrane mainly depends on its internal structure. The cross section of the PVDF membrane before and after modification was characterized by scanning electron microscopy. The internal microstructure of PVDF membrane before and after modification is shown in Fig. 2c and d. It can be observed that the PVDF membrane belongs to a typical asymmetric structure. From top to bottom, it is a dense porous surface layer, a finger-like channel layer in the middle, and a sponge-like layer at the bottom. Among them, it is not the finger-like pores that play the role of adsorption and filtration in the main structural layer in the middle, but the finer micropores that exist in the main structural layer (Fig. 2e). It is such a large number of micropores that exist in the main structure of the membrane. In the filtration process, sufficient adsorption sites and small enough micropores can be provided for adsorption interception to intercept pollutants with smaller molecular weight. In addition, compared with the base membrane and P-10K, it was found that after surface modification, the dense micropores on the

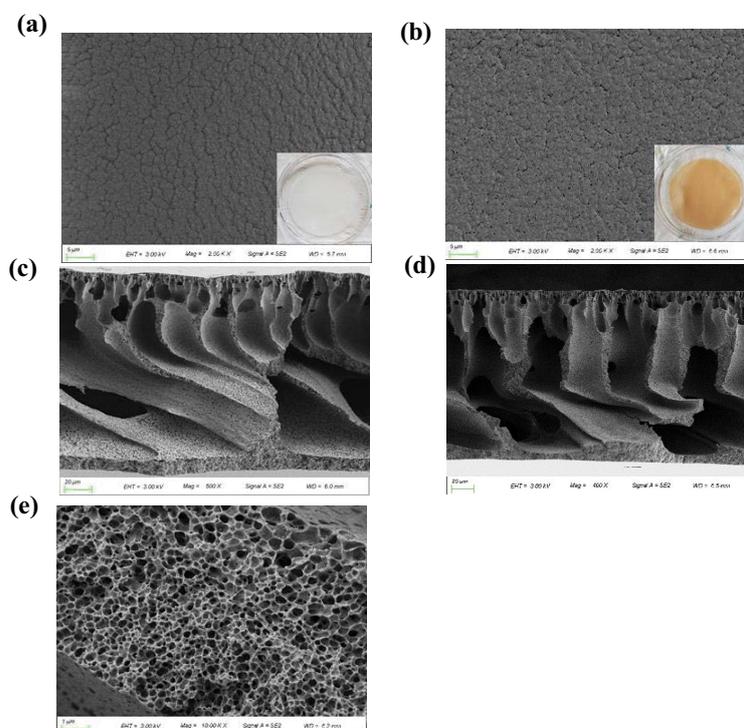


Fig. 2. Scanning electron micrographs of PVDF substrate membrane and surface cross-linked modified membrane ((a) and (c) are surface and cross-sectional micrographs of PVDF substrate membrane, respectively; (b), (d) and (e) are surface and cross-sectional micrographs of P-10K, respectively).

surface of P-10K increased and thickened due to the accumulation of PEI on the membrane surface. This result is to increase the microporous structure of the membrane, which is beneficial to improve the rejection performance of the membrane.

The pore size of PVDF original membrane and P-10K modified membrane was measured by capillary pore size analyzer, maximum and minimum pore size, average pore size, pore size distribution, etc. The results are shown in Fig. 3. The maximum pore size of PVDF membrane (20:3:77) was about 0.4  $\mu\text{m}$ , and the average pore size was 0.089  $\mu\text{m}$ . The maximum pore size of P-10K membrane is about 0.33  $\mu\text{m}$ , and the average pore size is 0.20  $\mu\text{m}$ . After modification, the maximum pore size decreased by 17.5%, while the average pore size increased significantly to 225%. Comparing the pore size distribution range before and after modification (Fig. 3b and d), the pore size above 0.20  $\mu\text{m}$  before modification accounted for 45.4%, and the remaining pore size was less than 20  $\mu\text{m}$ . The pore size above 0.20  $\mu\text{m}$  after modification accounted for 45.9%, of which the pore size of 0.32–0.33  $\mu\text{m}$  accounted for 41.3%, that is, the pore size of the modified membrane is mainly large pores, and the distribution is more uniform. There are two main reasons for this phenomenon. On the one hand, the surface modification is carried out at 50°C, and the substrate membrane expands due to uniform heating at higher temperatures, which makes up for the uneven distribution in the process of casting and phase transformation to a certain extent. Therefore, the pore size of the modified membrane becomes larger and the distribution is more uniform. On the other hand, polyethyleneimine was successfully attached to the surface and near-surface pores of the PVDF substrate membrane to modify the defects of the substrate membrane. In addition, through the analysis of the pore

size data, the results are consistent with the previous SEM images.

### 3.3. Study on the characteristics of PVDF modified membrane for removing antibiotics

The removal of target substances in membrane separation process generally involves spatial steric effect (screening effect), hydrophilic/hydrophobic effect, Donnan effect (under different conditions, the charged states of charged membrane surface and target removal substances are different, and the membrane interception effect is enhanced by adjusting the operating parameters to change their charged states), as well as the change of interception effect caused by membrane fouling [18].

#### 3.3.1. Number of cycles and operating pressure

Set the pressure gradient of 0.05, 0.10 and 0.15 MPa, and filter each group for 5 times. Supplementary Fig. S3 shows the membrane water flux is positively correlated with the transmembrane pressure. At the same pressure, the membrane flux decreased with the increase of the number of cycles. After three cycles, the flux remained relatively stable, and the flux fluctuation was the smallest at 0.10 MPa.

As shown in Fig. 4, the retention effect of PVDF modified membrane on SMX and TC is inversely proportional to the transmembrane pressure. The lower the pressure, the better the removal effect of target antibiotics. When the pressure is 0.05, 0.10 and 0.15 MPa, the removal rates of SMX in five cycles reach 73.8%, 67.7% and 52.8%, respectively, and the removal rates of TC reach 65.59%, 46.07% and 38.71%, respectively. By comparing the results under the same pressure conditions, it can be concluded that the

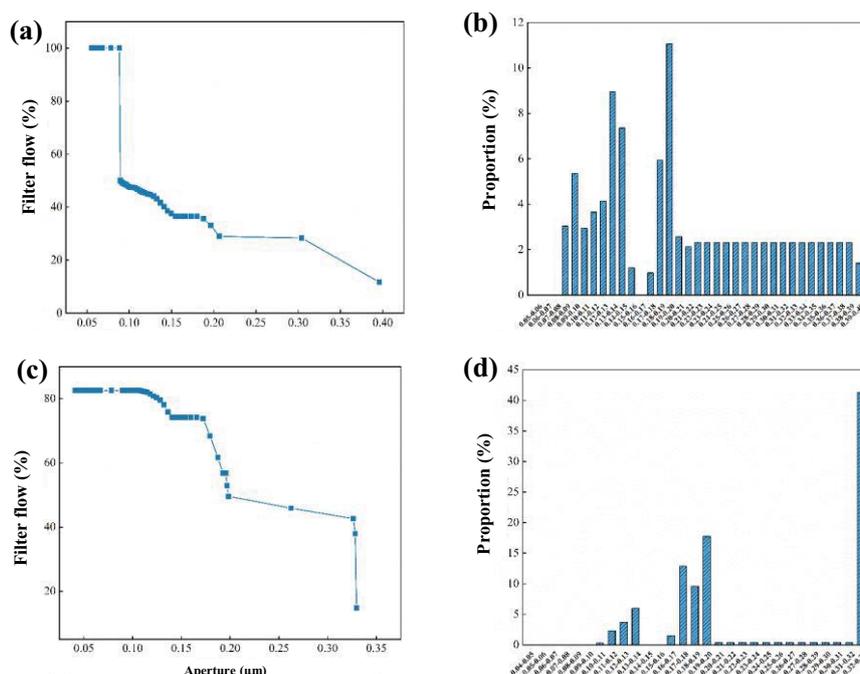


Fig. 3. Average pore size of PVDF substrate membrane and P-10K membranes.

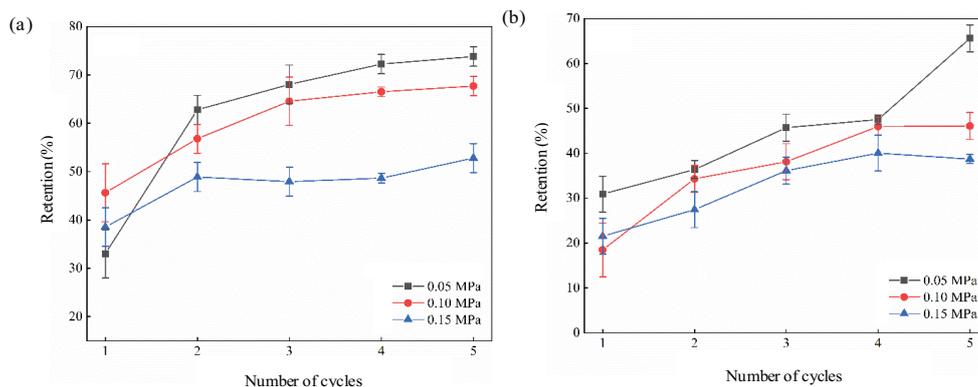


Fig. 4. Variation of removal of (a) SMX and (b) TC at different pressures ( $C_o = 100 \mu\text{g/L}$ ,  $\text{pH} = 7$ ).

more cycles, the better the removal effect of target antibiotics is, but the removal effect is basically stable after three cycles, and the subsequent increase of cycles contributes less.

In conclusion, when the transmembrane pressure is 0.10 MPa and the number of cycles is 3, the antibiotic removal effect is better.

### 3.3.2. Initial feed concentration

The most common problem in the practical application of membrane technology is membrane fouling, which will cause concentration polarization in severe cases. The main reason is that the solute accumulates on the membrane surface due to long filtration time or high feed concentration, which leads to the increase of concentration near the membrane surface and the formation of reverse solute gradient [19,20]. Concentration polarization will lead to a sharp decline in membrane flux, poor effluent quality, and increased operating costs. Therefore, after determining the pressure and cycle times, it is necessary to determine the appropriate initial feed concentration to reduce the occurrence of membrane fouling.

The flux changes with the initial feed concentration as shown in supplementary Fig. S4. When the initial feed concentration is 50, 100, and 500  $\mu\text{g/L}$ , the maximum difference of initial flux is 18.34  $\text{L}/(\text{m}^2\cdot\text{h})$ . At the beginning of the third cycle, the difference of flux is 63.4  $\text{L}/(\text{m}^2\cdot\text{h})$ , which is 2.5 times higher. At different feed concentrations, although the membrane will be cleaned after each cycle, the membrane flux still decreases. This shows that in the process of circulating filtration, the adsorption on the surface and inside of the membrane intercepts the target, leading to the decline of the recovery flux, and the higher the concentration of the filtrate, the greater the decline of the membrane flux.

According to the removal results of antibiotics in solution by P-10K (Fig. 5), the removal efficiency of target antibiotics is positively correlated with feed concentration and cycle times. It may be that the higher the initial feed concentration is, the more solutes will be trapped in the inner membrane at the same time, and the more pollutants will be adsorbed and accumulated on the membrane surface and inside, the easier it is to form pollutant groups to cause membrane fouling, which will lead to increased transmembrane resistance, blocked membrane pores, and decreased

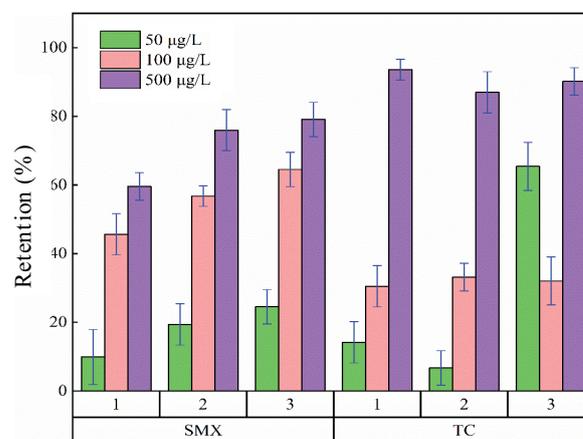


Fig. 5. Removal of SMX and TC by P-10K membranes at different initial feed concentrations (0.10 MPa,  $\text{pH} = 7$ , number of cycles = 3).

flux. However, a certain degree of membrane fouling is conducive to the screening and interception of pollutants by the membrane, thus improving its removal rate [21].

### 3.3.3. pH

pH is the main factor regulating the charge state of membrane surface and organic micro pollutants. This study conducted a pH gradient test to explore the changes in the removal effect of P-10K membrane on SMX and TC at different pH values (Figs. 6 and S5). It can be seen that the removal rate of P-10K on SMX decreases first and then increases in the pH range of 1–9. When  $\text{pH} = 1$ , the removal rate is the highest, and when  $\text{pH} = 5$ , the removal rate is the lowest. This is just the opposite of what Tadkaew et al. [22] found when  $\text{pH} = 5$ , the removal rate of SMX is the highest. This may be due to the different base membranes used. Similarly, the removal rate of TC by P-10K decreases first and then increases, but the overall removal rate is lower than that of SMX, and the trend changes gently. When  $\text{pH} = 9$ , the removal rate is the highest, 54.62%, and when  $\text{pH} = 7$ , the lowest. In addition, comparing the removal effects of three cycles of filtration on two kinds of antibiotics, it

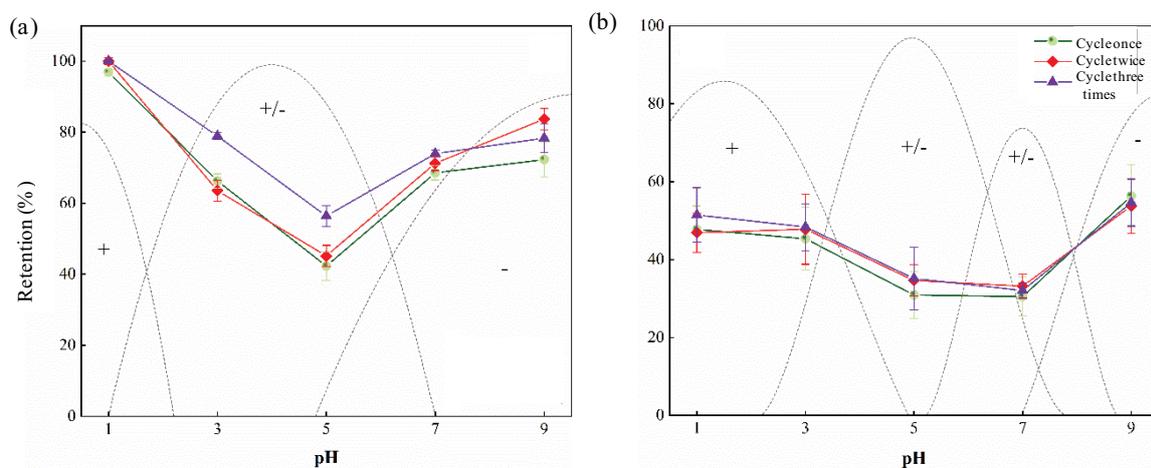


Fig. 6. Relationship between antibiotic removal and pH ((a) SMX and (b) TC; the dashed area illustrates the charge state of the antibiotic in that pH range).

is found that the difference between the removal rates of SMX and TC in three cycles is small, and the contribution of the second and third cycles to the removal rate is less than 10%, which also shows that pH has a more obvious impact on the membrane retention effect.

After the PVDF membrane is cross-linked and modified on the PEI surface, a layer of PEI is uniformly attached to the membrane surface, and the amino groups carried by the PVDF membrane show different charges at different pH values, so P-10K shows different charges [23,24]. Zhao et al. [25] also put forward in the study of PEI cross-linked P84 ultrafiltration membrane that the PEI modified membrane surface showed different strengths of charge under different pH conditions, and showed strong positive charge in the range of pH < 4. With the increase of pH value, the positive charge on the membrane surface weakened between 4–7. When the pH rose to 8–10, the positive charge on the membrane surface was extremely weak. Similarly, the charge of SMX and TC will change with the change of pH.

In a word, the optimal pH range for removal of SMX and TC by P-10K is 1–3 or above.

### 3.3.4. Ionic strength

There are many kinds of metal ions in the actual water body, which usually have a significant impact on the existing forms of pollutants in the water body and the removal process. According to the literature, obtain the concentrations of various common anions and cations in the Huangpu River water system, prepare ion antibiotic solutions with appropriate concentrations, and explore the impact of different ionic strengths on the removal of SMX and TC by P-10K [26]. The cations used mainly include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ , etc.

The change of filtration flux is shown in supplementary Fig. S6. The ionic strength is different. With the extension of filtration time, the membrane flux decreases. Under the conditions of 5, 10 and 20 mmol/L, the flux attenuation after the first cycle is 35.8%, 54.7% and 73.5%, respectively, and the flux attenuation after three cycles is 38.9%, 69.1% and

68.5%, respectively. During this period, the recovery flux after two membrane cleaning was basically close. And the greater the ionic strength, the smaller the flux during membrane filtration. The main reason is that  $\text{FeCl}_3$  added in the simulated water sample causes a great degree of pollution to the membrane during the filtration process. In addition, a variety of salts added to the water sample increase the concentration of solution ions. With the operation of the equipment, reverse solute infiltration is carried out, and the greater the ionic strength is, the greater the driving force of reverse osmosis is, thus reducing the effective osmotic pressure difference on both sides of the membrane. Therefore, adding cation to the antibiotic solution will reduce its filtration flux and the higher the ionic strength is, the greater the attenuation will be [27].

It can be observed from Fig. 7 that after the addition of metal ions, the retention effect of P-10K on SMX and TC is not good as a whole, only 30%–45% at the highest, and the decline rate increases with the increase of cation strength, that is, the retention effect of P-10K on SMX and TC is inversely proportional to the cation strength. In addition, compared with the effect of three cycles of filtration, it was found that multiple cycles had a small increase in the proportion of antibiotic retention. P-10K membrane is a porous medium, and its pores and effective adsorption sites will decrease with the increase of ionic strength, thus reducing the adsorption and removal of antibiotics by the membrane [28,29]. Secondly, the change of ionic strength in the aqueous solution system will affect the charge state of the membrane surface. When the pH is near neutral, the positive charge strength of the P-10K membrane surface is low, and SMX and TC are amphoteric or weakly negative. However, metal cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  will cause the double layer compression and charge shielding on the PVDF membrane surface, weaken the electrostatic interaction between the PVDF membrane and charged antibiotic molecules, and reduce the interception effect [30]. Moreover, due to the difference of dissociation constants, the positive charge intensity of TC is slightly higher than that of SMX in this interval, which can also explain why the retention effect

of TC decreases more when the ionic strength increases. In addition, relevant research shows that the increase of ionic strength in solution will form ion pairs between ions and solute ions, which will reduce the effective concentration of solute ions that can be removed by adsorption and affect the adsorption removal effect [31,32].

For common anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) in river water, the flux change is shown in supplementary Fig. S7. The trend is similar to that under the influence of cations, but the influence of cations on the flux attenuation is higher than that of anions. At the same time, the filtration flux of P-10K membrane decreased with the increase of anion strength. The effect of anion strength on membrane flux is similar to that of cation.

The influence of anionic strength on the removal of SMX and TC by P-10K is weaker than that of cations. As shown in Fig. 8, the removal rate of antibiotics by adding anions is basically higher than that by adding cations at the same strength. This may be because in the aqueous solution, cations generally exist in the form of hydrated ions, and there is a double-layer charge layer on the surface. The positive charge of the outermost layer can be combined with the antibiotics carrying amphoteric groups, thus achieving a higher impact rate. The anion is mainly related to the salt dissolution effect of aqueous solution, which can achieve the goal by affecting the solubility of antibiotics in water. Under different intensities, the removal efficiency of SMX and TC by P-10K is inversely proportional to the ionic strength. In addition, the data also shows that the last two cycles of filtration have a small contribution to the removal rate of antibiotics, and even have a negative contribution rate. There are three reasons for these situations. First, antibiotics are low soluble micro pollutants, while the salts added in the solution are highly soluble solutes. In the same solvent system, highly soluble solutes will seize the water molecules combined with low soluble substances, thus enhancing the hydrophobicity of antibiotic molecules, so reducing the removal effect of membrane antibiotics [33]. In addition, similar to cation, reverse osmosis process reduces

the removal rate of antibiotics while reducing the flux. Third, in the process of the test, under the near neutral or slightly alkaline conditions, the negative groups of SMX and TC gradually occupy the main advantage. At this time, the anion groups with the same negative charge in the solution generate ion competition, which then affects the removal of SMX and TC by P-10K. In addition, Dannon effect, compressed double electric layer and charge shielding may also affect the removal of antibiotics. To sum up, too high ionic strength is unfavorable for PVDF membrane filtration of antibiotics, and the ionic strength of the membrane needs to be controlled in actual operation.

### 3.3.5. Humic acid

There are a lot of humus in surface water (mainly including fulvic acid, fulvic acid, humic acid, etc.), which has a considerable impact on the membrane separation process. These effects include easy to cause membrane hole blockage, reduce membrane flux, increase transmembrane differential pressure, and increase operating costs. Therefore, humic acid is selected as a representative in this experiment to explore the impact of P-10K filtration on target antibiotics in the presence of humic acid.

As shown in Fig. 9, after adding humic acid in the membrane filtration process, the flux drops sharply at the beginning of the membrane separation process. The average initial pure water flux of P-10K membrane in the same batch was  $313.64 \text{ L}/(\text{m}^2\cdot\text{h})$ . When the humic acid concentration was 5, 10, and 20 mg/L, the initial filtration flux decreased to 304.5, 270.6, and  $208.64 \text{ L}/(\text{m}^2\cdot\text{h})$ , respectively, and the initial attenuation reached 3%, 14%, and 33.5%. That is, the higher the humic acid concentration, the higher the attenuation rate and attenuation rate of membrane filtration flux. After three cycles of filtration and cleaning, the final fluxes of the three decreased to 46%, 34.2% and 16% of the initial fluxes, and the corresponding filtration time was extended, which was in direct proportion to the concentration of humic acid added. It can be seen from Fig. S8 that the degree of

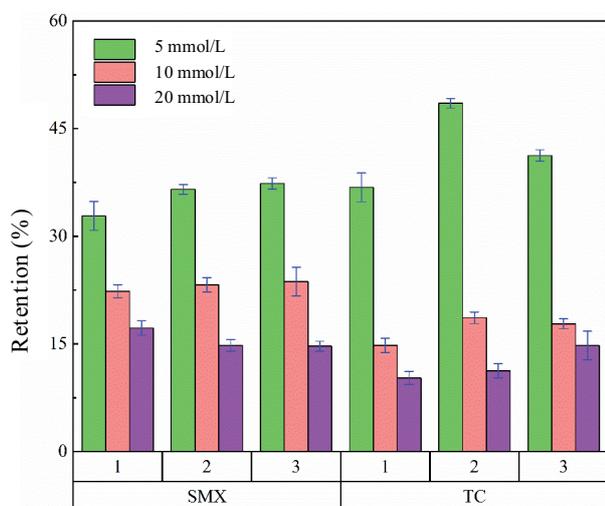


Fig. 7. Effect of cation concentration on antibiotic removal by P-10K (pH = 7, 0.10 MPa, number of cycles = 3).

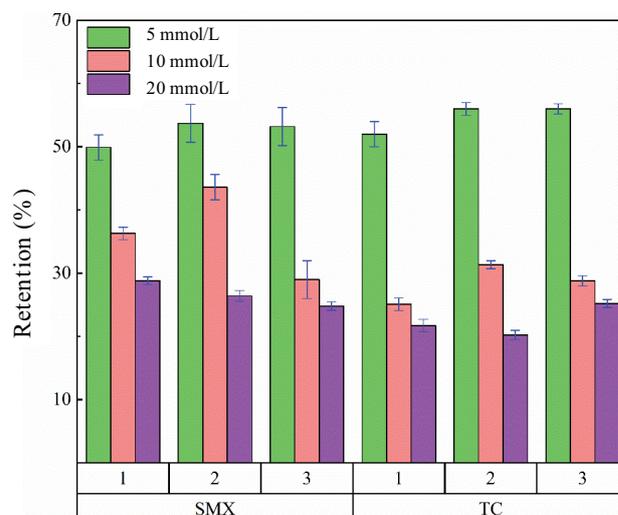


Fig. 8. Effect of anion concentration on antibiotic removal by P-10K ( $C_0 = 100 \mu\text{g}/\text{L}$ , 0.10 MPa, number of cycles = 3).

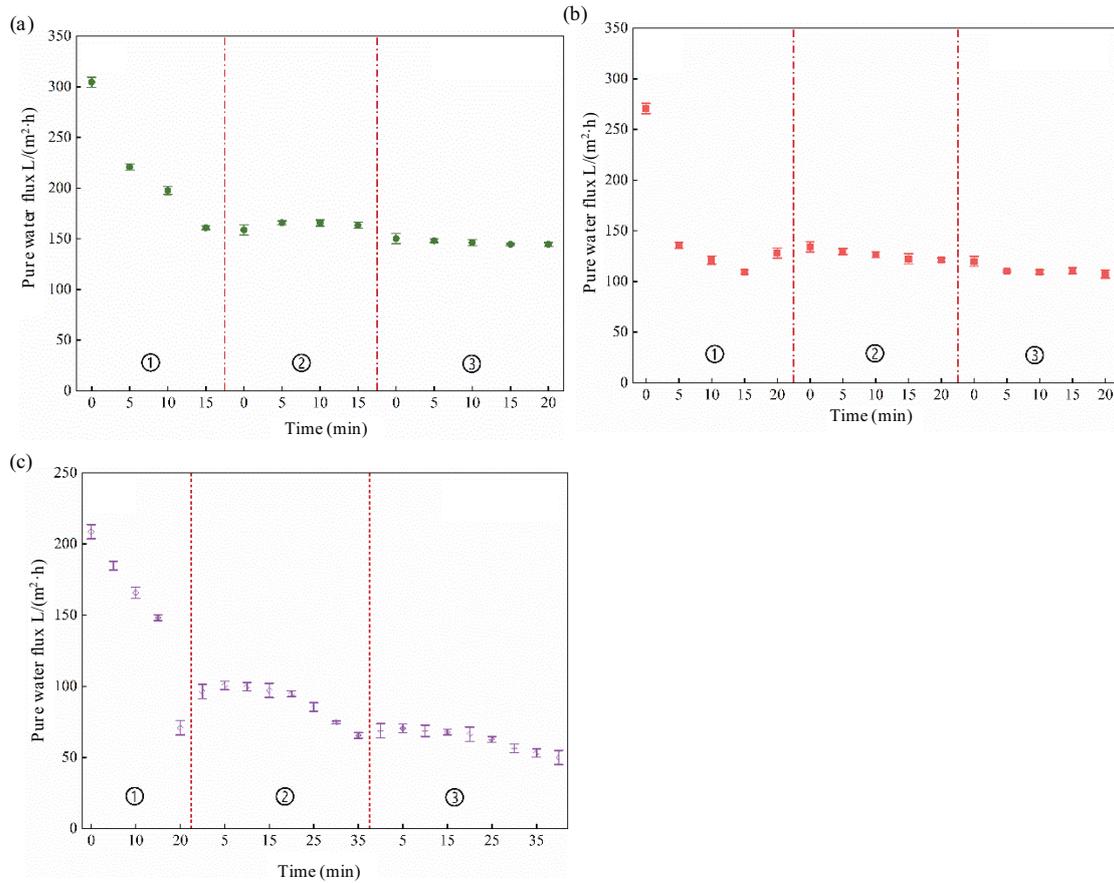


Fig. 9. Effect of humic acid concentrations (a) 5 mg/L, (b) 10 mg/L, and (c) 20 mg/L on membrane filtration flux ( $C_0 = 100 \mu\text{g/L}$ , 0.10 MPa, number of cycles = 3).

membrane fouling will increase with the increase of humic acid addition.

According to the quantitative test results of the water sample of the preserved permeate during the filtration process, humic acid has a positive impact on the retention of target antibiotics by P-10K (Fig. 10). For TC, the TC in the water sample after quantitative detection is lower than the detection limit. From the results of SMX removal, the higher the concentration of humic acid, the higher the removal rate of SMX by P-10K. Without humic acid and pH = 7, the removal rate of SMX by P-10K is only 64.55%. After the concentration of humic acid is 5, 10 and 20 mg/L, the removal rate of SMX by P-10K is 86.8%, 94.3% and 99%, respectively. In addition, by comparing the retention effect of three cycle filtration cycles, it is found that under the presence of humic acid, the primary filtration of P-10K can achieve a higher retention effect, and the subsequent two filters only contribute 9.3%, 18.3%, and 11% to the removal of SMX, combined with the data of flux attenuation. This shows that after adding humic acid, humic acid molecules quickly cause a high degree of membrane fouling to P-10K membrane, resulting in membrane pore plugging and flux reduction, thus creating favorable conditions for intercepting SMX molecules, and improving the removal effect of P-10K on SMX under the space steric effect.

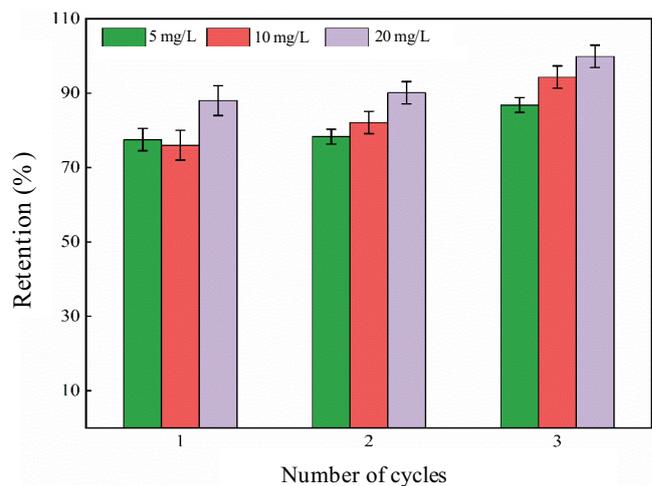


Fig. 10. Effect of humic acid on the removal of SMX by P-10K.

### 3.4. Removal of antibiotics from river water

The flux change of the river water sample filtered by P-10K is shown in Fig. S9. The initial flux is 321 L/(m<sup>2</sup>·h). After a filtration cycle, the flux drops sharply to 70 L/(m<sup>2</sup>·h),

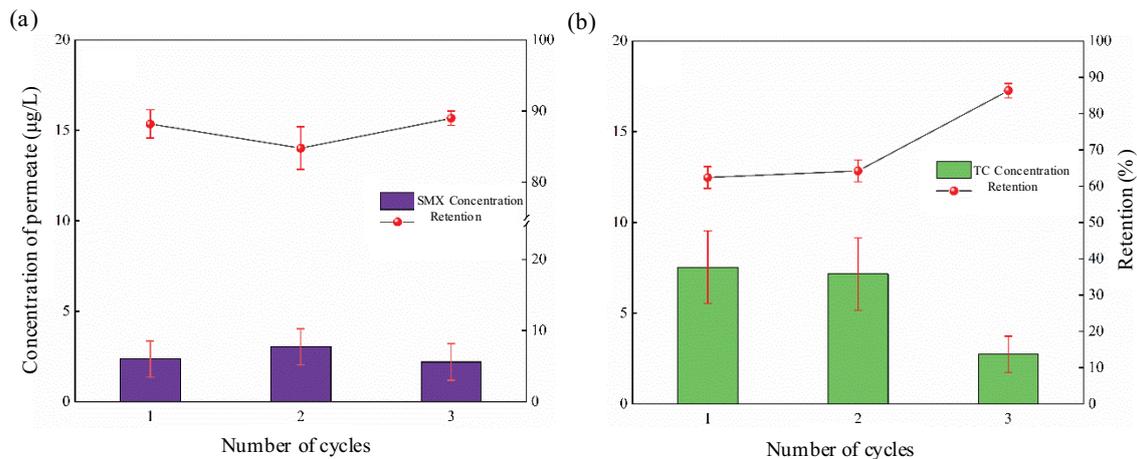


Fig. 11. Retention effect of P-10K on antibiotics in actual water samples ((a) SMX and (b) TC).

with a drop of 78.2%. After two subsequent cycles, the flux is basically stable, and the end flux is 40–50 L/(m<sup>2</sup>·h). The flux variation law when filtering the actual water sample is basically consistent with that in the simulation test, but the flux attenuation ratio of the former is higher than that of the latter. This is because compared with the simulated water sample, the actual river water quality is more complex, which contains various pollutants and is difficult to completely clarify the physical and chemical properties. Therefore, during the filtration process of P-10K, membrane fouling is formed more quickly, so the flux drops sharply, and the overall attenuation is high.

In addition to the sharp decrease of flux, membrane fouling also brings about the improvement of effluent quality. As shown in Fig. 11, after the first cycle is over, the concentrations of SMX and TC in the permeate decreased to 2.36 and 7.53 µg/L, and the interception rates reached 88.2% and 62.4%, respectively. At the end of the three cycles, the retention rates reached 89% and 86.3%, respectively, which was better than the results of simulated water sample filtration test. There are two reasons for this. On the one hand, the substances contained in the actual water sample are more complex, so the membrane fouling layer can be formed more quickly. Moreover, the membrane fouling layer can provide more adsorption points after the formation, and the effect will be better after it is superposed with the porous structure of the membrane, which is conducive to the removal of micro pollutants to a certain extent. On the other hand, the pH of the filtrate is adjusted to 1–3 through HCl and NaOH solutions before the test. According to the results of the previous test, this range is the best range for P-10K to remove SMX and TC, and the electrostatic effect dominates. With the combined effect of other charged substances that may be contained in the actual water sample, SMX and TC can be removed more effectively.

### 3.5. Membrane anti-fouling property test

At present, people pay much attention to membrane fouling, so the anti-fouling performance of membrane materials should also be considered in the application of membrane separation technology. The membrane materials

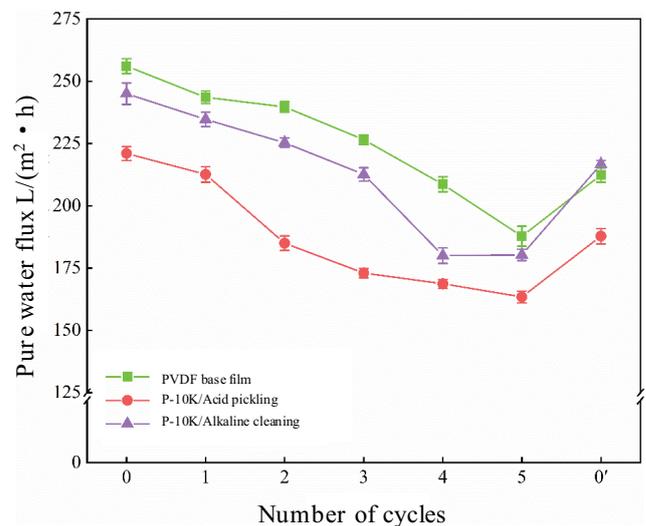


Fig. 12. Flux of membrane filtration and cleaning processes (0.10 MPa and  $C_0 = 100 \mu\text{g/L}$ ).

with good anti-fouling property can run for a longer time under the same conditions, thus prolonging the cleaning cycle, reducing the cleaning times, and achieving the goal of cost saving. Liu et al. [34] proved that CuO-CuS/PVDF membrane has good stability and reusability. Sun et al. [35] found that the blend film formed in the magnetic coagulation bath had better anti-fouling performance to the humic acid solution under ultraviolet light through the performance test of the PVDF modified film. Therefore, this study tested the anti-fouling performance of P-10K. Use the same batch of base membrane and modified membrane for filtration 100 µg/L antibiotic mixed solution, after circulating and filtering for 5 times, rinse with cleaning solution, and then test to recover the flux. As shown in Fig. 12, after five cycles of filtration, the PVDF base membrane flux decreased by 26.7%, and the P-10K modified membrane decreased by 26% and 26.4%, with similar attenuation; However, after the base membrane was washed with pure water, the flux recovered to 212.48 L/(m<sup>2</sup>·h), 83%, while after the P-10K

modified membrane was washed with pH = 5 acid solution and pH = 9 alkali solution, the flux recovered to 187.8 and 216.7 L/(m<sup>2</sup>·h), respectively, with recovery rates of 85% and 92.3%, higher than that of the base membrane washed with clean water, especially the alkali solution, 7.3% higher than that washed with acid solution. The results showed that the anti-fouling performance of PVDF membrane was improved after surface cross-linking modification, indicating that PEI had a positive effect on the anti-fouling performance of the membrane.

#### 4. Conclusions

In this study, a modified membrane was prepared by surface cross-linking modification using PEI modified PVDF base membrane. A single factor variable rotation test was designed to investigate the flux change of the modified membrane under the influence of various factors (pressure, cycle time, pH, feed concentration, ionic strength, etc.) and the removal effect of two target antibiotics (SMX, TC) to determine the relatively optimal membrane separation parameters. The results showed that: (1) Modification temperature and PEI molecular weight have a significant impact on the microstructure and performance of the separation membrane. High modification temperature is not conducive to the flux stability of the separation membrane, and the flux of the modified membrane is inversely proportional to the molecular weight of PEI. The modified membrane prepared at 50°C can have removal rates of >57.5% and >10% for SMX and TC, with P-10K performing relatively best. (2) The SEM results showed that the surface microstructure of PVDF film modified by PEI was smoother, the pore distribution was more uniform, and the cross-sectional morphology showed that its internal structure was denser. Moreover, pore size analysis data show that the average pore size increases, and the pore size distribution becomes more uniform after modification, which is conducive to adsorption interception during the separation process. (3) The data of single factor variable rotation test and correlation analysis showed that the cation strength and humic acid concentration had the greatest influence on the flux and antibiotic retention of the modified membrane. (4) The experiment of removing antibiotics in actual river water by modified membrane showed that the removal rates of SMX and TC in actual water by P-10K reached 88.2% and 62.4%, but it was also accompanied by a large degree of membrane fouling. After the first filtration cycle, the flux decreased by 78.2%, indicating that the actual water body was more complicated, and the anti-fouling property of the membrane should be paid attention to in the application. In the anti-fouling performance test, the membrane flux can be restored to 85% and 92.3% of the initial flux after acid washing and alkali washing, indicating that the anti-fouling performance of the PVDF membrane after surface cross-linking modification has been improved. Polyethyleneimine has a positive effect on the anti-fouling performance of the membrane.

#### Acknowledgments

This work was financially supported by Key Projects of the Joint Fund of the National Natural Science Foundation

of China (U2240205); the USST Program of Science and Technology Development (2018KJFZ117).

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Supporting information

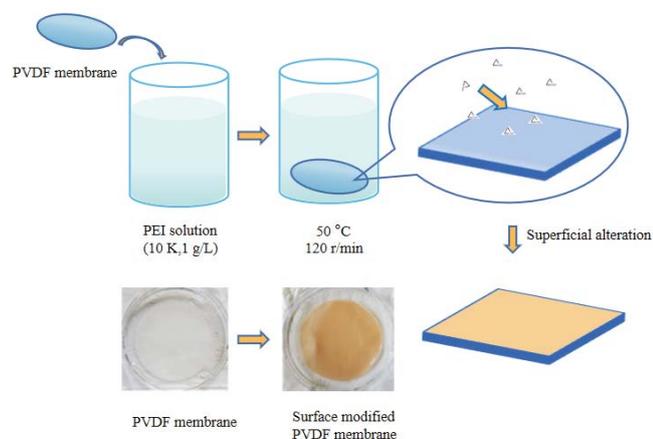


Fig. S1. Surface modification mechanism of PVDF membrane.

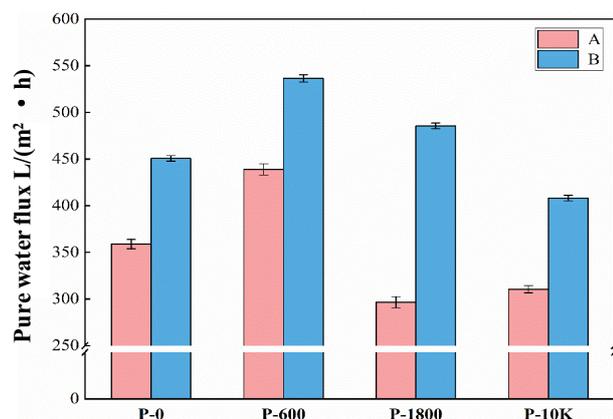


Fig. S2. Water flux of surface cross-linked modified PVDF membrane at different temperatures: A-50°C, B-70°C (0.10 MPa).

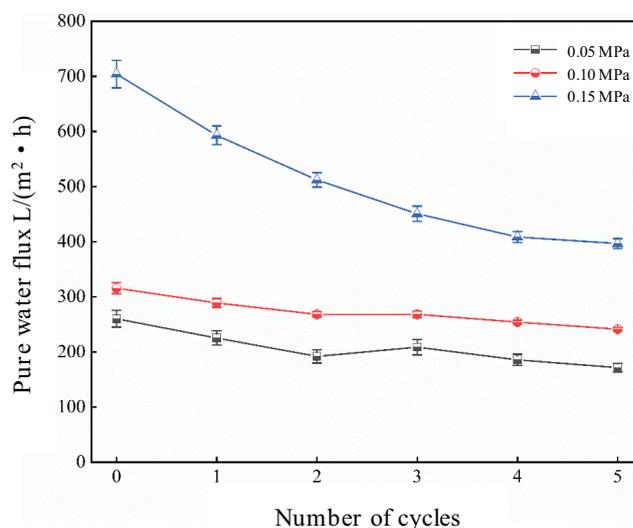


Fig. S3. Variation of circulating filtration flux at different pressures ( $C_0 = 100 \mu\text{g/L}$ ,  $\text{pH} = 7$ ).

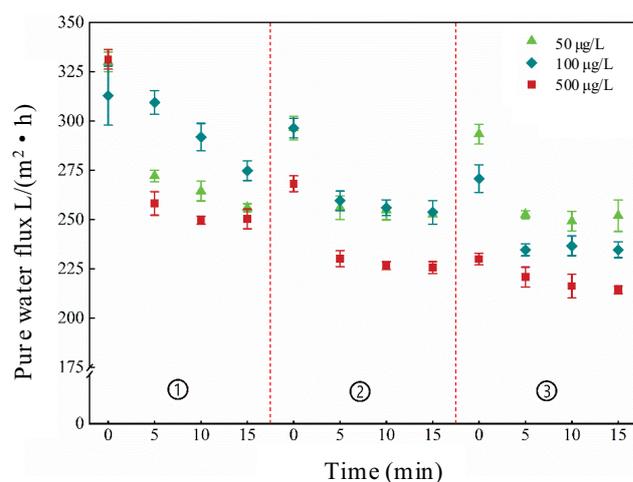


Fig. S4. Variation of flux with initial feed concentration ( $\text{pH} = 7$ , 0.10 MPa, number of cycles = 3).

Table S1  
Evaluation parameters of target antibiotic detection method

Antibiotic	Standard curve	Correlation coefficient	Recovery rate of spiking (%)	Relative standard deviation of spiked recovery	Limit of quantitation (ng/L)
SMX	$y = -0.0382725 + 0.00620518x$	0.9984	83.9	5.7	4.72
TC	$y = -0.00652143 + 0.0024038x$	0.9931	90.4	4.3	2,381.30

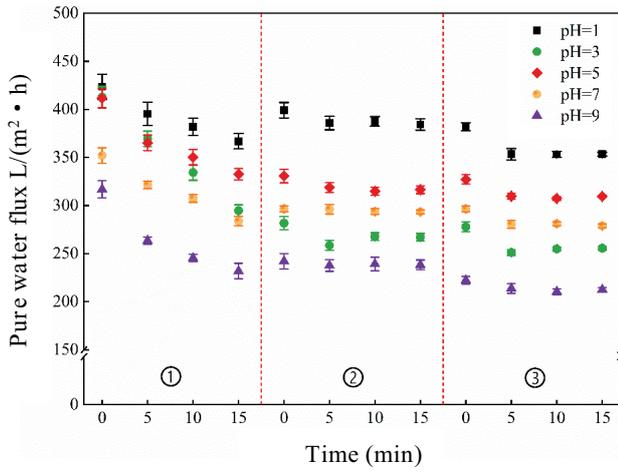


Fig. S5. Flux variation with pH ( $C_o = 100 \mu\text{g/L}$ , 0.10 MPa, number of cycles = 3).

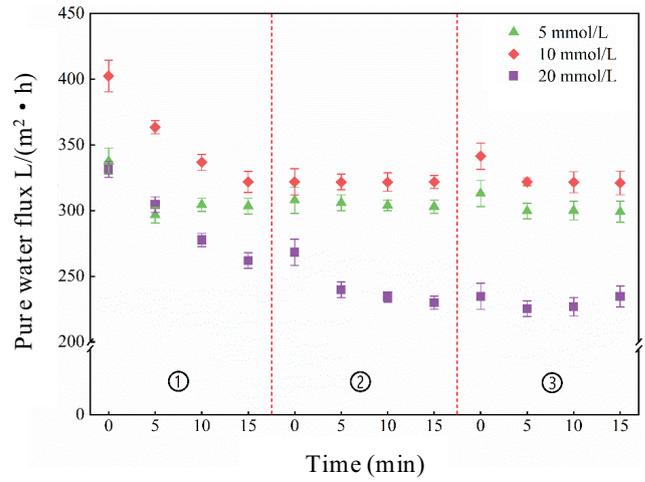


Fig. S7. Effect of the anion concentration on the membrane flux ( $C_o = 100 \mu\text{g/L}$ , 0.10 MPa, number of cycles = 3).

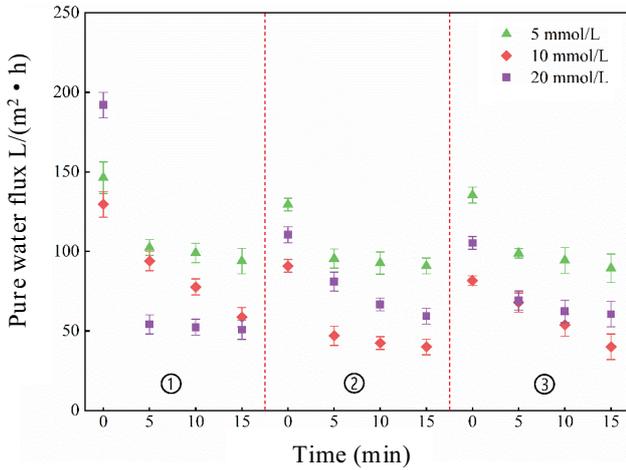


Fig. S6. Effect of cation concentration on membrane flux (pH = 7, 0.10 MPa, number of cycles = 3).

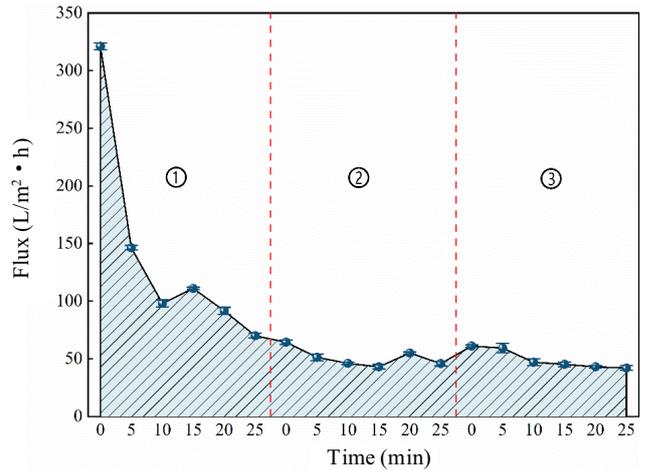


Fig. S9. Flux variation of actual water samples filtered by P-10K (0.10 MPa, numbers of cycle = 3, pH = 1~3).

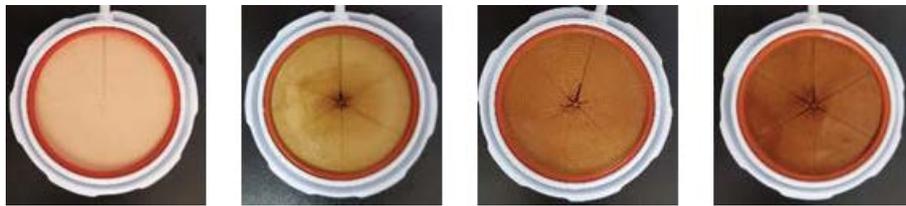


Fig. S8. Effect of humic acid on P-10K filtered antibiotics (P-10K original membrane, filtered membrane samples at humic acid concentration of 5, 10 and 20 mg/L, respectively).