

Study of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ -SAC/PVDF membrane for dye wastewater treatment under “double carbon” target

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ABSTRACT

In the context of “carbon peaking” and “carbon neutralization”, Fe_3O_4 -SAC magnetic carbon, a modified material prepared from fouling peat, was used to enhance the effectiveness of polyvinylidene fluoride (PVDF) membranes in treating dye wastewater. Three dyestuffs, methyl violet, malachite green and Congo red, were tested in terms of water flux, retention rate and pollution resistance to investigate the effect of the modified membranes on the treatment of dyestuffs. The optimal performance of the modified membranes was investigated by varying the ion concentration, initial concentration, and pH value. A group of modified membranes ($\text{TiO}_2/\text{Fe}_3\text{O}_4$ -SAC/PVP/PVDF) was made by adding 1.5 wt.% of TiO_2 to the casting solution and then adding different ratios of SAC- Fe_3O_4 to test the effect. The results showed that when the TiO_2 content was 1.5 wt.% and Fe_3O_4 /SAC content was 0.2 wt.%, the membranes had the best overall performance and could retain 71.24% of methyl violet, 75.62% of malachite green and 65.72% of Congo red, with fluxes of 827.35, 769.45 and 729.53 $\text{L}/(\text{m}^2\cdot\text{h})$, respectively), and the average Fe_3O_4 /SAC preparation using 1 kg of municipal sludge can reduce 1.94 kg of CO_2 emission, while using the modified membrane can reduce approximately 0.80~1.49 kg of CO_2 emission per 1 ton of dye wastewater treated.

Keywords: Ultrafiltration; Membrane; Carbon neutral; Magnetic carbon; Dye wastewater; Titanium dioxide

1. Introduction

The scientific and technological innovation in the fields of “carbon peaking” and “carbon neutral” involves all aspects, and in this context, wastewater treatment and resource utilization will also move towards the direction of “green and low carbonization”. In this context, the development of membrane wastewater treatment technology has brought serious challenges and important opportunities for technology renewal and iteration [1]. In nature, peatland is an important place for atmospheric-terrestrial material exchange, energy exchange, especially carbon exchange, and its strong primary productivity fixes atmospheric carbon into soil in the

form of photosynthesis [2], while the heterotrophic respiration of plants and microorganisms continuously converts greenhouse gas emissions into the atmosphere [3]. In the field of wastewater treatment, dewatered sludge also contains a large amount of organic carbon, which, if left directly in nature without treatment, is converted to the greenhouse gas carbon dioxide by biodegradation in nature and released into the atmosphere. If the sludge is modified by chemical co-sedimentation and converted into Fe_3O_4 /SAC magnetic carbon that can be used to improve the water treatment performance of polyvinylidene fluoride (PVDF) membranes through the pore-forming effect of peat volatilization and analysis during the preparation process [4], it can not only

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fix the organic carbon in the sludge and reduce the emission of greenhouse gases, but also be used to improve the effective treatment of organic dyes in the modified membrane and further reduce carbon emissions. This will help to achieve China's goal of peaking CO₂ emissions by 2030 and achieving carbon neutrality by 2060.

Dye wastewater is a type of industrial wastewater that is difficult to treat because of its high organic content, poor biochemical properties, and high variability in water quality [5–7]. Traditional methods of dye wastewater treatment include: physical, chemical, and biochemical methods to treat [8]. The effect of biodegradation or physical absorption methods is not ideal [9], and other technical methods for traditional wastewater treatment are physical, chemical (electrochemical, photochemical and photocatalytic oxidation, Fenton and Fenton-like oxidation, ozone oxidation), and biological (anaerobic, aerobic, and combined anaerobic–aerobic methods) [10]. Membrane separation technology has the advantages of effective treatment of various organic substances, high water quality of produced water, and simple operation [11]. The experiments used three typical dyes, alkaline cationic methyl violet, malachite green, and anionic ion Congo red, to explore the effect of modified membranes on the treatment of dyes through three tests on water flux, retention rate, and anti-pollution properties.

2. Materials and methods

2.1. Materials and equipment

2.1.1. Main experimental materials

PVDF, analytical purity, Shanghai Sanfu New Materials Co., Ltd., (Shanghai, China); polyvinylpyrrolidone K30 (PVP), analytical purity, Tianjin Chemical Reagent Co., Ltd.; concentrated hydrochloric acid (HCl), analytical purity, Chengdu Kelong Chemical Reagent Factory (China); dimethylacetamide (DMAc), powdered activated carbon (PAC) 300–700 nm, sodium hydroxide (NaOH), 95% ethanol, methyl violet, malachite green, Congo red, analytical purity, Tianjin Comio Chemical Reagent Co., (Tianjin, China) self-made.

2.1.2. Main experimental equipment

Electronic Balance, FA-2004, Mettler-Toledo Instruments (Shanghai) Co., Ltd; Thermostatic Heating Magnetic Stirrer, DF-101S, Gongyi Yuhua Instruments Co., Ltd; Thermostatic Shaker, SHY-100, Changsha Xiang Yi Centrifuge Instruments

Co., Ltd; Blast Dryer, DZF-620, Shanghai Yao's Instrument and Equipment Factory; UV Spectrophotometer, UV757CRT, Ltd. Shanghai Precision Scientific Instruments Co., Ltd; Flat membrane Small Timer, FiowMem0021-HP, Xiamen Fumei Technology Co., Ltd; field-emission scanning electron microscopy, Hiitachi-s-470, Hitachi, Japan.

2.2. Preparation of Fe₃O₄/SAC

In this study, Fe₃O₄/SAC magnetic carbon was prepared by chemical co-precipitation method [12–15]. Dissolve NiSO₄·6H₂O and FeCl₃·6H₂O in ultrapure water in a molar ratio of 1:2, and stir magnetically for 10 min to make the mixture homogeneous, and the resulting solution is recorded as A. A certain proportion of peat was added to solution A. The main metal element contained in peat is Fe [16], and the sludge activated carbon (SAC) was shaken for 10 min to mix well with solution A. In addition, a certain amount of NaOH was dissolved in ultrapure water and recorded as solution B. Solution B was added to A drop by drop with a rubber-tipped dropper under the condition of magnetic stirring, stirred for 20 min, reacted at a suitable temperature for a certain time, cooled, filtered, washed and dried at 105°C for 4 h, and Fe₃O₄/SAC was obtained.

2.3. Preparation of TiO₂/Fe₃O₄-SAC magnetic mass carbon/PVP/PVDF membrane

Take 200 mL DMAc and add it into 250 mL conical flask. And weighed 18.0 wt.% PVDF powder, 5.0 wt.% PVP, 1.5 wt.% TiO₂ and 0.2 wt.% SAC-Fe₃O₄ mixed and dissolved in DMAc, respectively, and sonicated for 30 min to make them fully dissolved. Then put the rotor into the oil bath at 80°C for 1 h, adjust the temperature to 60°C and continue stirring for 12 h to get the homogeneous PVDF solution. Then put it into the oven at 60°C for 12 h to get the stable cast membrane solution. The cast membrane solution was evenly scraped on a glass plate with a 200 μ membrane maker, waited in air for 30 s, and then quickly immersed in deionized water for phase conversion. After membrane formation, the membranes were placed in fresh deionized water and the water was changed every 8 h interval and kept for 7 d continuously and then stored for use. Studies have shown that the PVDF membranes prepared with different concentration ratios have different structures [17], and the experimental ratios of TiO₂/SAC-Fe₃O₄/PVP/PVDF ultrafiltration membranes used in this study are shown in Table 1.

Table 1
Experimental ratios of TiO₂/SAC-Fe₃O₄/PVP/PVDF ultrafiltration membrane

Number	Polymers	Dispersants	Additives	Solvent	Gel bath
M0	PVDF (18%)	PVP (5%)	TiO ₂ /SAC-Fe ₃ O ₄ (0%/0%)	DMAc	Pure water
D1	PVDF (18%)	PVP (5%)	TiO ₂ /SAC-Fe ₃ O ₄ (1.5%/0.05%)	DMAc	Pure water
D2	PVDF (18%)	PVP (5%)	TiO ₂ /SAC-Fe ₃ O ₄ (1.5%/0.10%)	DMAc	Pure water
D3	PVDF (18%)	PVP (5%)	TiO ₂ /SAC-Fe ₃ O ₄ (1.5%/0.15%)	DMAc	Pure water
D ₄	PVDF (18%)	PVP (5%)	TiO ₂ /SAC-Fe ₃ O ₄ (1.5%/0.20%)	DMAc	Pure water
D5	PVDF (18%)	PVP (5%)	TiO ₂ /SAC-Fe ₃ O ₄ (1.5%/0.25%)	DMAc	Pure water
D6	PVDF (18%)	PVP (5%)	TiO ₂ /SAC-Fe ₃ O ₄ (1.5%/0.30%)	DMAc	Pure water

2.4. Test method

Prepare several solutions of methyl violet, malachite green and Congo red dyes at 10 mg/L, install the membranes for testing the retention rate in the testing machine, measure the retention rate of the membranes with 10 mg/L of methyl violet solution instead of pure water, run at 0.2 Mpa pressure, collect the solutions at 10, 20, and 30 min, take 1 mL with the cuvette, respectively, at the wavelength of 552 nm. The absorbance was tested, and then calculated using the following formula, three membranes were taken for each ratio, and each membrane was tested three times, after which the average value was taken and the retention rate was calculated according to the formula.

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \quad (1)$$

where r_m is the average pore size of the membrane (nm); ε is the porosity (%); η is the viscosity of water at room temperature (8.9×10^{-4} Pa·s); l is the thickness of the membrane (m); Q is the volume of filtered water per unit time (m^3/s); A is the effective filtration area of the membrane (m^2); ΔP is the operating pressure (MPa). Afterwards, the methyl violet dye was replaced with malachite green and Congo red dyes, and the absorbance was adjusted to test the retention of methylene blue and Congo red, respectively. Experiments were conducted with different ratios of membranes separately, and the membrane ratio with the best treatment effect was obtained.

2.5. Test principle

Since the polymer (PVDF), the solvent and the modifier are not mutually soluble at room temperature, the components are dissolved by heating and stirring. When the cast membrane liquid system meets the Gibbs free energy less than 0 ($\Delta G_m < 0$), entropy change (ΔS) to temperature (T) of the second-order partial derivative less than or equal to 0 and other thermodynamic phase fusion conditions, the cast membrane liquid system has thermodynamic stability, the components are uniformly distributed.

Subsequent preparation was performed using the immersion precipitation phase transformation method. When the thermodynamically stable cast membrane liquid system is immersed in the gel bath, the mutual diffusion and exchange between the solvent and non-solvent are used to make the solvent and non-solvent diffuse each other at the cast membrane liquid/gel bath interface. When the exchange between solvent and non-solvent reaches a certain level, the cast membrane solution becomes a thermodynamically unstable system and phase separation occurs [18].

3. Results and discussion

3.1. Water flux retention rate test of composite membrane on printing and dyeing wastewater

From Figs. 1–3 it can be seen that when the $TiO_2/SAC-Fe_3O_4$ content is 1.5%/0.2%, the membrane has the best test results, with 71.24% retention of methyl violet and

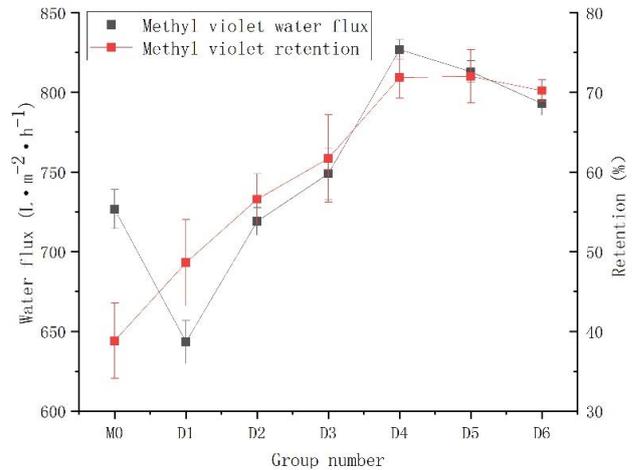


Fig. 1. Membrane flux and retention rate (methyl violet).

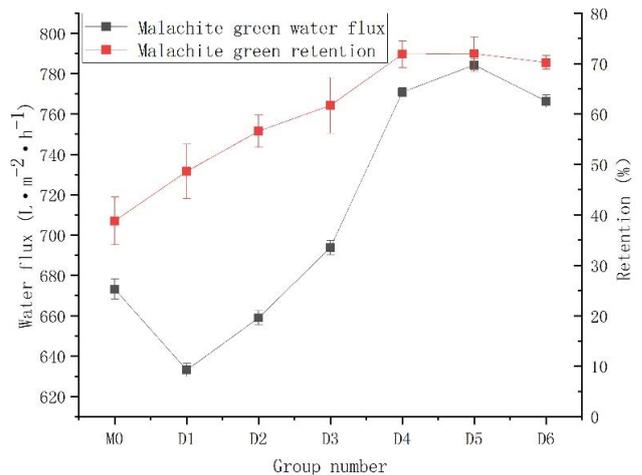


Fig. 2. Membrane flux and retention rate (malachite green).

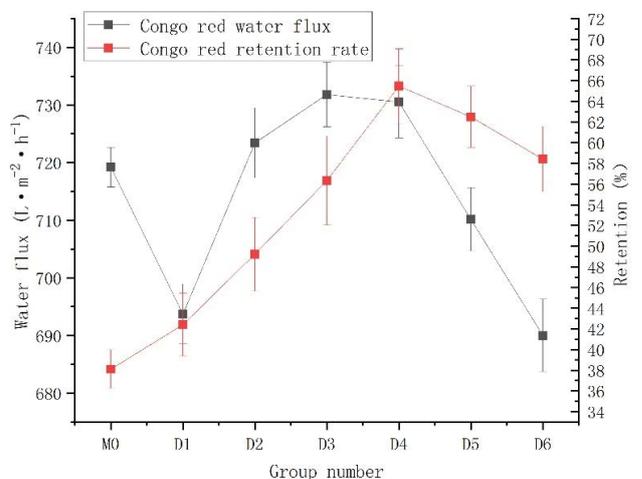


Fig. 3. Membrane flux and retention rate (Congo red).

827.35 L/(m²·h) flux; 75.62% retention of malachite green and 769.45 L/(m²·h) flux; 65.72% retention of Congo red and the flux was 729.53 L/(m²·h). This is due to: (1) the formation of a strong hydrogen bond between SAC-Fe₃O₄ and dye molecules, which enhances hydrophilicity and thus improves the water flux through the membrane. The hydrophilic functional groups form a hydration layer on the membrane surface, allowing only water molecules to enter, thus enhancing the retention rate of the membrane; (2) the aggregation of dye molecules forms a concentration polarization phenomenon on one side of the membrane [19], which prevents dye molecules from passing through the membrane pores; (3) SAC-Fe₃O₄ has an adsorption effect on dye molecules, and when the content of SAC-Fe₃O₄ is too high, it forms an agglomeration on the membrane surface, causing the dye decrease in flux.

3.2. Analysis of the anti-pollution properties of modified membranes

3.2.1. Flux recovery rate

As shown in Figs. 4–6, the best flux recovery was obtained for the modified membranes in group D₄ with a flux recovery rate (FRR) of 62.12% for methyl violet, which was 12.88% higher than that of the pure membrane, and 65.56% for malachite green, which was 19.16% higher than that of the pure membrane. The FRR for Congo red was 83.25%, which was 26.54% higher than that of pure membrane. This is because the pure PVDF membrane surface pores are dense and the membrane pore size is small, and the pollutants gather in the membrane pore size after passing through the dye wastewater, which leads to the reduction of membrane flux recovery rate. The composite particle TiO₂/SAC-Fe₃O₄ can change the membrane pore size, so that the membrane pore distribution is uniform and the pore size becomes larger to improve the membrane water flux. TiO₂/SAC-Fe₃O₄ composite additive contains a large number of hydrophilic functional groups, and it is known that hydrophilic functional groups can improve the resistance of the membrane to contamination after a study [20].

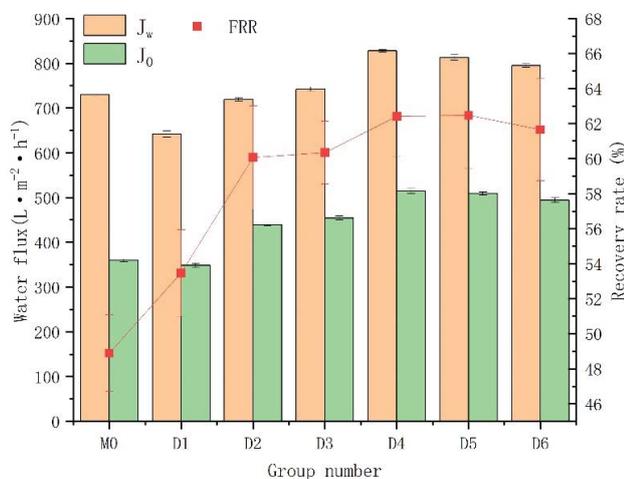


Fig. 4. Flux recovery rate of membrane (methyl violet).

3.2.2. Flux decay rate

Figs. 7–9 show that when TiO₂/SAC-Fe₃O₄ is used as an additive, it can significantly improve the membrane's resistance to contamination. The modified membranes of group D₄ had the best anti-pollution performance, and the reversible contamination rate (R_r) for methyl violet was 54.32% (30.3% for pure membrane) and the irreversible contamination ratio (R_{ir}) was 37.65% (69.42% for pure membrane); the reversible contamination rate for malachite green was 57.85% (41.27% for pure membrane) and the irreversible contamination ratio was 35.23% (59.21% for pure membrane); the reversible contamination rate for the reversible contamination rate of Congo red was 53.45% (37.42% for pure membrane), and the irreversible contamination ratio was 43.21% (63.35% for pure membrane). The reason is that when the additive content is too high, it will lead to a lower mass transfer rate between solvent and non-solvent and pore blockage, thus reducing the membrane's resistance to contamination. The best effect on dye solution treatment is achieved when the TiO₂/SAC-Fe₃O₄ content

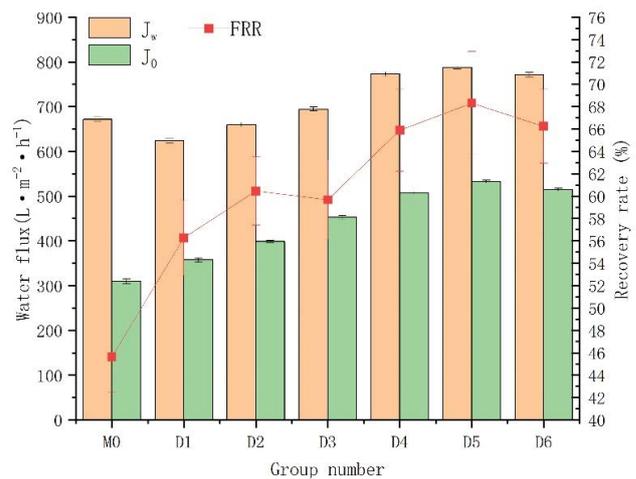


Fig. 5. Flux recovery rate of membrane (malachite green).

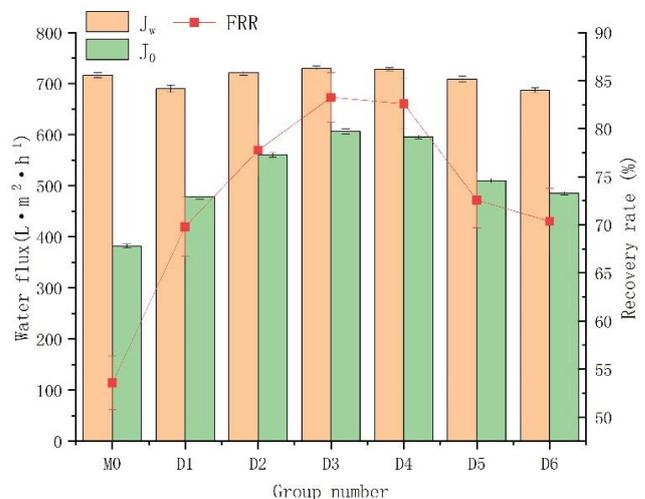


Fig. 6. Flux recovery rate of membrane (Congo red).

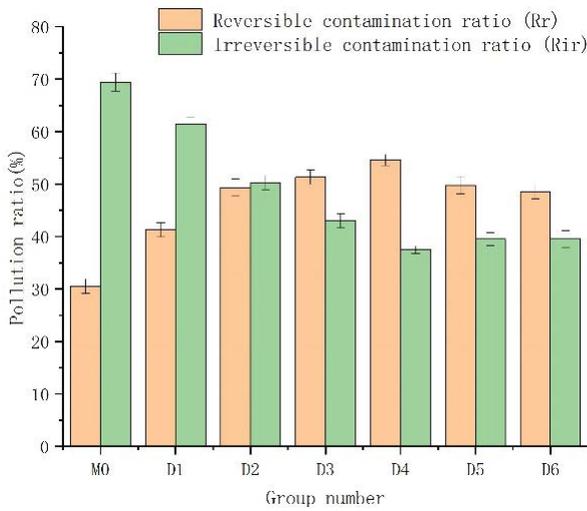


Fig. 7. Flux decay rate of membrane (methyl violet).

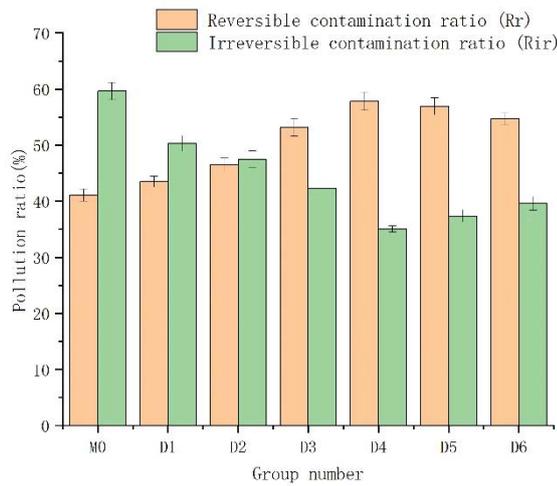


Fig. 8. Flux decay rate of membrane (malachite green).

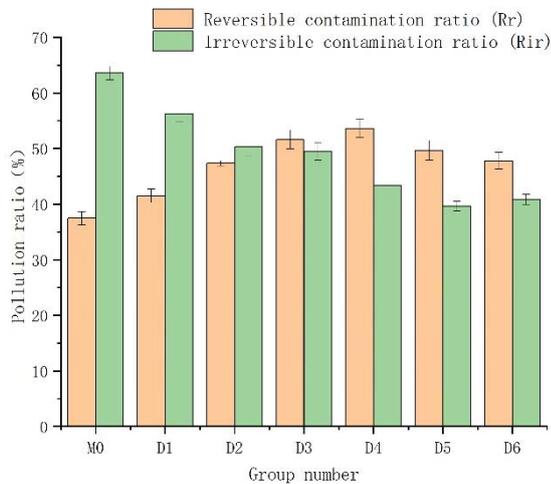


Fig. 9. Flux decay rate of membrane (Congo red).

is 1.5%/0.2%, so the following tests will be performed with the D₄ group modified membranes.

3.3. Effect of different conditions on membrane retention performance

3.3.1. Effect of different initial concentrations on the retention performance of dyes

Figs. 10–12 show that the retention performance of the modified membranes for the cationic dyes methyl violet and malachite green tends to decrease with increasing concentration; the retention of the anionic dye Congo red solution increases. The best retention of methyl violet and malachite green dyes at a concentration of 10 mg/L was 68.45% and 62.34%, respectively, an increase of 20.93% and 19.08% over the pure membrane (47.52% and 43.26%); the best retention of Congo red dyes at a concentration of 40 mg/L was

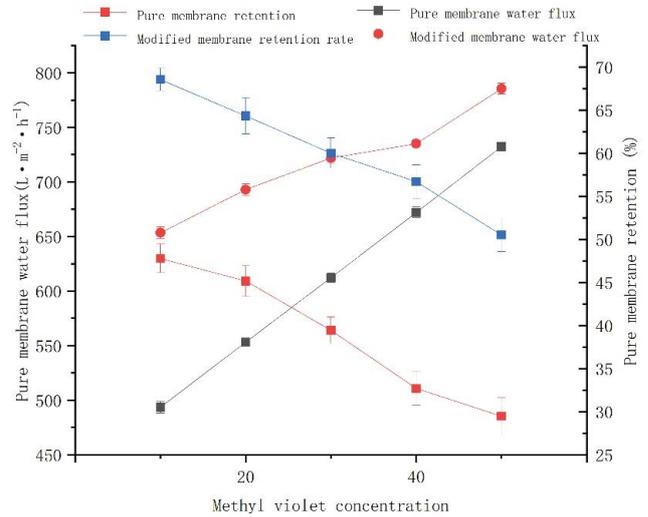


Fig. 10. Effect of initial concentration (methyl violet).

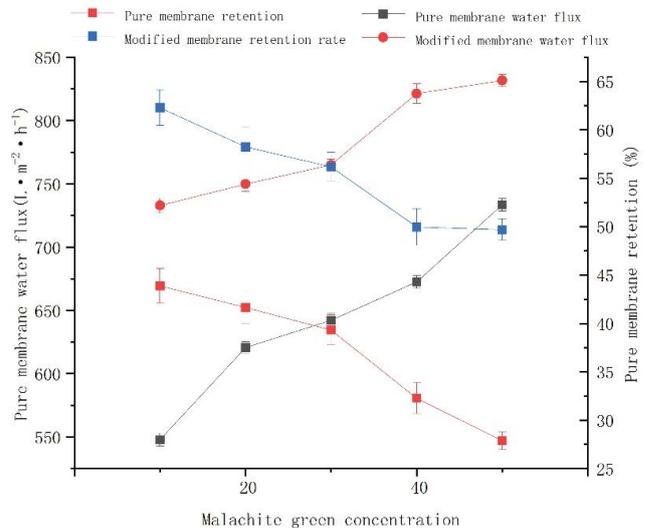


Fig. 11. Effect of initial concentration (malachite green).

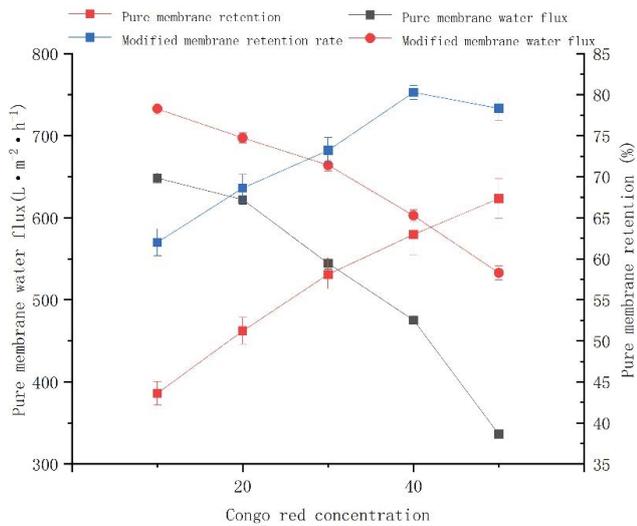


Fig. 12. Effect of initial concentration (Congo red).

79.21% (62.43% for the pure membrane). This is because cationic dyes generate positively charged colored particles in solution that are more easily adsorbed on the surface of the membrane. With the increase of the initial concentration of dye molecules, the contamination of the membrane surface is accelerated, causing the blockage of the membrane pores and leading to a decrease in the retention rate. It also tends to form a concentration difference phenomenon on one side of the membrane [21]. The anionic dyes have the effect of active agents, so the retention of Congo red dye is improved with increasing concentration. The composite modifier TiO₂/SAC-Fe₃O₄ contains a large number of hydrophilic functional groups and easily forms a gel layer through which only water can pass, thus enhancing the water flux of the modified membrane [22].

3.3.2. Effect of different pH values on dye retention performance

Figs. 13–15 show that the retention performance of the modified membranes for the cationic dyes methyl violet and malachite green showed a decreasing trend with increasing PH; the retention of the anion Congo red showed an increasing trend. The best retention of methyl violet and malachite green dyes at pH = 4 was 73.21% and 65.93%, respectively, which were 16.84% and 22.78% higher than that of the pure membrane (56.37% and 43.15%); the best retention of Congo red dyes at pH = 10 was 72.1%, which was 31.09% higher than that of the pure membrane (41.01%) 31.09%. Mainly because the pH value can change the catalyst particles on the membrane surface and the nature of the membrane surface, when pH < 6.3, TiO₂ particles on the membrane surface are positively charged, which reduces the adsorption of cationic dyes on the membrane surface, and the charge groups will lead to a looser membrane surface due to electrostatic repulsion, lower resistance and lower retention rate. When pH > 6.3, TiO₂ particles on the membrane surface are negatively charged, which promotes the adsorption of cationic dyes on the membrane surface and increases the resistance of the

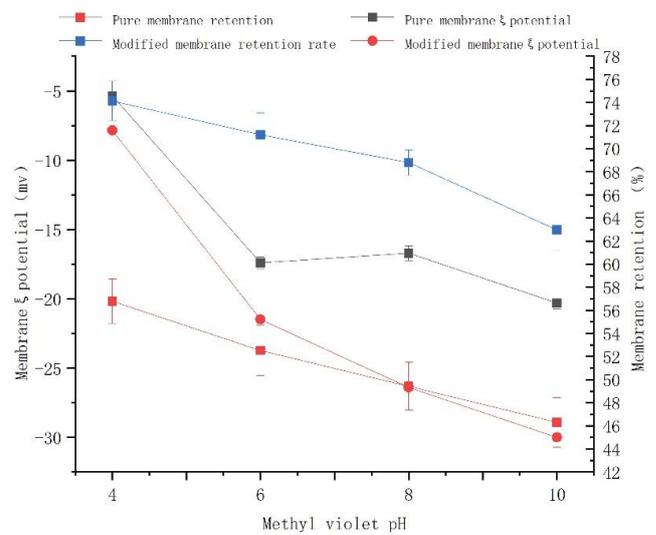


Fig. 13. Effect of pH value (methyl violet).

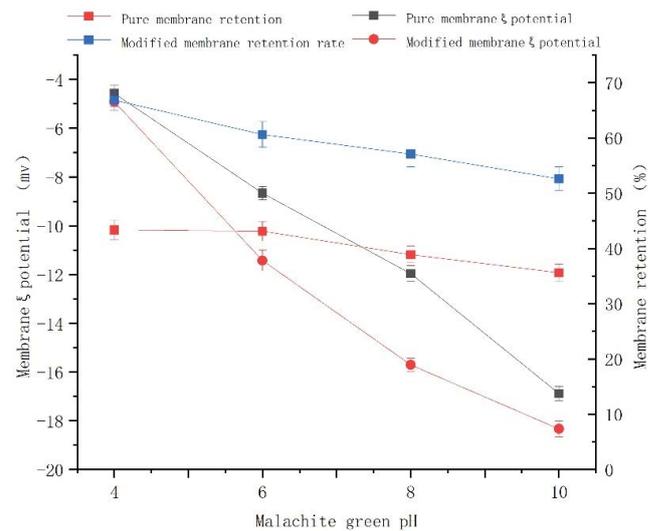


Fig. 14. Effect of pH value (malachite green).

membrane, and the membrane surface is prone to agglomeration of particles, thus blocking the membrane pores and reducing the retention rate. The anionic dye Congo red is negatively charged and is more easily repelled by the negatively charged TiO₂ particles on the membrane surface, so that the dye molecules cannot come into contact with the membrane surface and do not easily pass through the membrane, thus making the retention rate increase.

3.3.3. Effect of different ion concentrations on the retention performance of dyes

Existing studies have shown that inorganic salt ions can have an effect on membrane performance [23]. The inorganic salt used in this study was NaCl at concentrations of 0, 0.3, 0.6, and 0.9 mol/L. Figs. 16–18 show that the retention rate generally tended to increase as the ion concentration

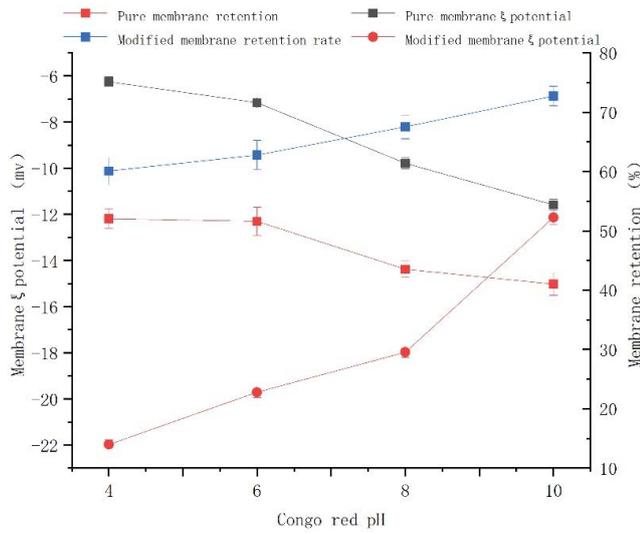


Fig. 15. Effect of pH value (Congo red).

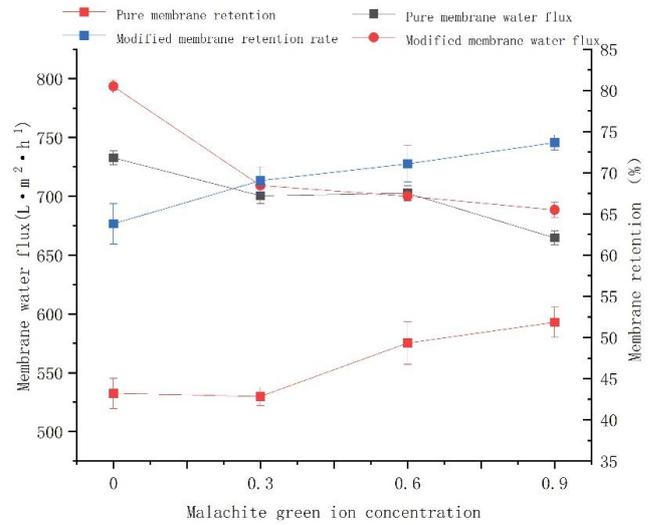


Fig. 17. Effect of ion concentration (malachite green).

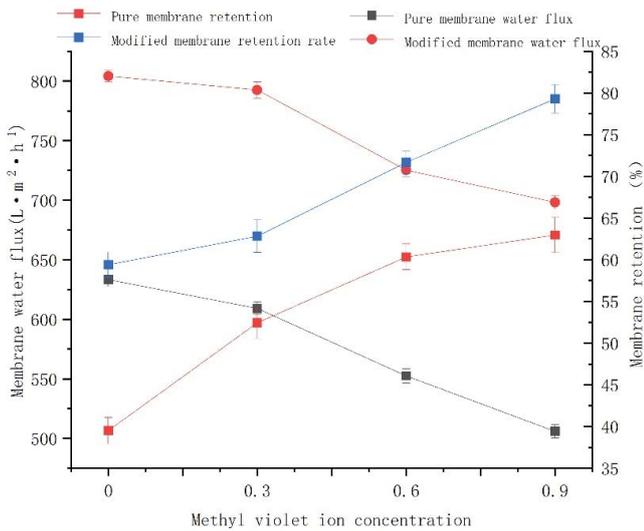


Fig. 16. Effect of ion concentration (methyl violet).

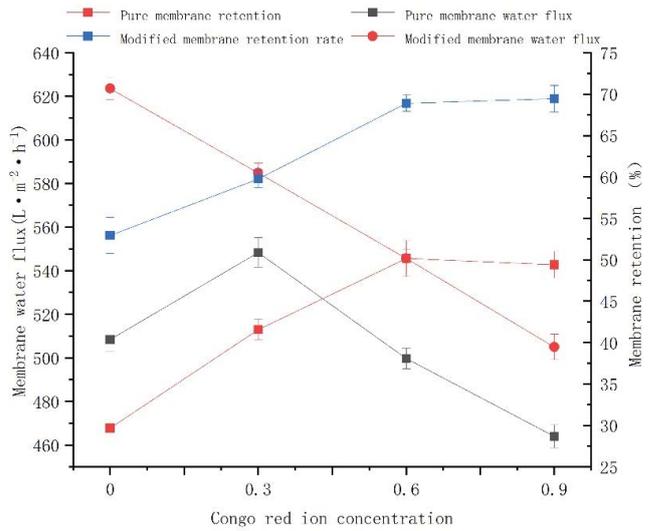


Fig. 18. Effect of ion concentration (Congo red).

increased. The modified membranes showed the best retention of methyl violet, malachite green and Congo red dyes at ion concentrations of 0.9 mol/L, with retention rates of 79.66%, 73.01% and 69.41%, respectively, which were 16.49%, 21.76% and 19.65% higher than those of pure membranes (63.17%, 51.25% and 49.76%). Therefore, compared to pure membranes, when the ion concentration increases, the retention of the three dyes by the membrane increases and the flux decreases. This is due to the fact that the concentration of NaCl in the solution is many times higher than that of the dyes, and the large amount of Na⁺ introduced into the solution will reduce the number of water molecules around the otherwise attracted polar or charged groups of the dyes, resulting in a weakened hydrophilicity of the dyes and a decrease in water flux. With the increase of inorganic salt ions, the retention rate increases due to the large number of ions accumulated on the membrane surface and in

the membrane pores. Also due to the increase of ions in the membrane pores, an electroviscosity effect is formed, which increases the viscosity of the solution and the resistance of the dye solution through the membrane increases and the retention rate rises [24]. When NaCl causes an increase in hydrophobicity of the dye to a greater extent than its reduction of the electrostatic gravitational force between the SAC-Fe₃O₄ surface and the dye, the rate of cationic dye adsorption by SAC-Fe₃O₄ increases due to the increase in ion concentration [25].

3.4. Evaluation of membrane anti-pollution performance

The flux recovery of the contaminated membranes was performed by physical and chemical cleaning [26]. Figs. 2–19 show that the flux recovery rate of the membranes after contamination with all three dyes began to decrease with

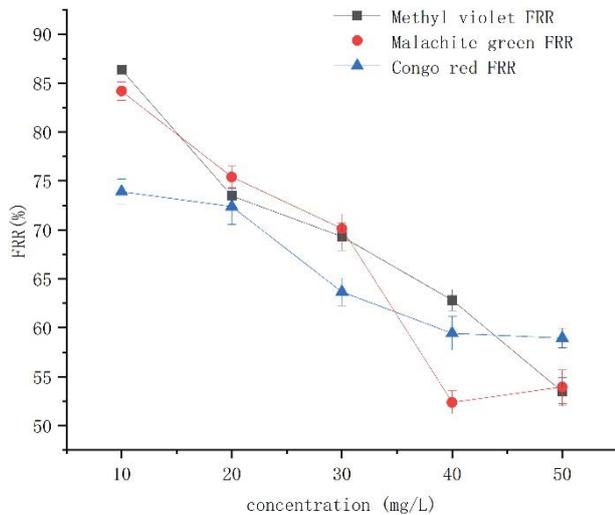


Fig. 19. Different initial concentrations.

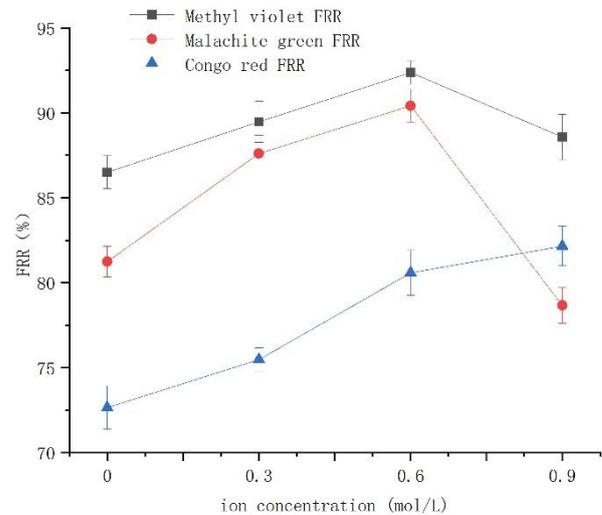


Fig. 21. Different ion concentrations.

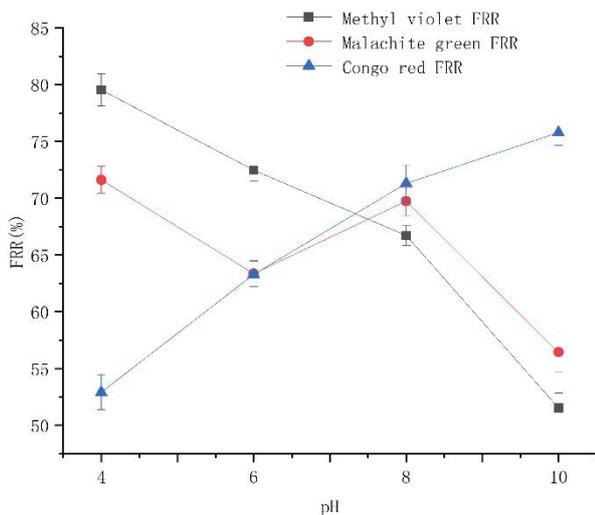


Fig. 20. Different pH values.

increasing initial concentrations. This is due to the fact that when the dye molecule concentration increases, it destroys the gel layer formed by the hydrophilic groups in TiO_2 and $\text{SAC-Fe}_3\text{O}_4$, which makes the membrane pores blocked and the flux recovery rate decreases. Therefore, the anti-pollution performance was optimal when the dye concentration was 10 mg/L, at which time the membrane flux recovery rates after contamination by methyl violet, malachite green and Congo red were 86.52%, 84.31% and 73.26%, respectively. Figs. 2–20 show that the flux recovery rate of the modified membranes contaminated by methyl violet and malachite green showed a decreasing trend when the pH value increased, and the flux recovery rate of the two contaminated membranes was optimal at pH = 4, 79.31% and 71.23%, respectively; the flux recovery rate of the membrane contaminated by Congo red showed an increasing trend, and the flux recovery rate of the contaminated membrane was optimal at pH = 10, 75.89%. This is due to the positive

charge of the cationic dye, and as the pH increases, the ξ potential of the modified membrane gradually decreases and generates a negative charge and then interacts with the cationic dye, causing the contaminants to be adsorbed on the membrane surface causing the membrane pores to be blocked; the anionic dye has a negative charge, and as the pH increases and the ξ potential of the modified membrane decreases, it generates a negative charge and then repels each other with the anionic dye, so that the contaminants are no longer in direct contact with the membrane surface, which enhances the membrane resistance to contamination. The anti-pollution property of the membrane is enhanced. Figs. 2–21 show that the flux recovery rate of the modified membranes also gradually increased after the ion concentration increased, and the best anti-pollution performance of the modified membranes was achieved when the ion concentration was 0.6 mol/L, and the flux recovery rates were 90.32% and 88.43% after contamination by methyl violet and malachite green, respectively; in the Congo red solution, the best anti-pollution performance of the membranes was achieved when the ion concentration was 0.9 mol/L, and the flux recovery rate was 82.13%. The reason is that the ion concentration in the solution increases, the inorganic salt ions increase, and a large number of ions accumulate on the membrane surface and in the membrane pores, and when rinsing, NaCl is easily dissolved in water, which makes the flux recovery rate of the modified membrane increase.

3.5. Field emission scanning electron microscopy (SEM) characterization of the modified membranes of group D_4

As shown in Figs. 22 and 23, the finger pore structure is more regular after the addition of $\text{TiO}_2/\text{SAC-Fe}_3\text{O}_4$, and even sponge-like pores appear at the bottom. This is due to the presence of many oxygen-containing functional groups in $\text{SAC-Fe}_3\text{O}_4$. Such functional groups use the coordination effect between $\text{SAC-Fe}_3\text{O}_4$ and TiO_2 to promote the crystallization of PVDF, increase the number of pores on the surface

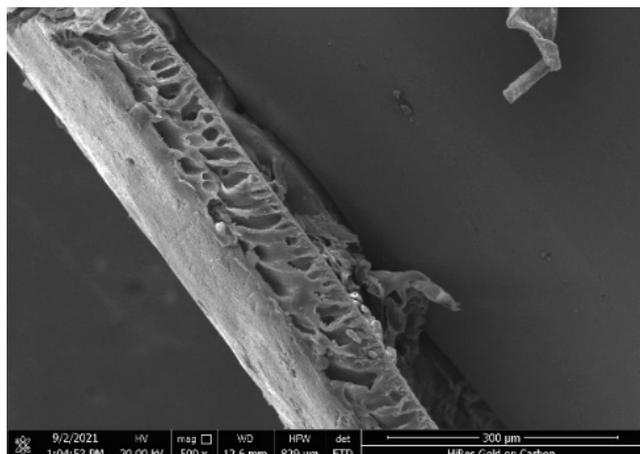


Fig. 22. Electron microscope images of modified membrane cross-section of group D₄.

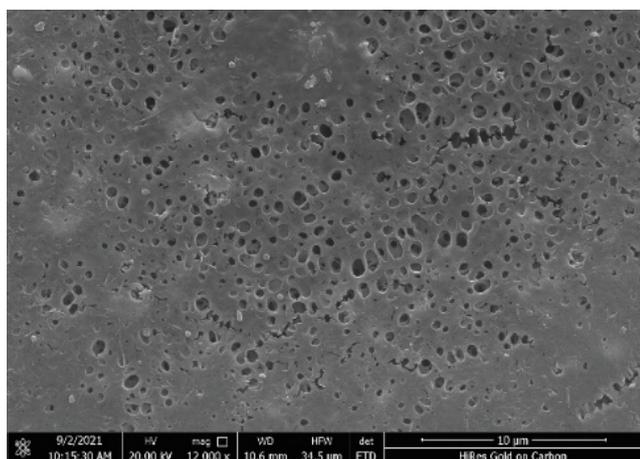


Fig. 23. Electron microscope images of modified membrane surface in group D₄.

of ultrafiltration membranes, and increase the number and size of finger-like pores and surface roughness. The introduction of hydrophilic functional groups without changing the basic structure of the membrane improves the water flux and retention rate of the membrane.

3.6. Contribution of modified membranes to carbon emission reduction

3.6.1. Contribution of preparation of Fe₃O₄/SAC magnetic carbon to carbon emission reduction

Since the sludge from municipal wastewater treatment plants contains more carbon, the objective conditions for the preparation of activated carbon are available. Therefore, the raw material for the preparation of Fe₃O₄/SAC magnetic carbon is mainly taken from the sludge after municipal wastewater treatment, which has a high carbon content, and its composition can be expressed by the molecular formula C₅H₇NO₂ with a theoretical carbon content of about 53% [27]. For every 1 kg of municipal sludge used to prepare

Table 2
Retention rates under different dye conditions

	Methyl violet retention rate	Malachite green retention rate	Congo red retention rate
Different initial concentrations	68.45%	62.34%	79.21%
Different pH values	73.21%	65.93%	72.10%
Different ion concentrations	79.66%	73.01%	69.41%
Average retention rate	73.77%	67.09%	73.57%

Table 3
Concentration equivalents of the three dyes

	Concentration equivalent
Methyl violet, mg/L	404.76
Malachite green, mg/L	332.03
Congo red, mg/L	1000

Fe₃O₄/SAC magnetic mass carbon, 1.94 kg of CO₂ emissions can be reduced.

3.6.2. Contribution of interception of organic dyes to carbon emission reduction

The effect of modified PVDF membranes on the retention of three organic dyes (methyl violet, malachite green and Congo red) under different conditions was investigated, and the retention rates under different dye conditions are shown in Table 2.

Potassium dichromate (K₂Cr₂O₇) or potassium permanganate (KMnO₄) is commonly used as an oxidizing agent according to the standard method for testing chemical oxygen demand (COD). However, the standard method further utilizes toxic reagents such as Ag⁺ and Hg²⁺ salts for COD assessment, and the COD concentration of a dye wastewater from a plant used was measured by electrocatalytic and photocatalytic oxidation techniques to be 850 mg/L. Also, according to the conversion factor equation for the theoretical calculated value of COD:

Conversion factor

$$= \frac{\left(\begin{array}{l} \text{Number of carbon atoms} \times 2 \\ + \text{Number of hydrogen atoms} \times 0.5 \\ - \text{Number of oxygen atoms} \end{array} \right) \times 16}{\text{Relative molecular weight}} \quad (2)$$

The COD conversion factors for methyl violet are: 1 mg/L methyl violet = 2.1 mg/L COD; 1 mg/L malachite green = 2.56 mg/L COD; 1 mg/L Congo red = 0.85 mg/L COD. Therefore, the COD of 850 mg/L in the used dye wastewater was converted to the concentration of each of the three dyes, as shown in Table 3.

The average retention rate of the three dyes by the modified PVDF membrane was used to calculate the reduction of greenhouse gas carbon dioxide emissions. The amount of greenhouse gas CO₂ emitted to the atmosphere if the dyes are completely decomposed by natural degradation processes is 0.80, 0.62, and 1.49 g-CO₂/L, respectively.

In summary, the use of modified PVDF membrane can reduce the emission of 0.80–1.49 kg of CO₂ into the atmosphere for every 1 ton of dye wastewater treated.

4. Conclusion

- TiO₂/SAC-Fe₃O₄ can improve the water flux, retention rate, porosity, etc. of the membrane, and the anti-pollution performance becomes stronger.
- The best retention performance of the modified membrane was achieved when the content of TiO₂/SAC-Fe₃O₄ was 1.5%/0.2%, with 71.24% retention and 827.35 L/(m²·h) flux for methyl violet; 75.62% retention and 769.45 L/(m²·h) flux for malachite green; 65.72% retention and 729.53 L/(m²·h) flux for Congo red. 729.53 L/(m²·h).
- With the increase of dye concentration, the retention performance of modified membranes of group D₄ for methyl violet and malachite green showed a decreasing trend; the retention rate of Congo red solution increased, and the highest retention rate was 68.45% and 62.34% for methyl violet and malachite green at a concentration of 10 mg/L, respectively, and the best retention rate was 79.21% for Congo red dye at a concentration of 40 mg/L.
- When the pH value increased, the retention rate of the modified membranes of group D₄ for the cationic dyes methyl violet and malachite green showed a decreasing trend, and the retention rate for the anionic dye Congo red solution showed an increasing trend. The best retention of methyl violet and malachite green at pH = 4 was 73.21% and 65.93%, respectively; the best retention of Congo red at pH = 10 was 72.1%.
- When the ion concentration increased, the retention of dyes by the modified membranes in the D₄ group showed an increasing trend. The best retention was achieved for methyl violet, malachite green and Congo red with ion concentration of 0.9 mol/L, and the retention rates were 79.66%, 73.01% and 69.41%, respectively.
- When using TiO₂/SAC-Fe₃O₄ modified PVDF to treat dye wastewater, 1.94 kg of CO₂ emissions can be reduced for every 1 kg of municipal sludge used to prepare Fe₃O₄/SAC magnetic mass carbon; and about 0.80 to 1.49 kg of CO₂ emissions can be reduced for every 1 ton of dye wastewater treated with COD concentrations similar to those tested.

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