**Abstract:** Membrane fouling is a key factor limiting the application of a membrane bioreactor (MBR), and membrane-surface modification holds the potential to control membrane fouling and solves this problem. In the research, novel nanocomposite membranes were designed and fabricated using antimicrobial copper nanoparticles (CuNPs) coupled with powdered active carbon (PAC) to mitigate membrane fouling. The successful coating was confirmed by SEM, XRD, and FTIR analysis. Compared with a pristine membrane, the functionalization of CuNPs and PAC improved the hydrophilicity of the modified membrane but led to a lower permeate flux. The result of antimicrobial adhesion experiments showed that the modified M-CuOC displayed high antibacterial activity with the bacteria count decreased by 72%. In MBR operation, the modified M-CuOC leads to the removal efficiency of chemical oxygen demand (COD) increasing to 93%, with better filtration performance under a lower TMP rise. The fouling-resistance analysis demonstrated that, although the intrinsic membrane resistance of modified M-CuOC slightly increased, the reversible and irreversible fouling resistances obviously decreased by 45% and 90%. Moreover, the membrane flux recovery efficiency of the modified M-CuOC also increased by 35%. Overall, these results indicated that, in addition to an improvement in antifouling performance, the functionalization of CuNPs and PAC also enhanced the membrane flux recovery efficiency, revealing a good antifouling potential in a practical application.

**Keywords:** ceramic membrane; powdered active carbon; copper nanoparticles; antifouling

1. Introduction

Membrane bioreactors (MBRs), as an integration of activated sludge and membrane filtration process, have been widely employed for municipal and industrial wastewater treatment over the past three decades owing to simple operation, small space requirement, and less residual sludge [1–4]. The treatment performance of MBRs relied highly on the synergism between the membrane and feed solution. Therefore, the physicochemical properties of membranes have an important impact on the performance of MBRs. Ceramic membranes are recognized to be better than organic polymeric membranes for the MBR treatment of various wastewaters because of their high mechanical strength, strong hydrophilicity, and excellent chemical stability [5,6]. However, like organic polymeric membranes, ceramic membranes also struggle with membrane fouling during operation, which restricts their applications [7,8].

Membrane fouling mainly occurs due to the adsorption or accumulation of pollutants and microorganisms on the membrane surface or pores and, then, subsequent formation of the cake layer [9–11]. The formation of the cake layer will result in the decline of
permeate flux or the evaluation of the transmembrane pressure. Strategies for controlling membrane fouling of ceramic membranes include pretreatment of feed solutions, regulation of operating parameters, and surface modification of ceramic membranes, in which the surface-modification method can regulate the surface structures and physicochemical properties of ceramic membranes to improve ceramic membranes’ water flux and fouling alleviation [12–14]. Therefore, surface modification of ceramic membrane technology has attracted more and more attention in recent years.

Many studies have demonstrated that predeposition of micro- or nanomaterials, including carbon based [15,16] and metal based (e.g., Ag, Au, and CuO) [17–19], on the surfaces of ceramic membranes can regulate topography and hydrophobic and hydrophilic behavior, as well as antifouling/biofouling performance. Among these materials applied, carbon-based materials attracted increasing attention in controlling membrane fouling owing to their abundance on Earth, good absorption ability, and great resistance toward acids and bases. For example, activated carbon [20], granular activated carbon (GAC) [21], reduced graphene oxide (rGO) [22], and carbon nanotubes (CNT) [23] have been deposited on surfaces of ceramic membranes to enhance membrane performance. Jafari et al. [20] demonstrated that the predeposition of activated carbon on tubular ceramic membranes could significantly enhance the removal efficiency of oil during the treatment of oily wastewater. Tran et al. [24] synthesized carbon-nanotube-modified tubular ceramic membranes to filter wastewater with phenol and found that the permeability of the modified ceramic membrane and the removal of phenol are greatly higher than the pristine ceramic membrane. This result was due to the high specific surface area and stronger adsorption ability of the carbon nanotube. Notably, Song et al. [25] found that the deposition of reduced graphene oxide on the surfaces of ceramic membranes improved the hydrophobicity of membranes and might compromise the permeability of the membrane. Moreover, owing to the adsorption of carbon materials, microbes may enrich on the membrane surface and aggravate membrane biofouling, leading to an increase in fouling resistance.

Recently, several studies have reported that the immobilization of metal nanoparticles (e.g., Ag [12,26], Cu [27], and Au [28]) with antibacterial activity on the surfaces of membranes is a good way to mitigate biofouling [29]. Compared with other metal nanoparticles, copper nanoparticles (CuNPs) with high antibacterial activity and relatively low cost attract increasing attention [30]. It has been well-documented that blending CuNPs in the casting solution can adjust the surface roughness, porosity, wettability behavior, and antifouling/biofouling properties of polymeric membranes [31–33]. In addition, Lv et al. [34] found that CuNPs could improve the hydrophilicity of ceramic membranes due to the presence of a surface hydroxyl group. Hence, the deposition of CuNPs on carbon-modified ceramic membranes has the potential to alleviate membrane biofouling and compromise the improvement of hydrophobicity.

The purpose of this study is to prepare copper nanoparticles coupled with fine powdered active carbon (CuNPs@AC)-modified ceramic membranes and to investigate the performance of modified ceramic membranes. First, CuNPs@AC-modified ceramic membranes were prepared via the modified sol–gel impregnation calcination method, and the physicochemical characteristic of the prepared membranes was analyzed. Second, the antibacterial experiment was conducted to evaluate the antifouling property of the modified membranes. Then, to study the long-term performance of the modified membranes, the membrane bioreactors with modified membranes were constructed to treat synthetic wastewater. Finally, the influence of physical cleaning and acid cleaning on the modified membrane flux was assessed.

2. Materials and Methods

2.1. Materials and Chemicals

Copper nitrate (Cu(NO₃)₂·3H₂O), citric acid (C₆H₈O₇), sodium acetate (C₂H₃NaO₂), and potassium dihydrogen phosphate (KH₂PO₄) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Powder activated carbon (PAC) was sup-
plied by Green Source Co., Ltd. (Langfang, China) and the details can be found in Table A1. The ceramic membrane marked as M0 with the effective filtration size of 120 mm × 80 mm × 6 mm was provided by the Advanced Ceramic Research Institute of the Zibo High-tech Industrial Development Zone (Zibo, China). The composition and characteristic parameters of the ceramic membrane are shown in Table A2. Unless otherwise specified, ultrapure water (18.2 MΩ·cm) prepared by a Milli-Q system was used for solution preparation.

2.2. Membrane Modification and Characterization

The modified membrane was fabricated via a modified sol–gel impregnation calcination and deposition method (Figure 1). First, the base membranes were dipped into the mixture solution of 0.5 mol/L Cu(NO$_3$)$_2$·3H$_2$O and 1.2 mol/L C$_6$H$_8$O$_7$ with the reaction for 1.5 h, and the obtained membranes were dried over 24 h at 60 °C in oven. Second, the modified membranes were placed into a muffle furnace and treated at 750 °C for 2 h with a heating rate of 5 °C/min. Then, the CuNPs@AC-modified ceramic membranes were prepared through a vacuum-suction method. In brief, one side of the prepared CuNPs-modified ceramic membrane was sealed, and the opposite end was linked to a vacuum pump. Then, the modified ceramic membrane was added to 1 g/L of fine-powered active carbon solution and sucked by the vacuum pump. And then, the treated membrane was dried over 24 h at 60 °C in a vacuum. Finally, the obtained CuNPs@AC-modified ceramic membranes (M-CuO$_x$) were calcined at 200 °C for 2 h. In addition, single nanocopper particles or micro-fine-powered activated carbon-modified ceramic membranes were also prepared using the same method and were labeled as M-CuO and M$_C$.

Figure 1. Schematic representation of the membrane-modification protocol.

The surface morphology and elements of the virgin and the modified ceramic membranes were analyzed by a scanning electron microscope (SEM, Phenom Prem, Eindhoven, The Netherlands) equipped with an energy-dispersive X-ray scattering (EDX) spectrometer. A powder X-ray diffractometer (XRD, D8 Advance, Saarbrucken, Germany) was used to investigate the crystal structure of the in situ CuNPs. The Fourier transform infrared spectra were obtained using a Fourier infrared spectrometer (FTIR, Nicolet is50, Thermo Fisher Scientific, Waltham, MA, USA). The hydrophobicity of different membranes was assessed using contact-angle measurements (DSA 30, KRUSS, Hamburg, Germany). The contact angle was determined at 5.0 s after a droplet (2 μL of DI water) evenly spread on the membrane surface. Twenty random locations on the tested membranes were measured for each evaluation.
2.3. Membrane Performance

2.3.1. Anti-Biofouling Performance Evaluation

Static antibacterial assays were conducted, referring to previous studies [32], using *E. coli* as the model bacteria. Specifically, bacteria cultures were reared for 24 h in lysogeny broth (LB) at 37 °C; then, the bacteria suspension was diluted with fresh LB medium and further cultivated to the exponential phase (determined by a growth curve). The culture was centrifuged and washed with phosphate-buffered saline (PBS) three times to separate the cells from the culture medium. Finally, the bacteria were resuspended and diluted with PBS to a concentration of 10^6 colony-forming units per milliliter (CFU·mL⁻¹) for later use. Membrane samples (1 cm × 1 cm) were installed in custom-made membrane holders, and then, these holders were placed in the prepared bacteria suspension at 37 °C with a rotary shaker (200 rpm) for 10 h. After this, membrane samples were withdrawn and inoculated onto an LB solid medium, then were cultured for 12 h under 37 °C to count the bacteria colonies.

2.3.2. Membrane-Bioreactor Setup

As shown in Figure A1, the MBR has a working volume of 50 L. The CM membranes with an effective area of 0.0192 m² were immersed in the bioreactor vertically and run with the peristaltic pump. An air diffuser was set under the membrane module to provide continuous aeration to maintain the dissolved oxygen (DO) concentration in the range of 3–5 mg/L. The collection of effluent was controlled by a timer with the mode of 10 min on/2 min off, and the water outlet was equipped with a pressure sensor and paperless recorder to record the change of TMP in real time. The activated sludge inoculated in the bioreactor was obtained from the secondary sedimentation tank of the Sewage Treatment Plant in Jinan, China. The water quality of synthetic wastewater and the operating conditions of the MBR are shown in Table A3 and Figure A1. During the experiments, the mixed liquid–suspended solid (MLSS) was maintained at 3200 mg/L; the HRT was 12 h. The constant flux of 2.08 L/h was controlled through a peristaltic pump, and the TMP was recorded at the scheduled time. After cleaning, the cleaned membranes were returned to the MBR system. The next filtration run then began. The time taken for the membrane to reach its cutoff TMP was termed the filtration period.

2.4. Membrane-Fouling Resistances and Cleaning

2.4.1. Membrane-Fouling Resistances

The resistance-in-series model based on Darcy’s law was used to analyze the fouling resistance [35]. The fouling resistance could be expressed as:

\[ R_t = \frac{\text{TMP}}{\mu J} = R_m + R_r + R_{ir} \]  

where \( R_t \) represents the total membrane-fouling resistance (m⁻¹), \( R_m \) is the intrinsic membrane resistance (m⁻¹), \( R_r \) and \( R_{ir} \) are defined as reversible and irreversible fouling resistance (m⁻¹), respectively, \( \text{TMP} \) is transmembrane pressure (kPa), \( \mu \) is the dynamic viscosity for feed solution, and \( J \) is the permeation flux.

In our experiments, the permeation flux of the virgin membrane with DI water was recorded as \( J_0 \); the permeation flux of the modified membrane at the end of the operation was defined as \( J_f \). Therefore, the \( R_t \) and \( R_m \) could be calculated as the following equation:

\[ R_t = \frac{\text{TMP}}{\mu J_f} \]  

\[ R_m = \frac{\text{TMP}}{\mu J_0} \]
In addition, the permeation flux of the modified membrane after rinsing with deionized water was recorded as $J_g$, and the reversible fouling resistance was counted as follows:

$$R_r = \frac{TMP}{\mu J_f} - \frac{TMP}{\mu J_g} \quad (4)$$

After the calculation of $R_t$, $R_m$, and $R_r$, the irreversible fouling resistance was obtained by subtracting $R_m$ and $R_r$ from $R_t$, as shown in the following equation:

$$R_{ir} = R_t - R_m - R_r \quad (5)$$

2.4.2. Membrane Cleaning

After the operation, the two-step membrane-rinsing method was performed. Briefly, the contaminated membrane was rinsed with deionized water with 1 L/min to clean the concentration polarization layer, and then, the contaminated membrane was further washed using a HCl solution (pH = 2.5) for 3 h to remove the gel layer, followed by washing with deionized water to a neutral pH. The permeation fluxes of different membranes with DI water were computed to evaluate the permeability recovery after each rinsing process, where the permeability recovery was defined as the following equation:

the permeability recovery = $\frac{J_f}{J_0}$ \quad (6)

where $J_f$ and $J_0$ were the permeation fluxes of the fouled and pristine membranes, respectively.

2.5. Analytical Methods

The COD and NH$_4^+$-N concentration of the influent and effluent was measured by standard methods [36]. The pH of the solutions was monitored by a pH meter (Mettler Toledo Pro2Go, Zurich, Switzerland). A DO meter was applied to measure the DO concentration and temperature. The measurement was performed at least three times with the standard deviation of less than 10%.

3. Results and Discussion

3.1. Membrane-Surface Characteristics

The membrane-surface morphology was investigated by SEM analysis. As shown in Figure 2a, the primitive ceramic membrane surface was porous, smooth, and shiny with some large particles. Compared with the morphology of the pristine membrane, the membrane surface of $M_C$ was covered with some irregular particles and became rougher, which indicated that micro-fine-powered active carbon was successfully deposited on the surface of the ceramic membrane (Figure 2b). After CuNPs immobilization, the surface of $M_{CuO}$ was relatively dense, and some clusters of spherical nanoparticles were observed on the membrane surface (Figure 2c). As presented in Figure 2d, irregular particles and nanoparticles were present on the surface of the $M_{CuOc}$. Compared with $M_C$ and $M_{CuO}$, $M_{CuOc}$ was more porous and ordered. The EDS analysis of the different membranes suggested that the content of the C and Cu elements in $M_{CuOc}$ was obviously higher than that in the pristine membrane (Table A4), further confirming the successful deposition of C and Cu elements on the membrane surface.
The XRD patterns of the pristine membrane and modified ceramic membranes are shown in Figure 3a to investigate the membrane’s chemical composition and lattice structure. As presented in Figure 3a, the characteristic peaks of rhombohedral Al$_2$O$_3$ were observed in the virgin ceramic membrane (M$_0$). Compared with the XRD patterns of M$_0$, the diffraction peaks of M$_{CuO}$ and M$_{CuOc}$ at 35.6° (11-1) and 38.7° (111) were the characteristic peaks of the rhombohedral CuO (JCPDS 48–1548) [37,38]. Similar diffraction peaks were also found in the copper oxide-modified ceramic hollow-fiber membrane, suggesting that CuO was successfully deposited on the surface of the ceramic membrane.

Figure 3. (a) XRD pattern of M$_0$, M$_{CuO}$, M$_c$, and M$_{CuOc}$, (b) FT-IR infrared pattern corresponding to M$_0$ and M$_{CuOc}$ samples.

Figure 3b shows the FTIR spectrum of the pristine membrane and the modified CuNPs@AC ceramic membranes. Compared with the FTIR spectrum of the pristine membrane, the vibrational peaks at 450–500 cm$^{-1}$, 1450 cm$^{-1}$, 1626 cm$^{-1}$, and 3400–3500 cm$^{-1}$ were seen in the FTIR spectrum of the prepared CuNPs@AC membranes. According to previous studies [39–41], the bands at 450–500 cm$^{-1}$, 1450 cm$^{-1}$, and 1626 cm$^{-1}$ were indexed to Cu=O structure, C=O, and C=C groups, demonstrating that CuNPs and the
MFPAC functional layer were successfully covered on the surfaces of ceramic membranes. Moreover, the presence of a band at 3400–3500 cm$^{-1}$ was ascribed to hydroxyl groups or absorbed H$_2$O, indicating that the prepared CuNPs@AC-modified ceramic membranes had good hydrophilicity.

To analyze the membrane-surface hydrophilicity of different membranes, the water contact angle was measured. As shown in Figure 4a, the contact angle of the modified ceramic membranes was significantly increased from 40.0° to 79.8° when the micro-fine-powered activated carbon was coated on the surface of the virgin membrane. Previous studies have demonstrated that a large contact angle indicates a relatively high hydrophobicity of the membrane and the mean severe membrane-fouling potential during filtration. Hence, the deposited activated carbon on the surface of the membrane might aggravate fouling, which was not conducive to membrane filtration. Notably, the function of the copper nanoparticles modifying the membrane became more hydrophilic with a lower contact angle of 22.7°. This result could be ascribed to the hydrophilic nature of the surface hydroxyl group of CuO. When the surface of the membrane was covered by copper nanoparticles and fine powdered active carbon, the water contact angle reduced from 40.0° to 32.6°. This suggested that compared with the virgin membrane, the CuNPs@AC-modified ceramic membranes were relatively hydrophilic and beneficial for alleviating the membrane fouling in filtration.

In addition, the permeate flux of the varied membranes was measured under constant pressure. As shown in Figure 4b, the permeate flux of the virgin membrane was 352.63 LMH, and the permeate flux of the modified membrane showed varying degrees of decrease, in which the permeate fluxes of Mc, M-CuO, and M-CuOc were 306.5 LMH, 269.1 LMH, and 207.4 LMH, 13%, 23%, and 41% lower than that of the pristine membrane, respectively. Similar results have been reported in previous studies, which might be ascribed to the fact that the modification process increased the surface-layer thickness resulting in the mass-transfer-resistance enlargement. Moreover, M-CuO and M-CuOc displayed a lower permeate flux than Mc because the CuO nanoparticles might congest the pore of the membrane, also leading to increased mass-transfer resistance.

![Figure 4](image-url)

Figure 4. (a) Water contact angles for the M0, M-CuO, Mc, and M-CuOc; (b) TDS and permeate flux of M0, M-CuO, Mc, and M-CuOc.

The stability of the modified components loaded on the membrane surface is an important factor for the sustainable operation of the membranes. Therefore, the TDS values of pure water after running for 5 d in the presence of different membranes were investigated. As shown in Figure 4b, the TDS values in the case of Mc, M-CuO, and M-CuOc were 37.9 mgL$^{-1}$, 7 mgL$^{-1}$, and 10 mgL$^{-1}$, and obviously higher than that (3 mgL$^{-1}$) of the pristine membrane, indicating that the stability of the modified components loaded on the membrane surface increased following the order of Mc < M-CuOc < M-CuO. This result could be attributed to the fact that the calcination process is beneficial for the modified elements more strongly loaded on the membrane surface.
3.2. Antibacterial Activity Assays

The adhesion of organisms on the surface is one of the main causes of membrane fouling. Therefore, the antimicrobial adhesion experiments were carried out to evaluate the anti-biofouling property of the modified membrane, in which E. coli were used as model organisms. After membrane samples were immersed in an E. coli bacterial suspension for 10 h, membrane samples were withdrawn and inoculated onto an LB solid medium within 12 h to quantify bacteria counts. As presented in Figure 5, the bacteria count in the presence of pristine CM and modified Mc was approximately 5.1–5.3 log, indicating that the pristine CM and modified Mc exhibited minimal antibacterial activity. Specifically, the modified M-CuO and M-CuOc showed high antibacterial activity for E. coli. As indicated in Figure 5, the bacteria count after filtration through modified M-CuO and M-CuOc was 67% and 72% lower than that of the pristine CM. This result clearly demonstrated that the layer of CuO nanoparticles on the surface obviously improved the antibacterial activity of the modified membrane, which highlighted the application potential to mitigate membrane biofouling.

![Figure 5. The bacteria count in LB solid medium in the presence of different membranes.](image)

3.3. MBR-Treatment Performance

3.3.1. TMP Analysis of Different MBR Systems

Several studies have proven that the variation of TMP can indirectly reflect the degree of membrane fouling in the case of constant flux. Hence, the TMP of pristine CM and modified CM was monitored (Figure 6). Notably, the initial TMP values of modified M-CuO, M-CuO, and M-CuOc were 24 Kpa, 22 Kpa, and 24 KPa, respectively, which was higher than that of pristine CM (21 Kpa). This finding was consistent with the lower permeate flux of modified CM (Figure 4b). A similar consequence has been reported in a previous study [41,42], which was due to the following reasons: (1) the modified layer on the surface was slightly compact and (2) the modified nanosized power might block the membrane pores. As shown in Figure 6, the increased rate of TMP of pristine CM was obviously higher than that of the modified membrane. The TMP of pristine CM continuously increased to 35 KPa within 150 h; meanwhile, the TMP of modified M-CuO, M-CuO, and M-CuOc only enlarged to 33, 27.35, and 25.2 KPa, respectively. Notably, the TMP of CuNPs@AC-modified CM first was maintained around 24 Kpa during the first 50 h; then, it slowly increased to 27 KPa during 199 h followed by sharply rising to 35 kPa during the operation of 200–250 h. Therefore, the filtration period of MBR systems was set to be 199 h in order to prolong the working time of modified membranes. These results indicated that CuNPs@AC-modified CM showed a lower fouling rate than the pristine CM, which was in line with the result of antibacterial activity assays and further certified the good antifouling ability of CuNPs@AC-modified CM.
3.3.2. Removal Efficiency of Pollutants in an MBR System

From the aforementioned results, it could be seen that the antifouling property of CuNPs@AC-modified CM (M-CuOc) was superior to other modified membranes. Hence, the CuNPs@AC-modified CM (M-CuOc) was selected as the optical modified membrane to assess the removal performance of a different MBR system. The concentrations of COD and NH\textsubscript{4}\textsuperscript{+}-N in the influent and effluent in the pristine CM and CuNPs@AC-modified CM system were measured during the operation of 31 d. The COD removal efficiency of CuNPs@AC-modified CM MBR was 92% slightly higher than that (85%) of virgin CM MBR. As seen in Figure 7a, the COD concentration in the influent was stable at 390 ± 5 mg/L for two MBR systems, and in the effluent from CuNPs@AC-modified CM was about 32 ± 2 mg/L, significantly lower than that (58 ± 4 mg/L) from the virgin CM. According to previous studies [12,27], the rise in COD removal efficiency for the modified M-CuOc might be ascribed to the adsorption of the fine powdered active carbon. The NH\textsubscript{4}\textsuperscript{+}-N concentrations in the influent and effluent were 37 ± 2 mg/L and 3 ± 0.5 mg/L for the two MBR systems, indicating that the removal efficiency of NH\textsubscript{4}\textsuperscript{+}-N was comparable in the two MBR systems (Figure 7b). In addition, the concentrations of MLSS in pristine CM and CuNPs@AC-modified CM systems were 3620 mg/L and 3590 mg/L, respectively. These results indicated that the CuNPs@AC-modified CM had little impact on the property of active sludge. Moreover, the removal efficiency of COD and NH\textsubscript{4}\textsuperscript{+}-N in the modified M-CuOc was compared with previous studies, where the MBRs were applied to municipal wastewater. As shown in Figure 7, the COD removal was close to that in previous studies, while the removal of NH\textsubscript{4}\textsuperscript{+}-N was slightly lower than that of previous studies. This difference might be ascribed to the higher influent NH\textsubscript{4}\textsuperscript{+}-N concentration in this study. Considering the positive effect of CuNPs@AC-modified CM on fouling reduction, it could be inferred that CuNPs@AC-modified CM would be highly effective in MBR application for wastewater treatment.
3.4. Membrane Fouling and Cleaning

To assess the antifouling property of modified membranes, the fouling resistances of pristine and modified membranes were analyzed. As shown in Figure 8a, the intrinsic membrane resistance and the reversible and irreversible fouling resistances of the virgin membrane after 199 h operation were $0.22 \times 10^{12} \text{m}^{-1}$, $6.55 \times 10^{12} \text{m}^{-1}$, and $0.98 \times 10^{12} \text{m}^{-1}$, respectively. Compared with the original membrane, the intrinsic membrane resistance of modified $M_C$, $M$-CuO, and $M$-CuOC increased to $0.29 \times 10^{12} \text{m}^{-1}$, $0.34 \times 10^{12} \text{m}^{-1}$, and $0.39 \times 10^{12} \text{m}^{-1}$, respectively. This result was in accord with the pure-water flux experiment, owing to some membrane pores might be blocked during the modified process. As can be seen from Figure 8a, the reversible and irreversible fouling resistances of modified membranes both decreased to a certain extent. Specifically, the $M$-CuO had a better antifouling property than $M_C$, which could be due to the high antibacterial activity of CuO nanoparticles to retard microbe adsorption on the membrane surface. Remarkably, the reversible and irreversible fouling resistances of $M$-CuOC decreased to $3.66 \times 10^{12} \text{m}^{-1}$ and $0.1 \times 10^{12} \text{m}^{-1}$ and were 45% and 90% lower than that of the pristine membrane, respectively. Generally, the functionalization of CuO nanoparticles and fine powdered active carbon outstandingly improved the antifouling performance of the modified membrane.

![Figure 7](image_url)  
**Figure 7.** The concentration and removal of (a) COD, and (b) NH$_4$\textsuperscript{+}-N in an MBR system with $M_0$ and $M$-CuOc.

![Figure 8](image_url)  
**Figure 8.** Analysis of membrane fouling (a) and the flux recovery efficiency (b) for different membranes.

The membrane flux recovery efficiency after the two-step membrane-rinsing method was explored to evaluate the durability of the modified membrane. As shown in Figure 8b, the membrane flux recovery efficiency after the same cleaning process increased in the following order, $M_0 < M$-CuO$ < M_C < M$-CuOC. The flux recovery efficiencies of modified...
M,C, M-CuO, and M-CuOC were 88%, 84%, and 92%, with 27.5%, 21.7%, and 35% higher than that of the virgin membrane (68%), respectively, which suggests that membrane modification raised the percentage of reversible fouling. This result indicated that, in addition to improvement in antifouling performance, the functionalization of CuO nanoparticles and fine powdered active carbon also enhanced the membrane flux recovery efficiency, revealing a good antifouling potential in practical application.

4. Conclusions

This paper proposed a simple and adaptable ceramic-membrane modification method via sol–gel impregnation and deposition of functionalization of CuO nanoparticles and fine powdered active carbon layer to resist membrane fouling, and their performances in an MBR system to treat wastewater were explored. The physical and chemical properties of a modified membrane were investigated by SEM, FT-IR, and XRD analysis. The results suggested that the CuO nanoparticles and fine powdered active carbon were successfully coated on the surface of a virgin membrane, improving the hydrophilicity of the modified membrane. The result of antimicrobial adhesion experiments showed that the modified M-CuOC displayed high antibacterial activity with the bacteria count reducing by 72%. During the long-running process of MBR, the modified M-CuOC membrane improved the removal efficiency of COD, while the removal efficiency of NH4+-N was comparable for the modified M-CuOC and virgin membrane. Notably, the modified M-CuOC membrane exhibited a significantly slower increase in TMP compared to the pristine membrane, indicating better filtration performance with a lower TMP rise. The reversible and irreversible fouling resistances of the modified M-CuOC decreased by 45% and 90% compared with the virgin membrane, further certifying the good antifouling ability of the modified M-CuOC. Moreover, the membrane flux recovery efficiency of the modified M-CuOC after cleaning was 92%, which was 35% higher than that of the virgin membrane. Overall, these results clearly demonstrated that integrating CuO nanoparticles with fine powdered active carbon to modify a ceramic membrane was a highly desirable option for utilization in MBR applications.

Author Contributions: Conceptualization, Q.Q. and S.S.; methodology, Q.Q., M.G. and Y.L.; writing—original draft preparation Q.Q. and S.S.; writing—review and editing, Q.Q. and M.G.; project administration, H.Z.; supervision, H.Z. and C.S.; All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data is contained within the article.

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Conflicts of Interest: Author Changtao Shao was employed by the company Shandong Industrial Ceramics Research and Design Institute. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Appendix A


<table>
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<tr>
<th>Subject</th>
<th>Coarseness (Mesh)</th>
<th>Iodine Absorb (mg/g)</th>
<th>Hardness (%)</th>
<th>Moisture (%)</th>
<th>Ash (%)</th>
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<tr>
<td>Index</td>
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<td>98</td>
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<td>≤5</td>
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Table A2. Characteristic parameters of the ceramic membrane.

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<td>Index</td>
<td>Ceramic membrane</td>
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<td>0.1 µm</td>
<td>12</td>
<td>Al₂O₃, SiO₂, TiO₂</td>
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Table A3. The water quality of synthetic wastewater.

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<th>TP (mg/L)</th>
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Table A4. Element contents on the membrane surface determined by EDS.

<table>
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<th>O (%)</th>
<th>Al (%)</th>
<th>Cu (%)</th>
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<td>44.76</td>
<td>38.10</td>
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<td>2.63</td>
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<td>2.32</td>
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Figure A1. MBR device.

References


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