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폐수중 항생제의 막기반 제거에 관한 연구: 검토

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Membrane Based Removal of Antibiotics from Wastewater: A Review

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요 약: 항생제는 과도한 사용으로 인해 폐수뿐만 아니라 다양한 수원에서 발견되는 새로운 오염 물질 중 하나입니다. 수중 항생제 오염 물질을 처리하기 위한 고도 산화 공정, 생물학적 처리 등 다양한 기술이 있습니다. 이 두 가지 공정은 비효율적이며, 부산물의 생성은 이 공정을 더욱 복잡하게 만듭니다. 오염 물질을 제거하기 위한 또 다른 대안으로 막 기술이 있습니다. 항생제와 내성 유전자의 제거를 개선하기 위해 막 생물 반응기는 NaClO와 탄소 물질로 변형됩니다. 풍부한 반응성 종의 생성은 항생제의 내성 유전자에 대해 활성입니다.

Abstract: Antibiotics is one of the emerging pollutants found in various water sources as well as wastewater due to its excessive use. Different techniques are available for treating antibiotics contaminants in water such as advanced oxidation process and biological treatment etc. These two processes are ineffective, and the generation of side products makes this process more complicated. Membrane technology is another alternative for the removal of contaminants. To improve the removal of antibiotics and their resistant gene, membrane bioreactors are modified with NaClO and carbon materials. The generation of abundant reactive species is active against the antibiotic's resistant genes.

Keywords: *antibiotics, tetracyclines, membrane, wastewater*

1. Introduction

This review paper encompasses a range of innovative technologies related to the membrane-based removal of antibiotics from wastewater. It begins by highlighting photocatalytic membranes, which effectively degrade various antibiotics, thereby reducing their environmental impact[1]. Ceramic nanofiltration membranes are then discussed, emphasizing their robustness and effectiveness in filtering out contaminants from both industrial and municipal wastewater[2]. The paper also explores the novel approach of using Dalbergia sissoo biomass-derived activated carbon for the adsorption of doxycycline, a common antibiotic, demonstrating a sustainable wastewater treatment method[3]. Biopolymer composites are examined for their capability to extract toxic organic compounds from

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pharmaceutical effluents[4]. The synergistic effects of solid carbon and manganese ore in enhancing the removal of nutrients and antibiotics in a denitrification system are then investigated, offering insights into improved wastewater treatment processes[5]. The effectiveness of IFAS-MBR bioreactors in treating wastewater contaminated with sulfonamide antibiotics is analyzed, highlighting their potential in maintaining water quality[6]. Additionally, the review assesses the use of commercial nanofiltration membranes to separate various drugs, including their efficiency under different conditions[7]. Lastly, the development and application of polyelectrolyte membranes, particularly for drug delivery, toxic metal ion removal, and fuel cell applications, are presented, showcasing their multifunctional capabilities[8,9]. In this review removal of antibiotics are discussed.

2. Removal of Antibiotics

The wastewater treatment can be enhanced by developing graphene oxide-cellulose nanocrystal hybrid membranes[10]. The study used graphene oxide (GO) nanosheets and cellulose nanocrystal (CNC) nanorods to create a novel GO/CNC hybrid membrane for wastewater treatment. The synthesis involved a modified Hummer's method for GO, followed by a combination with CNCs. These membranes displayed enhanced hydrophilicity and surface structure due to CNC incorporation, improving water permeability significantly (2~4 times higher than GO membranes). They effectively removed antibiotics like sulfamethoxazole, levofloxacin, and norfloxacin, with rejection rates of 74.8%, 90.9%, and 97.2%, respectively, while allowing nutrients like nitrate and phosphate to pass through. This performance was attributed to electrostatic repulsion and adsorption mechanisms. Density Functional Theory calculations further confirmed these interactions. The study highlights the membranes' potential in selective pollutant removal and nutrient recovery, outperforming other membrane types in antibiotic removal efficiency.

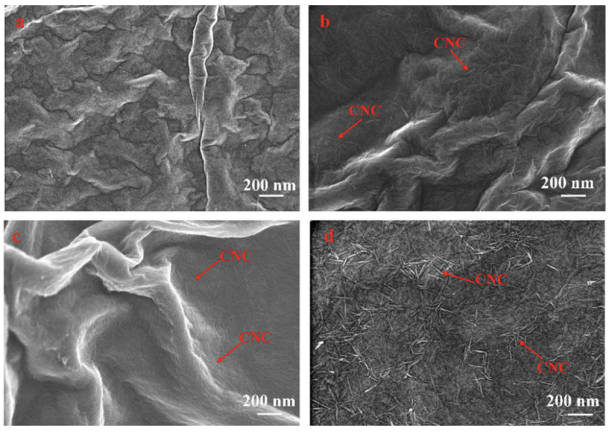

Fig. 1. SEM images of (a) GC100, (b) GC85, (c) GC75, and (d) GC65 (Reproduced with permission from Gao *et al.*[10], Copyright 2021, American Chemical Society).

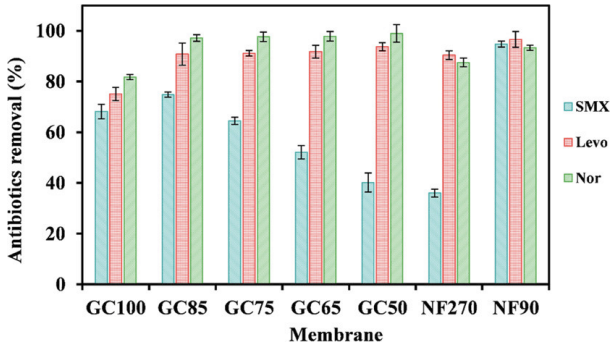

Fig. 2. Antibiotic separation performance of the hybrid membranes. Operational conditions: a mixture of SMX (C_0 = 1.0 mg/L), Levo (C_0 = 1.0 mg/L), and Nor (C_0 = 1.0 mg /L) serving as the feed solutions with an applied transmembrane pressure (TMP) of 60 psi and a running time of 4 h (Reproduced with permission from Gao *et al.*[10], Copyright 2021, American Chemical Society).

The escalating presence of residual pharmaceutical pollutants within wastewater has adverse repercussions on both the ecosystem and human well-being[11]. In this ongoing investigation, novel membranes comprising cellulose acetate/Mg-Al layered double hydroxide (Mg-Al LDH) nanocomposites have come up as an efficient mechanism for pharmaceutical substance removal from wastewater. We assessed the nanocomposite membranes' structure, porosity, surface characteristics, and heat resistance, varying the quantity of nanofiller incorporated, through techniques such as SEM, TGA, cCT, and contact angle measurements. The Mg-Al LDH

included in the polymer matrix nanofiller exhibited remarkable dispersion, as confirmed by TEM and XRD. We gauged their hydrodynamic properties and adsorption capabilities using pure water and water-based solutions containing tetracycline and diclofenac sodium. The nanocomposite membranes' enhanced permeability exhibition was discovered when compared to pristine cellulose acetate. Out of all of them, the membrane with 4 weight percent Mg-Al LDH showed the maximum water flux (529 vs. 36 L/m^2 · h) and the highest DS adsorption capacity, ten times more than the pure polymer. The main cause of this increase is clarified that it is due to the electrostatic interactions between the positively charged Mg-Al LDH layers and the negatively charged drug molecules. On the other hand, in the instance of TC, the drug molecule and the nanofiller exhibited hydrogen bonding interactions, which resulted in a more moderate increase in adsorption capacity.

Simultaneous elimination of antibiotics and antibiotic resistance genes (ARGs) is a crucial strategy for curbing the proliferation of antibiotic resistance[12]. A CeO_2-modified carbon nanotube electrochemical membrane was combined with NaClO (CeO_2@CNT-NaClO) to treat model water samples containing antibiotics and antibiotic-resistant bacteria (ARB). The CeO_2@CNT-NaClO system demonstrated a high efficacy in removing sulfamethoxazole, achieving a 99% removal rate. This was achieved using a CeO_2 to CNT mass ratio of 5:7 and a current density of 2.0 mA/cm^2. Additionally, the system was successful in removing tetracycline, with an efficiency rate of 98%. The outstanding performance of the CeO_2@CNT-NaClO system in simultaneously eliminating antibiotics and ARGs can be primarily attributed to the generation of multiple reactive species. This system utilizes the synergistic action of free radicals to inflict significant damage to cell membranes. This leads to an increase in intracellular reactive oxygen species (ROS) while concurrently decreasing superoxide dismutase (SOD) activity. As a result, this coordinated mechanism contributes to the system's enhanced efficiency in ARG removal.

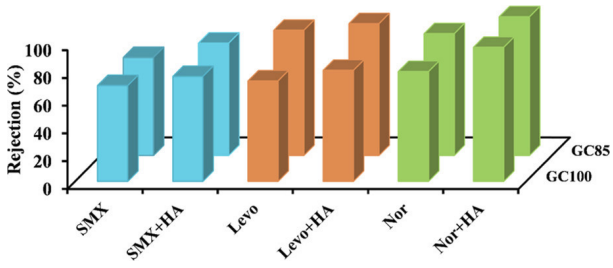

Fig. 3. Effect of HA on membrane antibiotic removal. The initial concentration of antibiotics is 1.0 mg/L for each, and HA concentration used in feed solutions is 10.0 mg/L. A transmembrane pressure (TMP) of 60 psi was applied to all the tests with a running time of 4 h (Reproduced with permission from Gao *et al.*[10], Copyright 2021, American Chemical Society).

Anaerobic-anoxic-aerobic (A_2O), membrane bioreactor (MBR), and modified biological nutrient removal (BNR) systems were among the biological wastewater treatment procedures in South Korea that were the subject of the study, which examined the amounts of 57 distinct compounds in various treatment units[13]. The objective was to comprehend the presence and destiny of personal care products and pharmaceuticals (PPCPs) in wastewater treatment plants (WWTPs). The findings showed that biological treatment processes were generally effective in removing most PPCPs, with some additional removal occurring during post-treatment stages. Notably, the A_2O system proved effective for PPCPs removal, except for the MBR process. To understand the removal mechanisms, mass balance calculations were performed for both the A_2O system and a laboratory-scale MBR process. The comparative analysis revealed that removal performance was significantly improved by biodegradation, especially in the lab-scale MBR, where compounds like bezafibrate, ketoprofen, and atenolol were effectively eliminated. On the other hand, it was discovered that substances like tetracycline, triclocarban, ciprofloxacin, and levofloxacin were extensively adsorbed to MBR sludge. Interestingly, the lab-scale MBR process showed enhanced biodegradability while having strong adsorption characteristics. In other biological treatment procedures, the removal of highly adsorbable chemicals

and non-degradable or persistent particulate matter pollutants (PPCPs) is probably made possible by the MBR process's improved biodegradation capacity.

Park *et. al.* looked into the effects of adding two coagulants to the membrane bioreactor (MBR) process: chitosan and polyaluminum chloride (PACl)[14]. The principal aim was to comprehend their impact on the fouling of the membrane and the elimination of personal care and pharmaceutical products (PPCPs). When these coagulants were added at carefully optimized dosages, several positive outcomes were observed. The membrane's permeability improved as a result of decreased concentrations of microbial products that are soluble in the liquor mixture, reduced levels of inorganic elements, and a decrease in fouling that is irreversible on the surface of the membrane. Over an extended operational period, the addition of PACl led to an increase in removal efficiencies for specific PPCPs, including tetracycline, mefenamic acid, atenolol, furosemide, ketoprofen, and diclofenac, with improvements ranging from 17% to 23%. A comparative assessment was conducted by calculating mass balances between the PACI-involved coagulation-MBR and the PACI-excluded control-MBR. This analysis revealed that the enhanced biodegradability of certain PPCPs played a pivotal role in enhancing removal efficiencies within the coagulation-MBR system. Furthermore, the rates of specific nitrification and higher oxygen uptakes have resulted in the coagulation-MBR. In summary, our findings show that combining MBR with coagulation has the dual benefit of reducing membrane fouling and thus extending the operational lifespan of the membrane, as well as improving the removal of specific PPCPs through improved biodegradability.

Shen et al. investigated that there is a possibility for carbon-fiber (CF) cloth decorated with C_3N_4 to enhance the activity of photocatalysis. CF is used as a flexible filter-membrane-shaped photocatalyst for wastewater degradation.[15]. Aiming to efficiently separate photogenerated carriers, the researchers introduced TiO_2 between the C_3N_4 and CF layers. They achieved this by growing TiO_2 nanoparticles (with a diameter ranging from 100 to 200 nm) in-situ on the CF cloth using a dip-coating/hydrothermal method. Additionally, C_3N_4 nanosheets (with a thickness of 30~50 nm) were prepared on the surface of the TiO_2-coated CF cloth through thermal polymerization. The resultant CF/TiO_2/C_3N_4 cloth had an absorption edge at about 450 nm and showed good visible photoabsorption. When exposed to visible light, this cloth outperformed CF/C_3N_4 and CF/TiO_2 cloth in terms of photocurrent and photocatalytic activity for the degradation of different organic pollutants (such as methylene blue, acid orange 7, 4-chlorophenol, and tetracycline hydrochloride (TC)) and reduction of heavy-metal ions (Cr(VI)). Using CF/TiO_2/C_3N_4 cloth as a filter-membrane to degrade wastewater flowing at a rate of 1.5 L/h resulted in an 87% removal efficiency for TC and an 88% removal efficiency for Cr(VI) after 7 cycles. These removal rates were higher than those achieved by CF/C_3N_4 cloth (60% TC, 28% Cr(VI)) and CF/TiO_2 cloth (8% TC, 7% Cr(VI)). Thus, CF/TiO_2/C_3N_4 cloth shows promise as an effective photocatalyst in the form of a filter membrane for the removal of heavy metals and other organic pollutants from flowing wastewater.

Numerous nanoscale photocatalysts have shown promise in efficiently treating antibiotic solutions within laboratory settings, but the issue persists of antibiotics being discharged into flowing rivers[16]. To address the challenge of photocatalytically degrading antibiotic wastewater in a flowing state, the development of a large-scale, highly photocatalytic-active flexible filter membrane is essential. In this study, carbon fiber (CF) cloth is utilized as a porous and flexible substrate and the successful BiOBr/Ag_3PO_4 heterostructures growth, in-situ, is reported. This involved the sequential synthesis of BiOBr nanosheets (with a thickness of approximately 10 nm and a diameter ranging from 0.5 to 1 μm) and Ag_3PO_4 particles (sized between 50 and 200 nm) on the CF cloth. A solvothermal-chemical deposition two-step method, for this achievement, has been adapted. The resulting CF/BiOBr/Ag_3PO_4 cloth exhibited remarkable visible photoabsorption, with an absorption edge at around 520 nm. When exposed to

visible light, a 4 × 4 cm^2 CF/BiOBr/Ag_3PO_4 cloth demonstrated the ability to degrade approximately 90.0% of tetracycline hydrochloride (TCH), serving an antibiotics-relevant model, within a 30-minute timeframe in a laboratory beaker. Notably, for degrading flowing antibiotic wastewater, this cloth, in a multiple photocatalytic setup, was also used as a filter-membrane. The removal efficiency of TCH increased from 12.8% during the first cycle to 89.6% after the sixth cycle. Additionally, the study proposed a photocatalytic mechanism for CF/BiOBr/Ag_3PO_4 cloth and outlined a potential decomposition pathway for TCH, drawing upon simulation and experimental results. In summary, this research provides valuable insights into the development of photocatalysts with flexible filter membranes for efficiently degrading flowing wastewater.

Le *et. al.* addresses the troubling issue of antibiotic residues, antibiotic-resistant bacteria (ARB), and antibiotic-resistance genes (ARGs) as emerging water contaminants, all of which pose potential risks to aquatic ecosystems and human health[17]. The study provides comprehensive data on the presence of 19 antibiotics, bacteria resistant to 10 antibiotics, and 15 ARGs in wastewater treatment stages ranging from raw influent to processes within conventional activated sludge (CAS) and membrane bioreactor (MBR) systems. 17 of the 19 target antibiotics were detected in raw influent, with concentrations reaching up to ten micrograms per liter. However, compared to raw influent, secondary effluent had far lower antibiotic concentrations. Antibiotics with high removal efficiency (median removal efficiency > 70%) by CAS or MBR systems included amoxicillin, azithromycin, ciprofloxacin, chloramphenicol, meropenem, minocycline, oxytetracycline, sulfamethazine, and vancomycin; trimethoprim and lincomycin, on the other hand, were less resistant, with a median removal efficiency in the CAS system of less than 50%. Similarly, target ARBs and ARGs were found to be prevalent in the raw influence, with average concentrations as high as 2.6 × 10^6 CFU/mL and 2.0 × 10^7 gene copies/mL, respectively. However, compared to the raw influent, the secondary effluent of the CAS system had much lower ARB concentrations, frequently by two to three orders of magnitude. Moreover, no ARB was found in the MF permeate of the MBR system. The results showed that the amounts of ARGs in secondary effluent/MF permeate varied from less than the method's quantification limit (MQL) to 10^4 gene copies/mL. The MF permeate of the MBR system still contained some ARGs, such as *ermB*, *intI1*, bla_{KPC}, bla_{SHV}, bla_{NDM}, *sul*, and *tetO*, with average amounts reaching 10^3 copies/mL. In summary, the MBR system outperformed the CAS system in eliminating ARB, ARGs, and the majority of the target antibiotics, demonstrating its efficacy in reducing the presence of these emerging contaminants in wastewater treatment processes.

3. Removal of Tetracyclin

Concerns have recently been raised about the antibiotics' fate, non-target organisms' impact, and an increase in antibiotic resistance in the wastewater treatment systems[18]. Despite their critical importance, the effects of biological nutrient removal in wastewater treatment plants (WWTPs) of these antibiotics remain unknown. Researchers conducted batch experiments using activated sludge samples obtained from two distinct membrane bioreactor systems: reciprocation MBR (rMBR) and air scouring MBR (AS MBR) to assess how antimicrobial substances impact the microbiome and the efficiency of nutrient removal. The activated sludge was exposed to varying concentrations of tetracycline (TET), ampicillin (AMP), sulfamethoxazole (SUL), and a combination of these antibiotics, including 0 mg/L, 0.1 mg/L, and 1.0 mg/L. Notably, the ammonia elimination efficiency was significantly reduced by the antibiotic combination., with a 5% decrease in rMBR and a 12% decrease in AS MBR. Furthermore, there was a significant decrease ($p < 0.05$) in the abundance of the amoA-AOB gene in AS MBR, whereas this gene was unaffected in rMBR. In the presence of antibiotics, the abundancy of gene amoA, from comammox, Nitrospira increased from 2.8 × 10^8

gene copies per gram of sludge (at 0 mg/L) to 5.0 × 10^8 gene copies per gram of sludge (at 1.0 mg/L). Correlation analysis of the relative abundance of prevalent taxa and antibiotic concentrations revealed that Compared to the rMBR microbiome, the AS MBR microbiome was more vulnerable to the antibiotics TET and MXD.

Guo *et. al.* discussed on addressing key micropollutants found in aquaculture wastewater, namely Cu^{2+}, tetracycline (TC), and related tetracycline resistance genes (TRGs), which pose significant risks to both environmental and human health[19]. In addressing this problem, the research developed a thin-film nanocomposite (TFN) forward osmosis (FO) membrane. This innovative membrane comprises an electrospun thermoplastic polyurethane/polysulfone (PSF/TPU) base and incorporates a UiO-66-NH_2 particle interlayer-modified active layer. The investigation explored how varying concentrations of Cu^{2+} influence the combined removal of TC and TRGs, including *tet*A/M/X/O/C, int1, and the 16 S rRNA gene, to gain a deeper understanding of Cu^{2+}'s function in the FO process. Furthermore, the rejection mechanism was thoroughly examined. The findings revealed impressive rejection rates, with TC and Cu^{2+} being rejected at rates of 99.53% and 97.99%, respectively. The study found that even when TRGs achieved rejection rates above 90%, with rates surpassing 99% for *tet*C, this occurred at a Cu^{2+} concentration of 500 μg/L using a 0.5 M $(NH_4)_2HPO_4$ draw solution. This high efficiency in rejection was attributed to complexation reactions between Cu^{2+} and TC, alongside electrostatic interactions, and the adsorption of Cu^{2+} on the membrane's surface. Consequently, the TFN FO membrane developed through this research shows remarkable potential in concurrently removing heavy metals, antibiotics, and resistance genes from actual wastewater, thereby presenting a hopeful approach to resolving water quality issues.

Proteins, azo dyes, and antibiotics are among the materials frequently found in wastewater from the manufacturing of active pharmaceutical ingredients (APIs), which significantly eutrophises water and promotes the growth of bacteria resistant to drugs[20]. A range of polyphenylsulfone (PPSU) membranes were created for this study in order to look into the relationship between pore structures and the ability of the membrane to separate foulants. The properties and functionality of these ultrafiltration membranes were also investigated in the study. A delayed liquid-liquid (L-L) demixing process changed the structure of the membrane's skin layer and its cross-sectional texture from being dense with finger-like macrovoids to taking on the appearance of a porous sponge. For the novel PPSU membranes, noncovalent bonding interactions took a crucial role when forming. These interactions selectively affected the surface polarity, the thickness of the layer, electronic repulsive force, and surface pore structure of the membrane. For organic foulants, all of the PPSU membranes demonstrated exceptional rejection capabilities, rejecting acid red 1 (AR1) about 90% of the time and bovine serum albumin (BSA) almost entirely (~100% rejection). Moreover, one of the membranes, denoted as M5, demonstrated a noteworthy 89% tetracycline (TC) rejection efficiency in the first cycle, clearly demonstrating the impact of pore size because of TC's small size. Furthermore, the pure water flux recovery rate (FRR) increased from 85% (for M1, water/ethanol: 100/0) to an impressive 99.9% (for M4, water/ethanol: 30/70) after BSA filtration. This enhancement was attributed to the weak nonsolvent, which reduced the membrane surface's roughness. Additionally, membranes produced with added ethanol (EtOH) exhibited excellent FRR values (99.9%) after AR1 filtration.

Wood membranes (WMs) modified with alkali-tolerant citric acid (CA) have emerged as a practical, cost-effective means of adsorbing tetracycline (TC) from water[21]. Despite limited comparisons of TC removal using modified wood membranes (WMs) with different types of wood channel walls, this study aimed to bridge this gap by focusing on the development of modified WMs using pinewood (PW) and basswood (BW). Before and after modification, both PW and BW WMs were characterized using SEM, EDX, XRD,

ATR-FTIR, TGA, contact angle, and zeta potential analyses. The modification process transformed the cellulose I in the raw WMs' cellulose crystal structures into cellulose II. It also increased the content of carboxylic groups in both PW and BW, enhancing the hydrophilicity of the WM surfaces. Notably, the modified BW WMs showed particle formation on the channel walls, including vessel pits, which introduced additional carboxylic groups. TC adsorption breakthrough curves indicated that the 6 wt% alkali-CA modified BW WMs had a filtration volume effectiveness of 1968 bed volumes (BV), which was higher than the 1205 BV achieved by the 4 wt% alkali-CA modified PW WMs under similar influent TC conditions, with breakthrough points set at 2 and 0.5 mg/L, respectively. At low pH levels, TC formed complexes with WM surfaces through Lewis acid-base interactions. Zwitterionic TC showed a preference for adsorption onto WMs through hydrogen bonding around a pH of 5. However, as the pH increased, TC adsorption efficiency decreased due to electrostatic repulsion. The study also evaluated the costs associated with these modified WMs. For low TC concentration effluents (0 to 0.5 mg/L), the costs for modified BW and PW were approximately 0.0054~0.0126 US$/$m^3$ and 0.01~0.024 US$/$m^3$, respectively. This research provides critical insights into the development of cost-effective and efficient adsorption WMs for removing contaminants from water sources.

Tetracycline (TC) was extracted from water by adsorptive-filtration using graphene oxide (GO) and poly(vinylidene fluoride) (PVDF) electrospun nanofibrous membranes (ENMs)[22]. Comparing to PVDF ENMs, the GO/PVDF ENMs showed a higher pure water permeation flux, ranging from 27,407 to 29,337 LMH/bar. The diameter of the flow pore continuously dropped as we raised the GO content in the GO/PVDF ENMs from 0 to 1.5 wt%. According to the Langmuir model, the maximum TC adsorption capacity of GO was determined to be 720.26 mg/g. This adsorption capacity persisted even after GO was added to GO/PVDF ENMs at a transmembrane pressure of 0.91 bar during water filtration. With 1.5 wt% GO ($GO_{1.5}$/PVDF) ENMs, the maximum experimental TC removal capacity ($q_{a,exp}$) was 17.92 mg/g, which was quite similar to the 18.03 mg/g value predicted by the modified dose-response model. Because the hydrophobic and π-π interactions brought about by hydrophobic organic carbon were improved, TC adsorption was enhanced when the natural organic matter was used. Furthermore, through cation bridging, the presence of Cu(II) enhanced the TC adsorption capacity in $GO_{1.5}$/PVDF ENMs, whereas Ca(II) had the opposite effect by impeding TC adsorption through electron shielding. During water filtration, the log removal values for *Staphylococcus aureus* and Escherichia coli bacteria stayed above 5 in order to evaluate the anti-fouling qualities of GO1.5/PVDF ENMs. Moreover, the addition of GO to PVDF ENMs inhibited the adsorption of bovine serum albumin (BSA) by making the ENMs more hydrophilic, generating an electrostatic repulsion between the negatively charged BSA and GO in $GO_{1.5}$/PVDF ENMs (zeta potential = -14.14 mV in deionized water at pH 6), and forming a hydration layer on the surface.

4. Conclusion

This review highlights advancements in wastewater treatment, focusing on the removal of antibiotics and antibiotic-resistance genes using novel membrane technologies. Techniques like graphene oxide-cellulose nanocrystal hybrid membranes and cellulose acetate/Mg-Al layered double hydroxide nanocomposites show promise in efficiently removing pharmaceuticals. The integration of materials like CeO_2-modified carbon nanotubes and eco-friendly polyelectrolyte membranes and the application of biological processes have also been effective. These innovations demonstrate significant improvements in antibiotic removal efficiency, nutrient recovery, and the reduction of environmental and health risks associated with pharmaceutical pollutants in water.

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