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Removal of Antibiotics from Wastewaters by Carbon Nanotube Filtration Membrane: A Review

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ABSTRACT

Water pollution by antibiotics is a global challenge requiring an affordable, readily available, efficient solution. Therefore, this review evaluates the role of carbon nanotube (CNT) based filtration membrane as an efficient solution to provide clean water free of antibiotic residues. The study considered the preparation of CNTs and CNT filtration membranes and their performance towards removing antibiotics from water. The study revealed that there are several methods for the preparation of CNTs, among which the chemical vapour deposition (CVD) is commonly used. It further revealed that three types of CNT-based membranes exist, which are vertically aligned (VA-CNT), bucky paper CNTs (BP-CNT) and CNT-based composite (CNT-CPS). Despite the high performance demonstrated by the membranes, there is a need to evaluate the cost-effectiveness, safety, and regeneration of the membranes. More studies are also required on a large scale to understand the behaviour of the membranes in the purification of ample water supply and the effect of interference from other co-pollutants in water in the real-life polluted water matrix. The study showed that CNT-based filtration membranes are promising membranes for the future, with reliable properties for effectively purifying contaminated water.

Keywords: Carbon nanotube, membrane, antibiotics, wastewater, removal

1.0 INTRODUCTION

The emergence of antibiotics in the water system has become a global threat to humans, animals, and the environment. Even though wastewater goes through wastewater treatment plants (WWTP), specific amounts of antibiotics are still found in the treated water due to the inefficiency of some of the WWTPs. The effluents emanating from the WWTP are often contaminated with traces of antibiotics. When discharged into the environmental water system (surface water), they pollute it [1-3]. Wastes from homes, hospitals, pharmaceutical industries, veterinary and animal husbandry and effluents from WWTPs are known core sources of antibiotics in environmental water systems [4, 5] The consumption of antibiotics is rising, and a previous study showed that more than 70 billion were consumed in 2010 [6]. In fact, for data generated in 2018, a study reported a global antibiotic consumption rate of 14.30 defined daily doses per 1000 population per day [7].

Table 1 shows some antibiotics reported in an environmental water system from some selected regions, suggesting the presence of antibiotics in water is a global challenge. Antibiotics may become persistent when they get into environmental

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water; this is also the case when they get into WWTP and may become difficult to remove via simple or conventional water treatment processes [21-23]. The presence of these antibiotics in water has many negative consequences, including the emergence of drug-resistant microorganisms and degradation to forms that can threaten humans and aquatic animals [24].

Table 1 Antibiotics reported from some selected regions of the world

Region	Countries	Antibiotics	Concentration ($\mu g\ L^{-1}$)	Reference
Africa	Kenya	Levofloxacin	0.040	[8]
	Ghana	Chlorotetracycline	0.044	[9]
	South-Africa	Metronidazole	0.962	[8]
	Nigeria	Erythromycin	1.000	[8]
	Mozambique	Trimethoprim	9.480	[10]
America	USA	Sulfamethoxazole	1.900	[11]
	Brazil	Cefalexin	0.133	[12]
	Canada	Lincomycin	0.730	[13]
	Brazil	Norfloxacin	0.051	[12]
	USA	Ampicillin	1.969	[14]
Asia-Pacific	Iran	Azithromycin	0.563	[15]
	Australia	Cefalexin	0.027	[15]
	Iran	Ciprofloxacin	0.657	[15]
	Taiwan	Sulfamethoxazole	14.300	[16]
	Japan	Clarithromycin	0.001	[17]
Europe	Croatia	Azithromycin	1.600	[18]
	Spain	Clarithromycin	0.010	[19]
	Croatia	Trimethoprim	1.100	[18]
	France	Oxytetracycline	0.680	[18]
	UK	Amoxicillin	0.552	[20]

Most standard water treatment methods can remove antibiotics in water to some level but not completely. Toxic side products may be formed during the treatment, indicating that the method used to treat antibiotic-contaminated water depends on the kind of antibiotics to remove. The goal is to achieve complete removal without forming a toxic side product. Membrane technology is often used to accomplish this purpose. Oxidation of organic pollutants in water may lead to the formation of toxic substances, although advanced oxidation process have been developed but the photocatalytic degradation may still produces small molecular weight molecules which can be removed my membrane technology [25-27]. Membrane technology ma combine processes such as adsorption and photocatalytic degradation to achieve this purpose [28, 29] A wide range of membranes has been prepared from different materials for this purpose [30]. The type of membrane used will also depend on its mechanism of action towards the target antibiotics. Membrane technology is one of the efficient ways of water purification due to its low energy consumption, high separation selectivity, continuous operation, zero chemical requirement and low energy consumption [31-33].

Despite the success of the use of membrane technology, it is challenged with the accumulation of contaminants on its surface and within its pores; which causes fouling, leading to a reduction in the efficiency of the membrane and, most times, a replacement of the membrane becomes unavoidable [34, 35]. The membrane may be regenerated for reuse; however, the performance reduces over the regeneration cycle [30]. In some situations, regeneration is expensive due to using regeneration chemicals or solvents. The high cost of membrane regeneration makes the membrane technology process costly and may need to be more sustainable in developing countries. The concept of combined methods has evolved in membrane technology. In the combined method, membrane technology includes other methods like oxidation, peroxidation, photocatalysis, etc., in its operation along with separation. The inclusion of these methods helps overcome the challenge of fouling. For example, materials for advanced oxidation may be included in the membrane film, forming a composite that promotes the decomposition of contaminants at the surface of the membrane.

Recently, most studies not only used separation by a membrane but a combination of different mechanisms of action, such as advanced oxidation, photocatalysis, peroxidation, and adsorption, to obtain a more efficient process using a membrane for the removal of antibiotics from water [36, 37]. Different materials have been used in membrane filtration, requiring improvement in many forms. A carbon nanotube (CNT) filtration membrane study has shown promising results. For example, caffeine, acetaminophen, carbendazim and triclosan were removed from water using a CNT filtration membrane [38]. A mixed matrix carbon membrane has been reported to remove tetracycline in water [39]. Single-walled CNTs (SWCNT) and multi-walled CNTs (MWCNT) containing nanocomposite were prepared and used for the removal of ibuprofen and triclosan from water [40]. A study reported the removal of norfloxacin and bisphenol A from drinking water with the help of CNTs and polyvinyl chloride membranes [41]. Using CNT as constituent material in filtration membranes has the advantage of combining different mechanisms of action by including other materials in preparing membranes and forming a composite. This allows the privilege of a combined mechanism of action for completely removing antibiotics. It helps overcome the challenges of fouling encountered in using conventional membranes. Therefore, this review aims to understand the potential of using CNT filtration membrane filtration to remove antibiotics from water.

2.0 CNT FILTRATION MEMBRANES

CNTs are porous adsorbents with high electrical conductivity and active sites for interacting with other molecules. They are cylindrically shaped carbon atom sheets, which may be single-walled (SWCNT) or multi-walled (MWCNT), as shown in Figure 1.

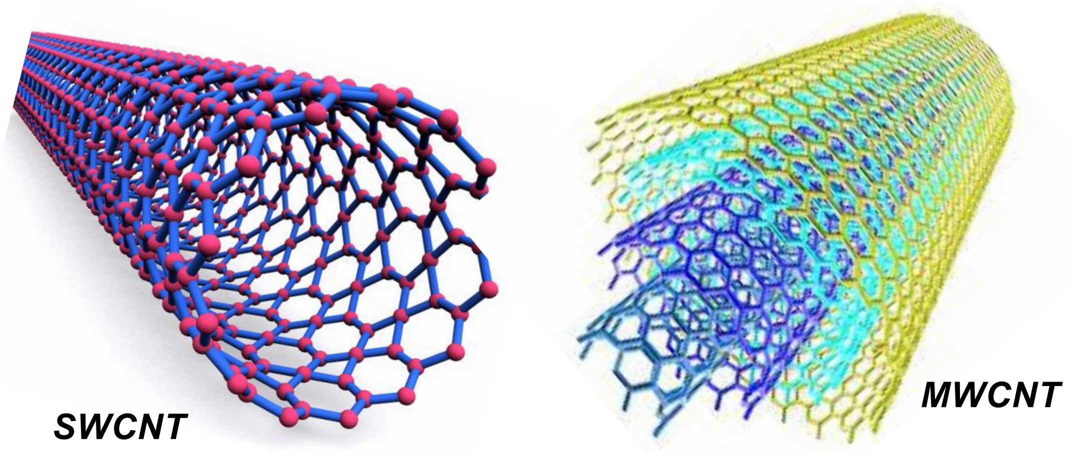

Figure 1 Diagrammatic representation of single walled (SWCNT) and multiwalled (MWCNT) shape carbon nanotubes

They exhibit unique properties such as high surface area, optical, vibrational, and mechanical stabilities. Due to their surface interaction with other molecules, they can be coupled with other materials for advanced oxidation processes, sometimes called CNT-electrocatalytic membranes [42]. The CNT-based electrocatalytic filtration membranes are efficient, stable and with a three-dimensional structure that enhances their performance [43, 44]. They have shown better activity than conventional membranes regarding regeneration, stability, and well-defined structure [44]. The performance has been shown to depend on electron transfer, physical adsorption, and mass transfer with a capacity to degrade organic pollutants [45].

2.1 Preparation of CNT

Several carbon sources are used in the preparation of CNT [46], while the common synthetic routes are arc discharge, chemical vapour deposition (CVD) and laser deposition methods [47]. The advantages and advantages of the three common methods are described in Table 2.

Table 2 Advantages and disadvantages of different synthetic routes for CNTs

Synthetic route	Advantages	Disadvantages	Reference
Arc discharge	Limited structural defect, and simple method	High temperature, required, short nanotube, and low production	[48]
Chemical vapor deposition	Low temperature, mass production, and economically viable for large scale industrial production	Best method for MWCNTs but not suitable for SWCNTs	[49]
Electrolysis	Process simplicity, easy control, low energy consumption, use of cheap raw materials, easy control of product structure and morphology	Destruction of graphite cathode during process, accumulation of electrolysis products,	[50]

Synthetic route	**Advantages**	**Disadvantages**	**Reference**
Sono-chemical/hydrothermal	Process is green, easy size control of CNT, large scale production, cheap technique, short time	Low product yield, multi-steps are required, expensive equipment, inefficient energy	[51]
Laser deposition	High purity, very few structural defects	Intensive cost and labor required	[52]

Two other methods have also been developed for the synthesis of CNT: sonochemical or hydrothermal and electrolysis [53]. The type of method used depends on the quality and intended application of the CNT.

The CVD is usually used for large production of CNTs with high economic viability at low temperatures, unlike the arc discharge process, which requires high temperature [54-56]. Furthermore, most SWCNTs and MWCNTs are produced in large quantities via CVD. SWCNTs are formed when the catalyst size is less than 10 nm, while MWCNTs are made when the catalyst size is large [57]. Common catalysts are cobalt, iron, aluminium, molybdenum, and nickel. Impurities such as amorphous carbon, catalytic particles and nontubular fullerenes are produced along with the CNTs. When this occurs, there is a need to remove such contaminants. It is vital to ensure minimal impurities are generated during production to avoid the high cost of the separation step that may increase production costs. Gas phase CVD is always encouraged to prevent generating large amounts of impurities [58]. CVD is low-cost, scalable, and easy to control compared with the other methods.

A study synthesised CNT on a silicon substrate using nickel as a catalyst, while ethanol was a carbon source in the argon carrier gas [59]. The role of the catalyst was checked in the CVD process involving the addition of molybdenum to a cobalt catalyst [60, 61]. It was revealed that the type and amount of catalysts play a vital role in the yield of CNTs during the CVD method. In consonance with this, a high SWCNT yield was reported using iron and molybdenum catalysts supported on a magnesium oxide substrate [62]. A 75.40 % yield of CNT was reported by using methane as a carbon source in the presence of ferrocene and molybdenum hexacarbonyl as catalysts [57]. A recent study reported a floating catalytic CVD method as the state-of-the-art progress for controlling the growth of CNTs [49].

The laser deposition method involves the vaporisation of graphite target by pulse laser in a high-temperature reactor in the presence of inert gas. The method is referred to as physical vapour deposition and is suitable for producing SWCNT. The SWCNTs made via this means have high purity and excellent structural integrity [63]. Different laser energies were studied in the production of CNT from graphite immersed in deionised water [64]. Previously, a study reported using a 532 nm Nd: YAG laser to target graphite in deionised water in the presence and absence of ultrasonic waves [65]. A 10 min irradiation of graphite in distilled water with a pulsed Nd: YAG laser of wavelength 532 nm has been reported to yield CNT [66]. The laser's wavelength plays a vital role in the quality of CNT produced; apart from this, a study evaluated the effect of a liquid medium on the properties of

CNTs [67]. The study revealed that the nature of the liquid medium used influences the properties of CNT formed. Therefore, when utilising the laser deposition method, care must be taken when selecting the wavelength and the liquid medium for the process.

In the arch discharge method, graphite electrodes immersed in inert gas are exposed to a direct-current arc voltage to generate CNTs. The method favours the production of MWCNT using mixed metal catalysts [68]. A high degree of structural perfection is possible using the arch discharge method; however, a lot of variables and conditions are required, which makes it expensive [68, 69] since it may involve the use of electrodes and chemicals [70-73]. A study reported the synthesis of nitrogen and boron-doped MWCNT [70]. Although the method appears superficial, obtaining a high yield from the method is always challenging. The arc discharge method may produce both SWCNT and MWCNT [74]. However, it is most suitably used to create MWCNT. A study that used methane as feedstock to produce MWCNT revealed that high ambient pressure favours the growth of MWCNT [75]. Increasing the arc current from 50 to 90 A also favoured the growth of MWCNT. Vaporising graphite rods have been reported to synthesise CNT in the presence of Ni and a Ni/Y mixture as catalysts applying a voltage of 30 V, current of 95 A and electrical power of 2.25 kW. The study corroborated that as the catalyst increases, the yield obtained increases [76].

The hydrothermal process is advantageous over the other methods because it is environmentally benign and inexpensive [77]. The process uses lower energy and lower oxygen content; these advantages make it suitable for preparing CNTs. The method has been used to prepare CNT-titania composite and evaluated for its ability to degrade acetaldehyde under UV illumination [78]. Similarly, the method was used to prepare CNTs, which were applied as supercapacitors [79]. Using the hydrothermal method, CNT was recently reported from renewable sources at low temperatures [80]. The electrolysis method works by depositing the CNT onto the electrode during the electrolytic process. The solid graphite goes into the solution while the carbon cathode breaks down. This leads to the production of MWCNTs. The process is simple, easy to control, low energy consumption, ease of controlling the properties of the CNTs produced and ease of process optimisation are the advantages of the process [50]. However, there are some disadvantages to the method, which include undesired accumulation of electrolysis products on the electrodes, breakdown of graphite cathode during the process and deposition of carbon nanomaterials in the electrolytic bath [50]. To minimise the concerns about climate change, the electrolysis method used in producing CNT harnessed CO_2 in a molten electrolytic process as feedstock [81].

2.2 Preparation of CNT Filtration Membranes

Including CNT in membrane to form CNT based filtration membrane has emerged as an improved technique in separation technology. CNT filtration membranes use the combined unique properties of CNT and the separation power of the membrane, which produces enhanced membrane performance with improved permeability and selectivity. Therefore, when CNT is included in a membrane, it can change the membrane morphology, improve membrane porosity, improve mechanical properties, solve fouling problems, and solve trade-off issues between permeability and selectivity [82]. The nature of the CNT affects the final membrane performance. As the number of walls in CNT (SWCNT or MWCNT) is boosted, the membrane performance improves [83]. A study has shown that when CNTs have a low diameter, the smallest SWCNTs exhibit better water transport than MWCNTs with a similar inner diameter [83]. Interestingly, the low-diameter SWCNTs allow the fabrication of highly permeable and selective high-density membranes [84]. CNT-based filtration membranes may be divided into vertically aligned CNT (VA-CNT), bucky paper CNTs (BP-CNT) and CNT-based composite membranes (CNT-CPS) as previously described [85, 86]. The differences among VA-CNT, BP-CNTs and CNT-CPS are highlighted in Table 3.

Table 3 Comparison of the different types of CNT filtration membrane

VA-CNT	BP-CNT	CNT-CPS
Fabrication process is complicated	Fabrication process is simple	Fabrication process is simple
Mechanical strength is moderate	Mechanical strength is limited	Mechanical strength is excellent
The network is compact	The network is compact	Loosely fit
Arrangement is vertical	Arrangement is random	Arrangement is random
Special operating system is needed	Requires simple operating system	Requires simple operating system
High water flux rate	Moderate water flux rate	Moderate water flux rate

The VA-CNT membranes are perpendicularly arranged to form aligned and opened channels [87]. The membrane allows a high flux of water through its structure which is an additional benefit to its use [88, 89]. VA-CNTs are produced by engulfing CNT in a polymer matrix. The CVD method can also achieve this by growing the CNT and polymer matrix on a substrate. Since most CNTs come as powdered when produced in large quantities, it is vital to pre-align the CNTs because powdered CNTs are unsuitable for producing VA-CNTs. Care must be taken because the synthetic route affects the length, density, diameter, and number of walls produced [87, 90]. The most common methods used to synthesise VA-CNTs are CVD, arc discharge, and laser ablation. A study has shown that arc discharge and laser ablation are expensive, while the CVD method is economical and affordable [91]. A study reported using microwave plasma-enhanced CVD (MPECVD) to synthesise VA-CNT [92, 93]. The process generated high electron density, ensuring a higher VA-CNT quality and reasonable yield. During the synthesis of VA-CNT, both ends of the CNT are covered by fullerene caps, making fluid transport through its inner core difficult. Moreover, the interstitial spaces between CNTs are not narrow because the arrays are fixed on a substrate used during production. Therefore, direct use of VA-CNT may only be beneficial with modification during synthesis to enhance performance as the membrane. Recently, VA-CNT was synthesised via template-assisted pyrolysis of polybenzimidazole-Kapton in the pores of anodised aluminium oxide [94]. A comparison of the different synthetic methods for VA-CNT filtration membranes is shown in Table 4. The method of choice for the synthesis of VA-CNT depends on the properties desired and the specific applications. When small diameter of VA-CNT is required, alcohol-assisted CVD would be the method to consider. It can further be concluded that Si is the most common substrate used in the synthetic process which may be due to the stability of si that enhances the stability of CNT [95].

BP-CNTs may be described as buckminsterfullerene or freestanding porous CNT ropes bounded by weak Vander Waals' force [116-118]. Most BP-CNTs are prepared by vacuum filtration, which involves three steps. Firstly, CNT is dispersed in a suitable solvent (N-Methylpyrrolidone and N, N-dimethylformamide are commonly used) in the presence of a surfactant (Sodium dodecyl-sulfate and polyoxyethylene octyl phenyl ether are widely used). In the second step, the homogeneously dispersed solution is filtered, and in the final step, the filtered CNTs are deposited on the filter forming the membrane [119, 120]. The mechanical property is weak with Young’s modulus and tensile strength of about 0.2-2 GPa and 2-33 MPa [121-123]. However, this may be improved when incorporated into a polymer matrix [118]; the CNT composite usually formed has well-improved properties. A recent study reported such improvement using a metal-organic framework to achieve a double-layer superior membrane performance with high permeance up to 59.3 and 76.0 L m^{-2} h^{-1} bar^{-1} for water and methanol, respectively [124]. Another study has also demonstrated the preparation of an improved BP-CNT from a carboxylated CNT with further modification by incorporating a surfactant, which improved the hydrophilic properties [125].

CNT-CPS membranes are designed to exhibit advanced transport and selectivity features due to the uniqueness of their properties, such as conductivity, water transport, temperature stability, chemical inertness, and mechanical stability [126]. CNT-CPS are produced from the functionalisation of CNT with the inclusion of functional materials and, in some situations, polymeric materials forming a membrane with enhanced performance [127]. The radiation-induced method was recently reported for the modification of MWCNTS to produce polyvinyl alcohol imprinted MWCNT, which was further designed with cellulose acetate to obtain CNT-CPS with improved properties, which gave high filtration flux (approximately1660 L m^{-2} h^{-1} bar^{-1}) and oil-rejection (>99.1%) when applied on dodecane-in-water emulsions [128]. CNT-CPS was produced from self-supporting BP-CNT, which lasted for up to 40 h in continuous testing. The CNT-CPS exhibited a high permeability of 3.3 x 10^{-12} kg $(m.s.Pa)^{-1}$, having an average percentage salt rejection of 95% [129]. Poly(vinyl-alcohol)-carbon nanotube composite membranes were employed in electro-ultrafiltration, which enhanced sieving performance [130]. Further assessment based on zeta potential measurements, microscopy evaluation and permeate flux suggested significant performance of the CNT-CPS. The combination of membrane technology and advanced nanotechnology has shown effectiveness as a synergistic approach for treating polluted water.

Table 4 Comparison of the properties of CNTs emanating from some selected synthetic method, process catalysts and substrates

Synthetic Method	Catalyst	Thickness (µm)	Substrate	Diameter of CNT (nm)	Type	Reference
Thermal-enhanced CVD	Fe/Al_2O_3	1.2/10	Si wafer	7.4–13.6	MWCNT	[96]
	Al/Al_2O_3 Fe/Mo	0.5	n-type (phosphorus) Si (100) wafers	1.6–4.0	MWCNT	[97]
	Fe/Al_2O_3	10/10	Si (100) wafers	1.0-4.0	MWCNT	[98]
	Al/Co	0.8-3	Si	6-12	MWCNT	[99]
		15/1	n-type Si wafer coated with 300 nm thick of SiO_2	3-4	MWCNT	[100]
Laser-assisted CVD	Mo/Fe/Al	50–200	Si	1	MWCNT	[101]
	Fe	5-100	Si	30	MWCNT	[102]
Hot filament PECVD	Ni	15–60	Glass	20–400	MWCNT	[103]
	Fe/Al_2O_3	0.5	Si wafer	0.8–1.6	SWCNT	[104]
	FeNi	10	Glass substrate	10–30	MWCNT	[105]
	Ni	8	Glass substrate	10–30	MWCNT	[106]
Alcohol-assisted CVD	Fe/Co	1.2/10	Si wafer	0.8	SWCNT	[107]
	Ru	0.2	$Al_2O_3/SiO_2/Si$	0.84–1.26	SWCNT	[108]
	Pt	0.5	Si/SiO_2	1	SWCNT	[109]
	Co/Cu	1.8	Si/SiO_2	0.9	SWCNT	[110]
	Co/Mo	-	quartz substrate (25 × 25 × 0.5 mm^3)	0.9	SWCNT	[111]
Microwave plasma-enhanced CVD	Fe	10	n-type Si (100) wafer	15	MWCNT	[93]
	Co	2	Mo	30	MWCNT	[112]
	Ni	70	Si	10–35	MWCNT	[113]
	Co	3-50	Si	10–35	MWCNT	[114]
	Al_2O_3/Fe	30/1	Si wafer	3-5	DWCNT	[115]

Precisely, CNTs, due to their unique property in composite membranes, have played an essential role in water treatment [131-134]. This synergy has exhibited outstanding performance in catalytic, adsorption and electrochemical properties, which gives them application in water treatment to remove antibiotics in water. This way, the properties can be combined in a single water purification process.

3.0 CNT FILTRATION MEMBRANE AS A RESOURCE FOR REMOVING ANTIBIOTICS IN WATER

Several modifications have been developed to improve the performance of CNT-based filtration membranes for water purification. Many approaches have been embarked on, emanating from numerous products in literature. Some of the reported membranes are compared in Table 5. Most CNT-based filtration membranes in the literature exhibited high capacities for removing antibiotics in water. The presence of CNTs in the membrane structure improved the performance of many of the membranes. Including CNTs in the polymeric membrane is advantageous and should be encouraged. A study demonstrated the preparation of a carbon-based nanofiltration membrane with MWCNTs interposed between graphene oxide forming a three-dimensional structure (PDDA-MWCNTs/GO), which was used to remove tetracycline hydrochloride from water [135]. The PDDA-MWCNTs/GO is an efficient membrane that can filter antibiotics in water system via electrostatic interaction. It expresses a 99.23% removal capacity towards the studied tetracycline hydrochloride and a high-water permeation of 16.12 $L\ m^{-2}\ h^{-1}\ bar^{-1}$. This performance is better than some previously reported water purification processes [136, 137] which supports the concept of membrane technology being a promising technology for now and the future in water purification. The optical image of the PDDA-MWCNTs/GO is shown in Figure 2 [135].

The PDDA-MWCNTs/GO showed excellent mechanical flexibility and could be reused over 7 cycles without forming any apparent cracks. Electrochemical and carboxylated CNT were prepared by vacuum filtration to remove antibiotics and antibiotic resistance genes in the water system [33]. The preparation was achieved via a simple reaction route using polytetrafluoroethylene as a substrate. Another study revealed the modification of the SWCNT membrane by UV-initiated graft polymerisation [6]. A benzophenone initiator (photo-initiator) was used, while 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBM) in dioxane served as the monomer. A description is shown in Figure 3 [6]. The modification created a combined hydrophilic/hydrophobic layer in the membrane as a means of improving the performance of the membrane.

Table 5 Comparison of the efficiency expressed by some selected CNT based filtration membranes towards some antibiotics in water

Membrane material	**Contaminant**	**Observation**	**Remark**	**Efficiency**	**Effectiveness & reusability**	**Reference**
Reduced graphene oxide with tunable magnetic nanoparticles	Bisphenol A	High surface area and magnetic properties. Adsorption process that fitted for pseudo-second-order model	The process is favorable at ambient temperatures with great reusability	Low	Low cost & Reusable	[138]
Single and multi-walled carbon nanotubes	Oxytetracycline and ciprofloxacin	Adsorption capacity remained the same in cold and warm conditions. SWNCT had the highest adsorption capacity	Enhanced adsorption of oxytetracycline	Moderate	Low cost & reusable	[139]
Multilayer graphene	Phenanthrene	Possibility of exfoliation and fragmentation that increases adsorption capacity	It can be used for controlling thickness	High	Moderate cost & Reusable	[140]
Activated Graphene	Ciprofloxacin	Increased surface area	pH dependent process	Moderate	Low cost & Reusable	[141]
MWCNT and Powdered Activated carbon	Nitrofurazone	High efficiency that fitted for pseudo-second-order kinetic.	Temperature dependent performance	Moderate	Low cost & Reusable	[142]
SMWCNT functionalized by MWCNT	Sulfamethazine	Preparation by dip-coating and pyrolysis	Ultrasonication methods was more effective	Low	Low cost & Highly reusable	[143]
Magnetic rGO composite	Chlorophenols	Easily regenerated	Efficient in neutral and acidic pH	Moderate	Low cost & Reusable	[144]

Single walled carbon nanotubes = SWCNT, multi-walled carbon nanotubes = MWCNT, rGO = reduced graphene oxide

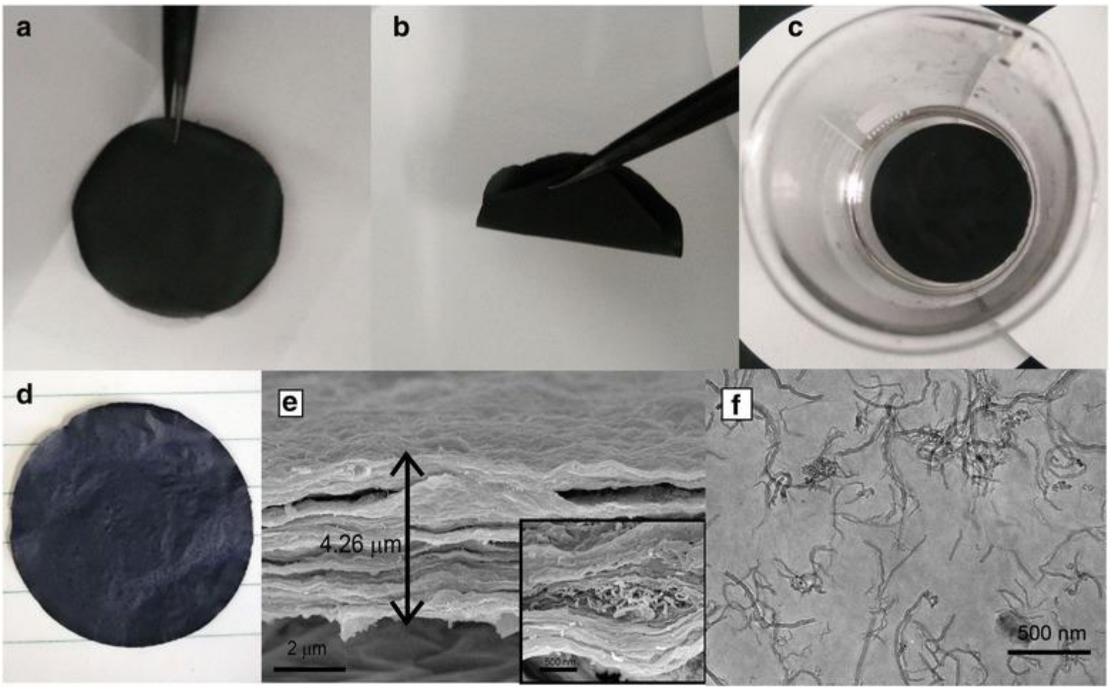

Figure 2 Optical images of PDDA-MWCNTs/GO membrane (**a**), image showing the flexibility of the PDDA-MWCNTs/GO membrane (**b**), image showing the stability of the PDDA-MWCNTs/GO membrane in water (**c**), image of the PDDA-MWCNTs/GO at more than 8th cycle of operation (**d**), SEM images of cross-sections of the PDDA-MWCNTs/GO membrane (**e**). The inset shows a higher magnification image of the PDDA-MWCNTs/GO membrane, TEM images of the PDDA-MWCNTs/GO membrane (**f**) [135]

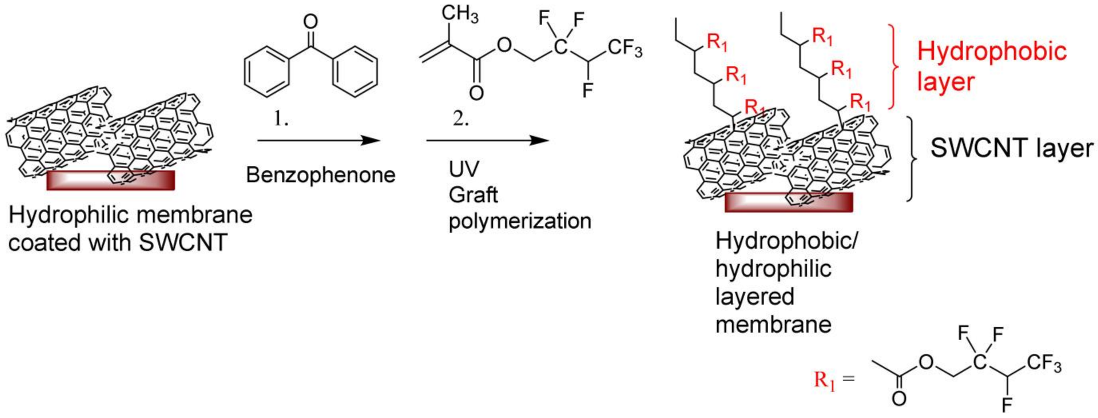

Figure 3 Modification of SWCNT membrane by UV-initiated graft polymerization [6]

The water permeation and adsorption capacity of some selected CNT-based filtration membranes are shown in Table 6.

The adsorption capacity expressed by the membrane towards antibiotics in solution is high. This suggests that CNT-based filtration membranes are membranes for the future in water purification. A hybrid carbon membrane was reported to remove tetracycline hydrochloride in drinking water [151]. The combined effort of graphene oxide (GO), CNTs and activated carbons (ACs) effectively removed 98.90% of tetracycline hydrochloride from water.

Table 6 Water permeation and adsorption capacity of some selected CNT based membranes

Membrane	**Antibiotic**	**water permeation ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)**	**Adsorption capacity (%)**	**Reference**
PDDA-MWCNTs/GO	TCH	16.12	99.23	[135]
SWCNT-MO	SMZ	-	98.80	[6]
	TMP		95.50	
	TC		87.00	
PES/ZrP	CIP	97.62	99.70	[145]
CeO_2@CNT	DCF	-	91.20	[146]
	SMZ		91.30	
	CIP		94.40	
	TC		99.30	
	CBZ		89.40	
TFC-FO	TC	-	99.30	[147]
PSF-PAA	AMX	108.30	91.00	[148]
PNF	TMP	21.10	>99.00	[149]
	SMZ		>99.00	
PCu_2W_{11}/NH_2-PVDF	TC	-	98.30	[150]

Tetracycline hydrochloride = TCH, - = Not reported, PDDA-MWCNTs/GO = Poly diallyldimethylammonium chloride-multi-walled carbon nanotubes-graphene oxide, sulfamethoxazole = SMZ, tetracycline = TC, trimethoprim = TMP, SWCNT-MO = Single-walled carbon nanotube-Mild oxidation, PES/ZrP = nano-composite adsorptive membrane based on Zirconium Phosphate (ZrP) adsorbent supported on Polyethersulfone (PES), CIP = ciprofloxacin, carbamazepine = CBZ, diclofenac sodium = DCF, TFC-FO = thin film composite- forward osmosis, PSF-PAA =polysulfone-polyacrylic acid, AMX = amoxicillin, PNF = Bifunctional photocatalytic nanofiltration, PCu_2W_{11}/NH_2-PVDF = polyoxometalate on ethylenediamine functionalized polyvinylidene fluoride

The AC was uniformly included in the GO for enhanced performance, as shown in Figure 4 [151], which revealed uniform insertion of CNTs and ACs in the GO structure. The inclusion improved the surface area of GO, which increased from approximately 86 $m^2\ g^{-1}$ to 414 $m^2\ g^{-1}$ for the GO-AC membrane and 326 $m^2\ g^{-1}$ for the GO-CNTs membrane. Recently, MWCNT electrochemical filtration membrane was prepared and applied to remove sulfamethoxazole, ciprofloxacin, and amoxicillin from the aqueous system [44]. The result further revealed high efficiency even in treating a mixed matrix of the combined antibiotics. Fortunately, the study showed that CNT-based filtration membranes might effectively treat a complex mixture of antibiotics matrix, which conventional membrane processes may find challenging.

4.0 CURRENT TREND AND FUTURE PERSPECTIVES

Many studies have investigated using VA-CNT, BP-CNT, and CNT-CPS as membranes for water treatment. There is no doubt that CNTs-based filtration membranes have the potential that may be improved for water treatment. Presently, membrane technology is used in many parts of the world for water treatment, most of which are based on reverse osmosis. One major challenge has been the replacement of the filters over time which many consider expensive and not sustainable in poor developing countries. Using CNTs-based membranes opens many opportunities for using them in water treatment.

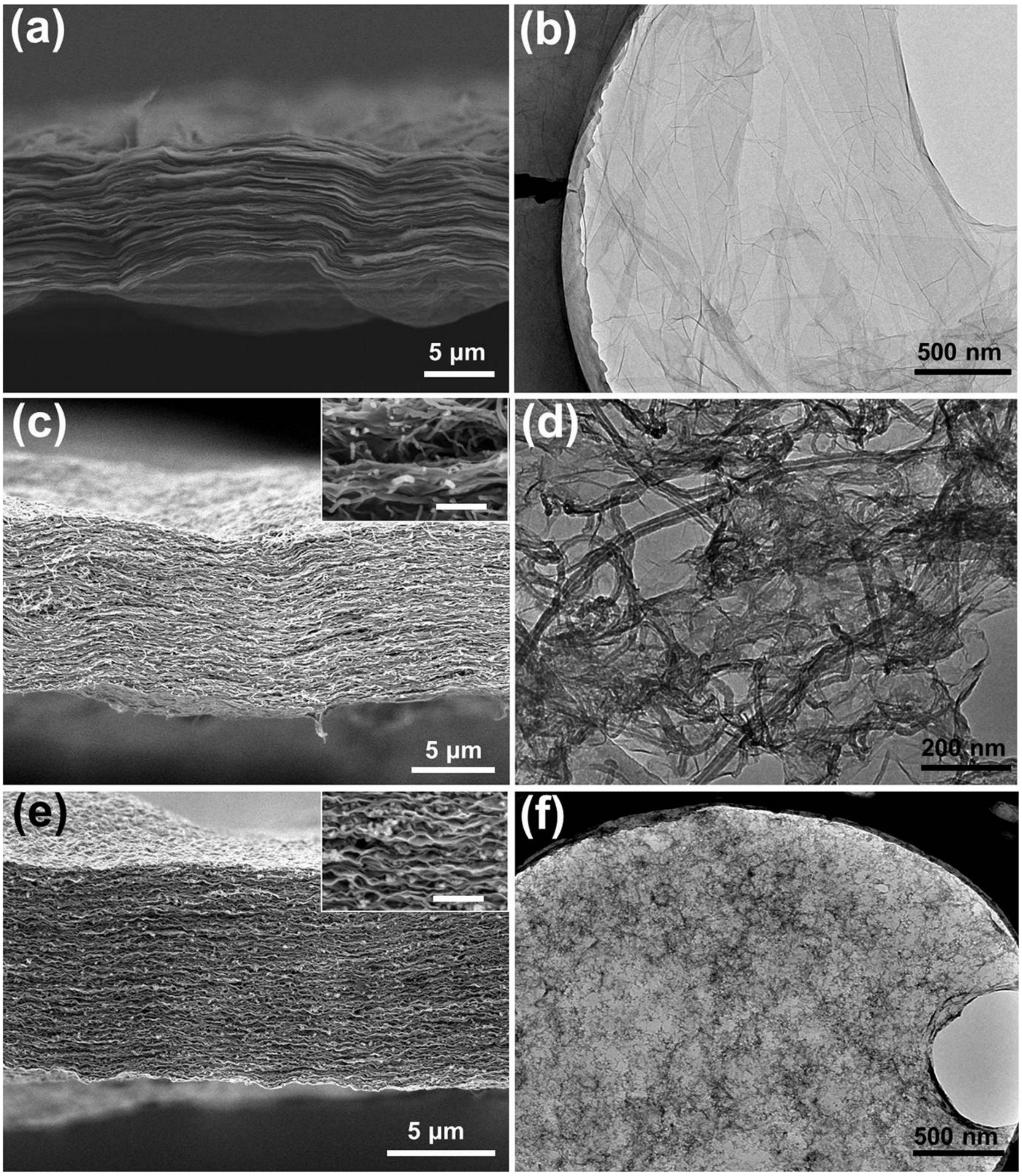

Figure 4 SEM images of a cross-section of (a) GO, (c) GO/CNT, and (d) GO/AC membranes, and TEM images of (b) GO, (d) GO/CNT, and (f) GO/AC membranes [151]

In the case of CNT-based membranes, it is possible to adsorb organic pollutants in water and oxidise the contaminant to simple molecules such as O_2 and CO_2; this possibility makes it easy to use the membrane over a long period. Unfortunately, most of the studies reported are on the laboratory scale. There is a need to conduct studies on a large scale to understand the behaviours of the CNT-based membranes on a large-scale application; studies in the future should focus on scaling up the process. This may also include a scale-up in the manufacturing of the membranes. It is necessary to do a cost evaluation of the manufacturing of the CNT-based membranes and the cost of running the water treatment with the membranes. A cost evaluation study is therefore required.

The cost of carbon in the market is expensive, making the presence purchase of carbon sources to produce CNTs expensive [152]. Although several studies use bio-sources, the process cost, such as energy, technology, and waste management generated during the process, are still makes it high [152]. It is crucial to attain the full potential of the process by developing cheap and affordable technology for carbon production. Most of the studies reported were based on the synthetic water system in the laboratory containing a single antibiotic pollutant. Real-life polluted water has a complex matrix of molecules with different behaviours. It is essential to understand the selectivity of the membranes in a complex matrix of a contaminated water system. Therefore, future studies should prioritise understanding the performance of the membranes in real-life polluted effluents and environmental water systems like rivers, streams, etc. This will help understand the behaviours of the membranes towards complex antibiotics matrix and interferences from other water pollutants.

Most of the studies focus on improving the wetting behaviour of membranes by surface modification through surface functionalisation by including different functional groups. This approach sometimes damages the CNT structure, which may decrease flux rate [82]. It is necessary to optimise modification processes that will not damage the CNT's structure or intrinsic properties; however, emphasis should be on developing freestanding and free CNT membranes with excellent properties for removing antibiotics from water. It is vital to check the recycling or regeneration of CNT-based membranes; most studies did not report the regeneration or recycling of the membrane, but a few. Checking this will further help to understand whether or not the membrane leached into the water after several uses. Future work needs to look in this direction. It is necessary to fact-check the toxicity of the membrane because after the membranes are completely spent, what happens to them is crucial. This may also include the membranes' biodegradability, environmental safety, and safety management when they are completely spent.

5.0 CONCLUSION

The review is focused on understanding the use of CNT-based filtration membranes to remove antibiotics from solution. Antibiotics have been detected in environmental water systems with the core sources being wastes generated from homes, hospitals, pharmaceutical industries, and effluents from WWTPs. The preparation of CNTs and CNT filtration membranes has been discussed. The study revealed that there are several methods for the preparation of CNTs, among which the CVD method is commonly used. It further revealed that three types of CNT-based membranes exist, VA-CNT, BP-CNT, and CNT-CPS, with several possibilities. The study showed that CNT-based filtration membranes are promising membranes for the future with reliable properties for effective purification of contaminated water. However, evaluating the cost-effectiveness, safety, and regeneration of the membranes is necessary. More studies are also required on a large scale to understand the behaviour of the membranes in the purification of large water supply and the effect of interference from other co-pollutants in the real-life polluted water matrix.

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