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# **A comprehensive review on micropollutants removal using carbon nanotubes-based adsorbents and membranes**

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## **Abstract**

Pharmaceuticals, steroids, personal care products, and disruptive endocrine substances are increasingly being used for healthcare objectives and to improve living conditions, resulting in the widespread presence of micropollutants in various water sources. Traditional water/ sewage and wastewater treatment plants are limited in their ability to cope with faced with these pollutants, making it challenging to supply safe and clean water for drinking and other domestic purposes. In this review, carbon nanotubes (CNTs) and CNTs related composites/ membranes have been considered suitable for settling this emerging issue. The existence of emerging micropollutants and their deleterious effects on human and animal health are discussed in this review. The efficient removal of micropollutants from different water sources using different

types of CNTs (pristine/ functionalized) and CNTs-based composites/ membranes have been reviewed and evaluated. Moreover, fabrication approaches CNTs- based composites/membranes are also presented with their merits and demerits. Lastly, the current barriers and future perspectives are discussed in detail. The present review provides an in-depth understanding of the removal of micropollutants from CNTs and CNTs related composites/ membrane and allows future researchers to resolve the barriers related to their applications at an industrial scale.

**Keywords:** *Micropollutants, carbon nanotube adsorbents, carbon nanotube membranes, free-standing membranes, carbon nanotubes, emerging disrupting compounds*

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## **1. Introduction**

The natural equilibrium of the ecology has been disrupted by continuous urbanization and industrialization, which has polluted every environmental source with a number of contaminants. As a result, access to safe and clean drinking water has become much more difficult, especially for third-world countries where environmental, societal, political, and economic factors also play an important role. Water-borne and non-fatal illnesses kill around 200 million people each year, according to estimates [1]. More than a billion people lack access to safe drinking water, resulting in serious global health challenges. Furthermore, the production of waste from poultry and dairy farms, as well as domestic, municipal, and industrial waste, is degrading world water supplies and reducing the supply of safe and clean water significantly. Micropollutants are a rising concern globally since they are among the pollutants that are posing grave danger to the global ecosystem [2]. The most commonly known

micropollutants, such as surfactants, solvents, pesticides, endocrine disrupting compounds, pharmaceuticals products, and personal care products, have often been detected in various water sources, such as drinking water and sewage water groundwater, and wastewater treatment plants. After disinfecting, few of the organic micropollutants transform into extremely toxic disinfection by-product through the addition of reaction or chlorine substitution, bringing chronic or acute disease for both human and animal [3]. Despite the adverse impacts and noxiousness, the level of micropollutants is expected to rise in the future due to the fast-growing global population, dependency on chemicals, and the non-biodegradability of most micropollutants [4]. Furthermore, many anthropogenic events, such as oil spills, municipal, industrial, and untreated wastewater effluents, deliver various micropollutants to the water bodies on a daily basis [5]. Therefore, designing advanced treatment techniques and materials for the effective elimination of organic pollutants is of great importance. Several techniques have been designed and implemented to decline the organic pollutants, for instance, adsorption [6], membrane filtration [7], and advanced oxidation processes [8].

Among these techniques, membrane separation has been known as the new generation water reclamation and purification technology because of its high separation capability, simple and continuous operation, low requirements of chemicals, and tiny footprint [9]. Nevertheless, highly selective pressure-driven membranes proficient in eliminating organic micropollutants are frequently dense and need high hydraulic pressure and energy consumption [10]. Membrane distillation could eliminate organic micropollutants because of their nominal pressure supplies, but the former is restricted to non-volatile organic micropollutants and subsequently needs regeneration of the draw solution [11]. Meanwhile, conventional membranes struggle from fouling, leading to a decline in flux and inclines in energy usage.

Hence, novel membrane materials fabrication and design have been substantially researched to overcome the trade-off between water purification capability and energy usage [12], [13].

Recently, innovative approaches to water and wastewater treatment with the support of nano-sized materials have been introduced. Nanotechnology assists in the advancement of future-generation water supply practices. Nanomaterials can adsorb and degrade different toxins such as pharmaceuticals, dyes, heavy metal ions, and pesticides and display interesting anti-microbial features against water-borne microbes. Unique aspects of nanomaterials backing up their potential for competent hydric resources remediation include strong mechanical strength, high surface area, economical cost, energy needs, higher chemical reactivity, recyclability, and convenient production modification approaches [14]. Carbon nanotubes (CNTs) are known as potential materials, especially for water purification. CNTs have been employed as catalyst support and adsorbents in advanced oxidization processes for different wastewater treatment applications. Moreover, CNTs have been incorporated with various materials to develop nanocomposites, for instance, CNTs-graphene, CNTs-magnetic graphene, and CNTs-bentonite for contaminants adsorption [15]. Reactive metals and oxides have also been embedded in CNTs, thus bringing diverse superoxide to form highly reactive oxygen species, for instance, superoxide radical. The reactive radicals can degrade a broad range of harmful organic contaminants into harmless carbon dioxide, mineralized salts, and water, following to regeneration of CNTs [16]. However, CNT-based composites have a poor adsorption efficiency, and CNT-based catalysis requires chemicals for catalyst and reactive oxygen species regeneration. CNTs in powder form, on the other hand, have a high risk of recontamination and are not suitable for reuse [17].

CNTs-based membranes have attracted tremendous attention, particularly as water purification candidates. CNTs membranes with interweaved nano-porous morphology have been developed by a grouping of self-assembly and filtration techniques [18]. In contrast, free-

standing CNTs membranes can also be fabricated through a facile vacuum filtration approach. Nevertheless, CNTs membranes are primarily employed for water treatment based on their adsorption and removal features, in which membrane fouling and performance regeneration are primary encounters [19]. It has been reported that the engineering adsorptive CNT-based membrane could overcome the disadvantages of typical CNT-based nanocomposites and membranes, allowing for the very effective removal of micropollutants [20]. Despite the prominence and importance of this area, there has yet to be a critical study that reports on the new CNT-based membranes for eliminating micropollutants.

This review attempts to bridge the gap in the literature by providing an overview of current CNTs and CNT-based composites/membranes, as well as their applications in micropollutants removal. The review mainly focuses on removing micropollutants via CNTs and CNTs-based composites/membranes rather than traditional adsorbents/membranes, i.e., membranes bioreactor, activated alumina, or silica gel. The review begins with a brief account of the existence of micropollutants, which is supported by various studies that determine their concentration in different water sources (surface water, groundwater, sewage, and wastewater treatment plant) around the world, as well as policies and regulation signed on their legal limits allowed in water resources, specifically EU policy, and their negative health and environmental effects. Fabrication methods for CNTs-based composites/membranes are also explored, as well as their benefits and drawbacks. In addition, current research studies have been evaluated for the removal of micropollutants by CNTs and CNT-based composites/membranes in a systematic manner. Finally, the hurdles to CNTs, and CNT-based composites/membranes are discussed, as well as future research opportunities. The paper lays forth a road map for future research by outlining the elements that could assist enhance the current state of CNTs and CNT-based composites/membranes.

## **2. Micropollutants**

Most surface water forms display many anthropogenically generated compounds; moreover, 10% of European lakes are only labeled 'very clean' based on their chemical grade [21]. Besides, the United Nations resolution in 2010 stated water as the 'new gold of 21st century'. There is currently an agreement in place that provides a long-term source of enhanced water quality, which is inextricably linked to marine eco-health and surrounding territory by providing essential eco-services. Furthermore, water pollution can cause a variety of problems, including the extinction of marine species, reduced biodiversity, and pathogenic eruptions, and it can harm marine species even at low quantities [22]. As a result, environmental concerns, including improving water quality, are one of the most pressing issues for present and future generations. By recognising and eliminating contamination sources, water quality could be improved in a sustainable and effective manner.

Up to date, Chemical Abstract Service (CAS) has labeled around 89,000,000 chemical compounds [23]. Because of the introduction of new items, the number of anthropogenic substances in water continues to rise daily, and this frightening situation becomes increasingly obvious with improved analytics. One of the rising fears is the 'emerging pollutants' or micropollutants [24]. The term micropollutants are described as anthropogenic chemicals found in the aquatic environment more than the usual natural level because human action, with trace concentrations i.e., ppt to ppb. Hence, micropollutants are described by their anthropogenic source and their existence at low concentrations. Most often, micropollutants are mentioned as anthropogenic trace compounds (ATC) [25]. Micropollutants may comprise uncontaminated synthetic chemicals or natural compounds, or estrogens. Micropollutants sources include agriculture, pharmaceuticals, steroid hormones, food products, and pesticides [26]. They are primarily introduced into the environment by effluents from wastewater

treatment plants and agricultural wastes. Micropollutants have been found in large quantities in water sources used to produce drinking water in the past [27].

The existence of micropollutants in various water sources has been reported widely [28]. It has been estimated that nearly 70% of the pharmaceuticals in the wastewater come from domestic households, 5% from hospital discharge, 20% from livestock farming, and the remaining derives from non-particular sources; nevertheless, geographical and seasonal variations on average take place. The concentration of micropollutants in different water sources is very much dependent on their physicochemical properties, for instance, octanol-water partition coefficient (LogP), dissociation constant (pKa), and water-solubility [29]. LogP and pKa are essential properties of micropollutants influencing their sorption affinity and charge. According to Rogers, the low and high sorption potential is determined by the value of LogP, i.e., the value of LogP less than 2.5 shows low sorption potentials and the LogP value greater than 4 shows high sorption potential [30]. A list of well-known micropollutants found in different water sources and their physicochemical aspects are listed in Table 1.

**Table 1:** The physicochemical features of the micropollutants

Compound	Molecular weight (gmol <sup>-1</sup> )	Density (gcm <sup>-3</sup> ) @25°C	Water solubility (mgL <sup>-1</sup> ) @25°C	pKa	LogP	References
Tylosin, Antibiotics (C <sub>46</sub> H <sub>77</sub> NO <sub>17</sub> )	916.1	~1.1424	211	7.73	1.633	[31]
Ibuprofen, Anti-inflammatory (C <sub>13</sub> H <sub>18</sub> O <sub>2</sub> )	206.29	1.03	21	4.47	3.84	[32]
Carbamazepine, Antiepileptic drug (C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O)	236.27	1.296 @115 °C	125	13	2.77	[33]
Pravastatin, Lipid (C <sub>23</sub> H <sub>36</sub> O <sub>7</sub> )	424.53	~4.2	6.065	4.2	3.1	[34]
Atenolol, β-blockers (C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> )	266.336	261	13300	9.6	0.16	[35]
Triclosan, Antibacterial (C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub> O <sub>2</sub> )	290	1.49	10	7.9	4.76	[36]



Methyl-paraben, Preservatives (C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> )	152.15	1.2	2.5x10 <sup>3</sup>	-	1.96	[37]
17-β ethinylestradiol, Hormones (C <sub>20</sub> H <sub>24</sub> O <sub>2</sub> )	296.4	-	11.3	10.4	3.67	[38]
Diazinon, Insecticides (C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> PS)	304.35	1.12	40	2.6	3.81	[39]
Butylhydroxytoluene, Food additives (C <sub>20</sub> H <sub>12</sub> )	220.35	1.05	0.6	-	5.1	[40]
Bisphenol A, Plasticizers (C <sub>15</sub> H <sub>16</sub> O <sub>2</sub> )	228.29	1.2	300	10.29	3.32	[41]
Tri(chloropropyl) phosphate, Flame retardants (C <sub>9</sub> H <sub>18</sub> C <sub>13</sub> O <sub>4</sub> P)	327.6	1.39	7000	-	2.82	[42]
Oxybenzone, Sunscreen (C <sub>14</sub> H <sub>12</sub> O <sub>3</sub> )	228.4	1.2	3.7	7.6	3.79	[43]
Homosalate, UV filters (C <sub>16</sub> H <sub>22</sub> O <sub>3</sub> )	262.34	1.04	<1	-	6.16	[44]
Chlorpyrifos, Fungicides (C <sub>22</sub> H <sub>17</sub> ClN <sub>2</sub> )	350.59	1.4	1.4	-	4.96	[39]
Tonalide, Cosmetics (C <sub>18</sub> H <sub>26</sub> O <sub>2</sub> )	258.41	0.96 @70 °C	1.25	-	5.7	[45]
Diuron, Herbicides (C <sub>9</sub> H <sub>10</sub> C <sub>12</sub> N <sub>2</sub> O)	233.1	1.48	42.1	2.68	2.68	[39]

Since micropollutants can be found everywhere and are usually used to enhance human life, it is not easy to maintain these compounds' sources in the water environment [46]. Many studies have testified micropollutants' availability at a significant level in drinking, ground, surface, and wastewater [47]. The conventional wastewater treatment procedures currently in use at plants are not designed to eradicate micropollutants, thus these chemicals remain in the processed water and wastewater run-off. Furthermore, micropollutant occurrence in the aquatic environment is linked to adverse effects, long- and short-term toxicity, endocrine-disrupting chemicals, and antibiotic resistance in micro-organisms [48]; [49]. Table 2 provides the list of well-known micropollutants that have been comprehensively studied and detected in different aquatic sources globally:

**Table 2:** Micropollutants detected in different water sources based on country

Micropollutant	Category/ Class	Aquatic Compartments	Research Country	Concentration (ngL <sup>-1</sup> )	References
17- $\alpha$ - Ethinylestradiol	Hormones	Surface-water	China	0.2-1.9	[50]; [51]
		Wastewater	Germany		
				South Africa	<1-8
Diclofenac	Non-steroidal anti-inflammatory	Grey-water	France	1.17-380	[52]; [53]; [54]
		Surface-water	Spain		
			Greece	0.8-1043	
			Costa Rica		
	United Kingdom	0.5-261			
2- ethylhexyl-4-methoxycinnamate	Sunscreens	Wastewater	Norway	4.7-505	[55]; [56]
		Surface-water	Japan	12-1040	
Methylparaben	Preservatives	Sewage-water	Spain	290-1000	[57]
Butyl-paraben	Parabens	Tap-water	Spain	28	[58]; [59]
Neonicotinoids	Insecticide	Surface-water	United States of America	1.1-105	[60]; [61]
			Spain		
		Wastewater	Australia	4.73-14.92	
Macrolide	Antibiotics	Surface-water	China	0.01-778	[62]; [63]; [64]; [52]
			Vietnam		
		Wastewater	Spain	54-1890	
			Slovakia		
			United States of America		
	Grey-water	China	0.2-20.5		
		Spain			
Butyl-methoxy-di-benzoylo-methane	UV-filters	Sewage-water	Hong Kong	289	[55]
17- $\beta$ - Estradiol	Hormones	Wastewater	Sweden	<1-88	[65]; [66]; [67]
			China		
		Grey-water	United States of America	0.3-147	

			France		
Ibuprofen	Non-steroidal anti-inflammatory	Surface-water	Costa Rica	5	[54]; [68]; [69]; [25];
			South Korea	15	
			Taiwan	5-280	
		Groundwater	Spain	185	
Oxybenzone	UV-filters	Tap-water	United States of America	14	[70]
N,N-diethyl-metoluamide	Insect repellents	Sewage-water	China	60	[71]
Carbamazepine	Anticonvulsant	Surface-water	Canada	3	[72]; [54]; [73]; [68]; [74]; [75];
			Costa Rica	1	
			United Kingdom	5-684	
			South Korea	4-595	
		Groundwater	Germany	-	
			United States of America	40	
Triclosan	Disinfectant	Sewage-water	India	892	[76]
			United States of America	540	
Gemfibrozil	Fibrates	Surface-water	Costa Rica	41	[69]; [77]
			Taiwan	1.9-3.5	
		Groundwater	Spain	165.3	
Sulfamethoxazole	Antibacterial	Groundwater	Spain	47.57	[78]
			United States of America	160	
Trimethoprim	Antibiotics	Surface-water	Taiwan	1	[79]
			United Kingdom	7-122	
			United States of America	9.1	
Triclocarban	Bactericides	Tap-water	United States of America	54	[70]; [80]
			Spain	13	

## **2.1 Present legislation and normative strategies**

In early days, there was a believe that the existence of micropollutants in the ecosystem induces a threat primarily for the natural water sources and the related marine species rather than for human being's health. As result, the primary concern with micropollutants is that the vast majority of them are not controlled or recognized by national or international legislation. Consequently, regulation and normative strategies through various organizations emphasize traditional pollutants to protect the quality of environmental systems, particularly associated with waters [81]. On the other hand, several institutions periodically create vital rules on various legislations and proposals features of substances with particular concerns "priority contaminants," for instance (JECFA) joint FAO/WHO expert committee on food additives, all focusing on micropollutants due to their risk based on the analysed or potential effects [82].

Till to date, a limited number of countries have implemented regulations on specific micropollutants; for instance, environmental quality standards (EQS) for nonylphenol and diiron (micropollutants) have been recognized by the EU Parliament [83]. Micropollutants, i.e., steroid hormones, pharmaceuticals, and personal care products (PPCs), are not stated on the controlled substance list. More research on micropollutants' effects on ecological and human health is required to create supervisory benchmarks for micropollutants. Many review papers have been issued concerning micropollutants occurrence in various water bodies, comprehensive studies on micropollutant occurrence are still needed [84].

Even though no defined standard determined the limits of the release of micropollutants, still few regulations have been issued. The first regulation marked in the EU water policy was Directive 2000/ 60/ EC [85]. This regulation mainly focuses on defining the high-risk substances as well as prioritized them. Directive 2008/ 105/ EC and EQS endorsed thirty-three priority substances (PSs) [86]. Furthermore, Directive 2013/ 39/ EU in 2013 suggested having a closer look at the monitorization and treatment options for 45 PSs, meeting

the safeguard of the human health and aquatic compartment [87]. In the same Directive, two pharmaceuticals and natural hormones were suggested in the initial watch-list of ten substances for EU monitoring, introduced within 2 years. On March 20<sup>th</sup> 2015, the watch-list of EU monitoring substances (Directive 2008/ 105/ EC) was revised in Decision 2015/ 495/ EU. The regular rate of pollutants of the emerging issue in the surrounding, helped the revision of the outline to cover a vast number of toxic compounds, besides endorsements for wastewater treatment phases or even innovative treatment states [88]; [89]; [65]. Table 3 lists the various European regulations stated for the legal bases of micropollutants handling:

**Table 3:** Legal bases for micropollutant's handling

<b>European Regulations</b>	<b>Description</b>	<b>Aim</b>	<b>References</b>
Water Framework Directive (2000/60/ EC)	The Directive was adopted on 23rd October'2000. A European directive promises that all European Union (EU) must attain all water bodies' good quantitative and qualitative rank. The completion date for the plan is 2027.	<ul style="list-style-type: none"><li>• Safeguard the transitional, in-land surface, ground, and coastal waters.</li><li>• Secure 'Good Status' for all kinds of waters at the targeted deadline.</li><li>• Water management regarding River Basins.</li><li>• 'Combined Approach' of discharge limit values as well as quality standards.</li><li>• Measures for decreasing the relevant contaminants/ contaminant group (VIII of WFD)</li><li>• Adequate water costing.</li></ul>	[85]; [90]
Plant Protection Product Legislation (1107/2009)	The legislation was published on 21st October '2009. The legislation states guidelines for the plant protection products (PPPs) authorization in marketable form and their setting on the market, use, and maintain within the community. Moreover, set regulations for active substances, synergists, and safeners approval, which PPPs comprise, and co-formulants and adjuvants rules. In short, it is legislation about PPPs that place in the EU market.	<ul style="list-style-type: none"><li>• Support high-level safeguard of the environment and human health.</li><li>• Improve operation of the internal market.</li><li>• Control as well as improve the competitiveness of the EU chemical market.</li></ul>	[91]; [92]
Groundwater Directive (2000/118/EC)	The Conciliation Committee accepted the Directive on 28th November 2006.	<ul style="list-style-type: none"><li>• Description of suitable groundwater chemical conditions.</li><li>• The sustained upward and significant reversal trend in contaminants concentration.</li><li>• EQS for pesticides as well as parameters for threshold values.</li><li>• Measure for controlling good water status and avoid/ decrease the pollutants input.</li></ul>	[93]; [94]

Marine Strategy Framework Directive (2008/ 56/ EU)	The Directive became official on 17th July 2008. It is established as a legal framework for safeguarding and managing EU seas and guarantees their long-standing, sustainable use. The legislation plan is to attain the excellent status of the EU's marine water by 2020.	<ul style="list-style-type: none"> <li>• Achieve good status of the marine water. [95]; [96]</li> <li>• Measures for controlling or decreasing relevant contaminants or contaminant groups.</li> </ul>
Regulation on Detergent (648/ 2004)	The regulation was officially presented on 31st March 2004. The regulation updates and merges the current Directive on detergent. The regulation executes a two-tier testing rule on the active detergent ingredient's bio-degradability, referred to as surfactants. Furthermore, the regulation introduces stricter labeling requirements on detergent producers.	<ul style="list-style-type: none"> <li>• Launch free movement of detergent and surfactants for detergents on the inner market, guaranteeing a high degree of safeguard of human health and environment. [97]; [98]</li> <li>• Bans on surfactants in terms of the bio-degradability two-tier testing rule.</li> </ul>
Directive on Industrial Emissions (2010/ 75/ EU)	The Directive was officially presented on 24 <sup>th</sup> November'2010. This EU Directive which pledges EU member state to maintain and reduce the industrial emission impact on the environment.	<ul style="list-style-type: none"> <li>• Establish guidelines on integrated prevention and pollution control are rising from industrial actions. [99]; [100]; [101]</li> <li>• Design rules to stop or decrease emissions into water, air, and land. Moreover, limit waste generation to attain a high level of safeguard of the environment.</li> </ul>
Regulation on Biocidal Products (528/ 2012/ EU)	The regulation was adopted on 22nd May'2012. The regulation relates to biocidal product use and place in the market, which is used to shield animals, humans, articles, or materials against toxic organisms such as bacteria or pests by the action of active constituents contained in the biocidal product.	<ul style="list-style-type: none"> <li>• Biocidal products authorization regarding environmental risk valuation of active biocidal products and substances. [102]; [103]</li> </ul>

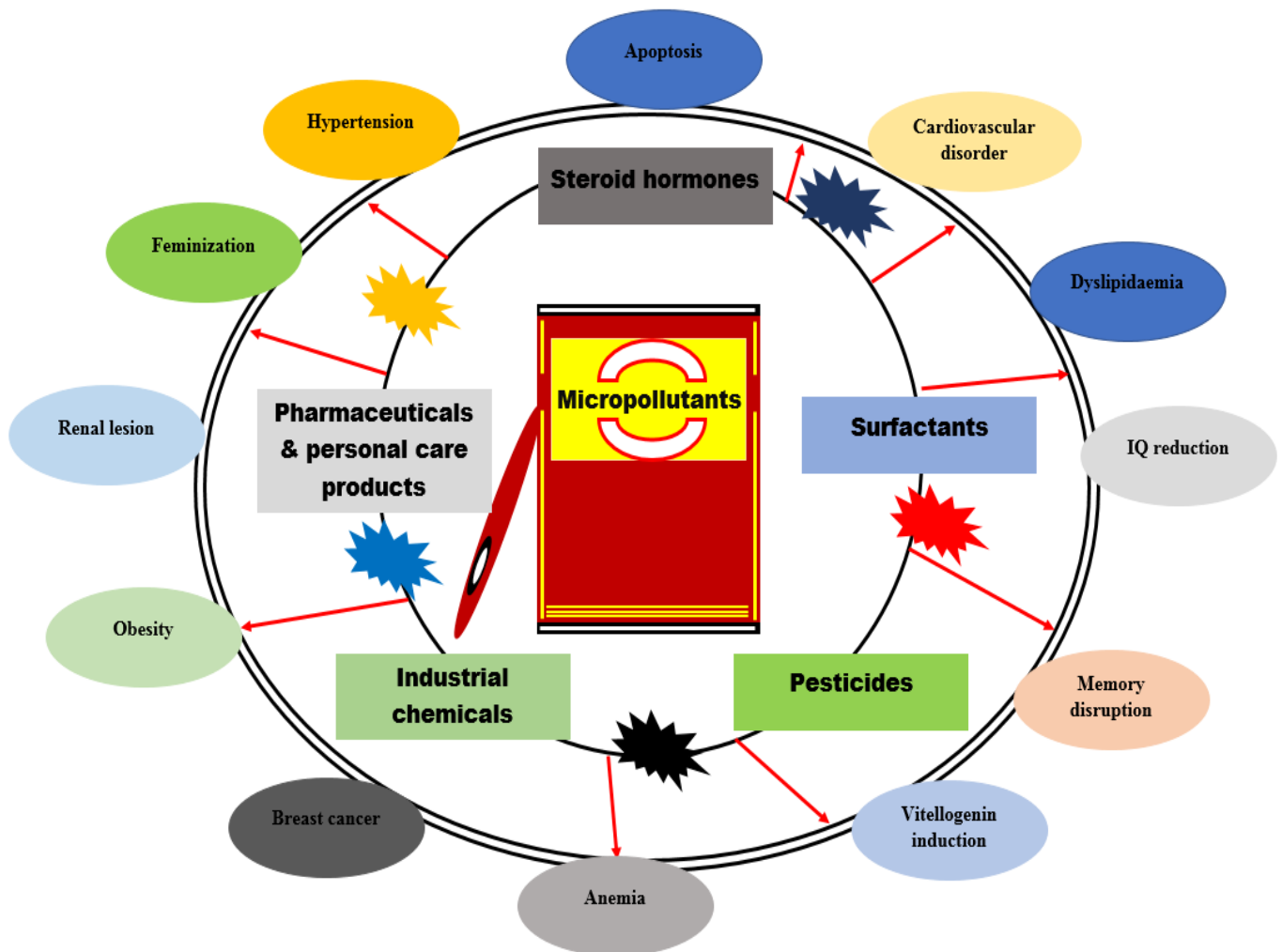
## **2.2 Environmental effects of micropollutants**

Environmental risk induced through substances mainly depends on their chemical and physical affinity and speciation for water and solid matter, which substantially impacts their bioavailability. Moreover, the risk to the biodiversity is also based on the mobility of materials and their potential to be transported into the food chain. The pollutants from suspended particles or water can be absorbed or incorporated into the tissues of aquatic organisms. Consequently, contaminants concentration in the tissues of marine species may be present at levels equivalent to or higher to the environment's concentration. The considerable variation in environmental conditions among water bodies might also be an important factor influencing bioavailability. Among these conditions, temperature, salinity, turbidity, or pH can be prominent. Moreover, the physicochemical aspects and sensitivity are also competent to affect the ability of bio-accumulate contaminants [104]. Even when exposed to identical quantities of certain pollutants, various organisms have varying potentials for bio-accumulation. Individuals of the same species exposed to a similar concentration of pollutants for the same amount of time may not accumulate elements at the similar rate. It is also linked with several other factors, for instance, size, sex, age, and physiological condition of the species. [105]

Data on the chemical concentration level in different water sources lack to investigate the risk to the environment. The results of chemical studies only offer specific information about the possible endanger to human beings and ecology. The environmental risk assessment to study the effects of micropollutants on plants, human health, ground/surface water quality, and aquatic species reported a broad spectrum of disorders posed by the exposure of micropollutants. These chemical elements in drinking water may cause serious, long-lasting effects and deliver irreversible mutations in human and wildlife beings [106]. A research performed on 24 individual post-mortem brain materials detected the accumulation of methylparaben, n-propyl paraben, triclocarban, bisphenol, and methylparaben in their white-matter



brain tissues [107]. A survey conducted in the US on 20 teenage girls, age 14-19, also found the accumulation of 16 noxious chemical compounds related to personal care products use, for instance, cosmetic products [108]. Fig. 1 depicts the known or suspected effect of micropollutants on human's health and the environment



**Fig. 1:** Major consequences and severe effects of micropollutants on human beings' health and the ecosystem

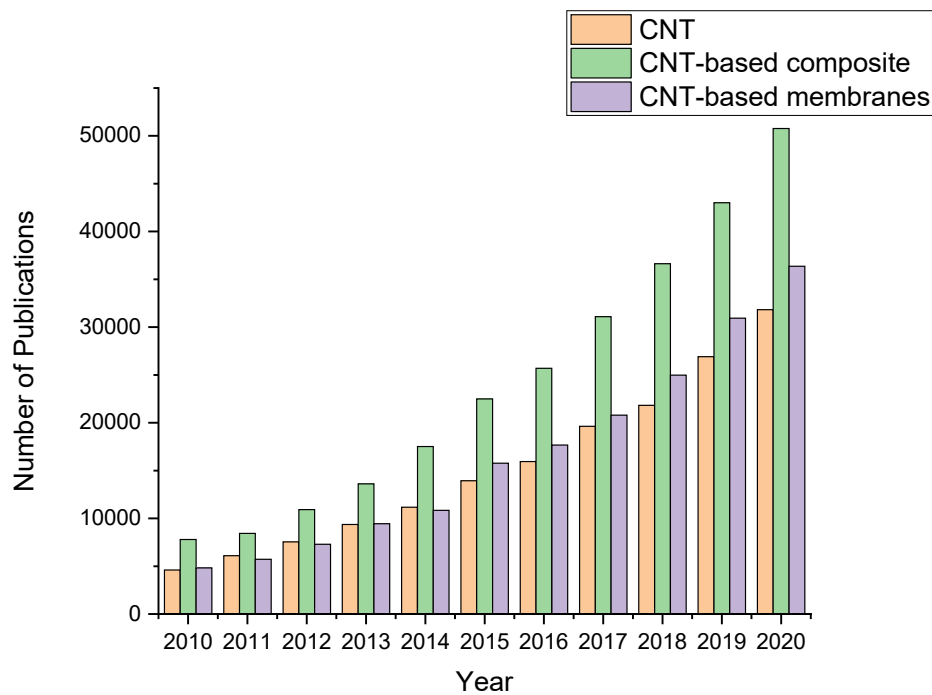
The organic compounds found in aquatic ecosystems are affecting the reproductive systems, threatening marine species growth. Aromatic micropollutants react with chlorine to produce chlorine by-products that are particularly toxic to living organisms. According to Chan and co-workers' research, the formation of different chlorine by-products during chlorination is extremely harmful to living organisms [109]. Antibacterial triclosan disturbs the hormonal functions, causing the metabolism and reproductive systems in human beings. Studies

performed by Kay and associates have discovered that the micropollutant, specifically endocrine-disrupting compounds, can modulate endocrine functioning, i.e., damage fertility, menstrual cycle malfunctions, and endometriosis [110]. Desai and co-associates' [111] study explained the role of endocrine-disrupting compounds in metabolic illnesses, for instance, dyslipidemia, cardiovascular, obesity and insulin resistance diseases in human beings. A separate study performed by Giulio and co-associates [112] elucidated the ability of endocrine-disrupting compounds on the pathogenesis of breast disease even at minor concentrations. The effect of chronic and acute exposure on the reproductive system, histopathological changes, and body organs of fishes, mammals, snails, and birds [113] has also been described.

### **3. Role of nanotechnology in micropollutants removal**

Improving wastewater quality and management is one of the primary focuses of nanotechnology. As a result, nanotechnology has been reported in the literature as the utmost advanced process for wastewater treatment. A few of the major nanotechnology techniques via water treatments are membrane filters with nanoparticles, nano-adsorption, and photocatalysis using nanoparticles [114]. Das and co-associates studied the trends in nanomaterials usages in environmental remediation and monitoring and highlighted the effectiveness of these nano-tools and the requirement to restrict beyond environmental pollution due to their habit [115]. Likewise, Karn and co-associates described nanomaterials' advantages and possible risks and stated that nanotechnology must be customarily seen as advantageous than destructive [116]. Several nano-scale materials have introduced environmental applications, such as metal oxides, carbon nanotubes, zeolites, and different noble metals. In contrast to all, CNT-based composites/ membranes have gotten substantial consideration for water and wastewater treatment applications; therefore, numerous researches have been performed by the scientific community over the past few years. The popularity of CNT-based composites/ membrane for water-related applications can be revealed by the number of articles that have been published

till now and it kept on increasing each year according to the search engine web of science database as depicted in Fig.2:



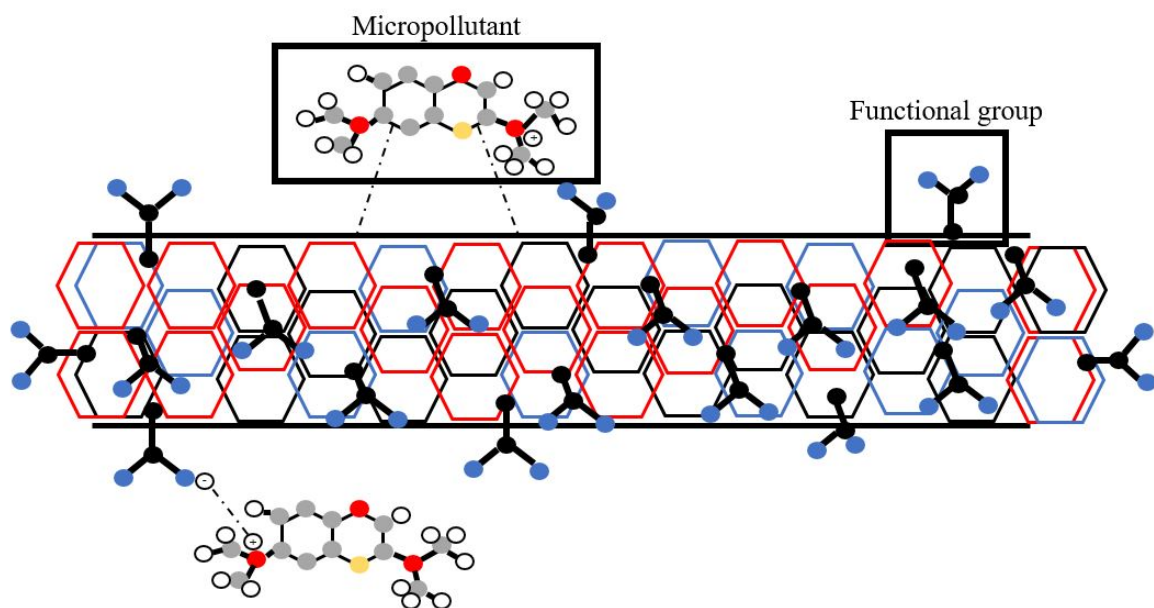
**Fig. 2:** Growth of CNT and CNT-based composites/ membranes for the period of 2010-2020

The above graph is constructed based on the employment of CNT and CNT-based composites/ membranes for water and wastewater treatment applications such as heavy metal, dyes, salt, and micropollutants removal between 2010 to 2020. It is apparent that there have been substantial studies conducted on CNT and CNT-based composites/ membranes. Given the popularity of CNT and CNT-based composites/membranes, the later section mainly focuses on CNT and CNT-based composites/ membranes that have been utilized for water-related applications, particularly micropollutants removal.

### 3.1 Carbon nanotube-based composites

With the rapid interest in nanotechnology, nano-structure materials have gained substantial applications in several sectors, especially environmental remediation and wastewater treatment. They have been introduced in different forms, such as nanotube, nanofiber,

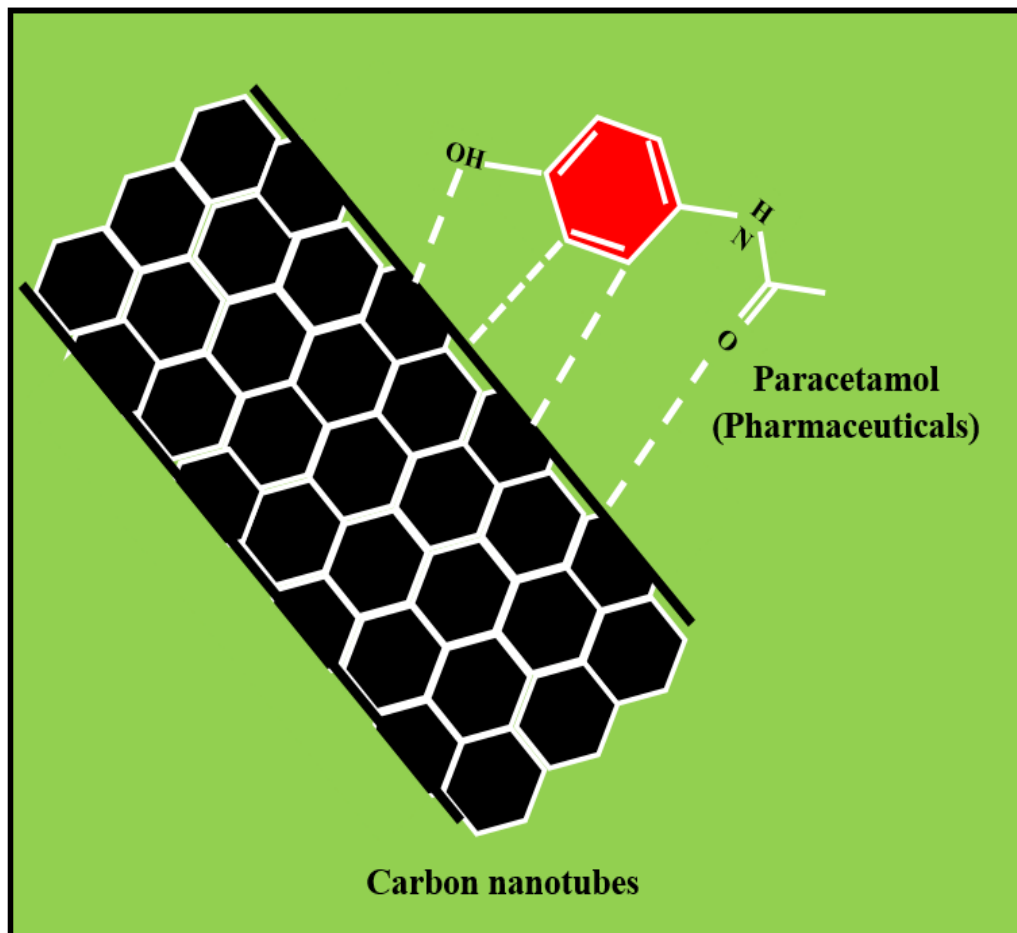
nanoparticle, and nanowire [117]. These nanomaterials have demonstrated higher adsorption capacity for most water pollutants than other bulk materials [118]. Among different nanostructured materials, carbon-based nanomaterials have shown remarkable attention as future-generation materials for different applications because of their unique physicochemical features, excellent mechanical, electrical conductivity, and thermal properties [119]. The outstanding properties of carbon-based nanomaterials lead them to a revolutionary technological breakthrough towards a diverse range of applications, such as electrically conductive materials, biomedical fields, catalyst supports, and biosensors [120], [121], [122]. Furthermore, carbon-based nanomaterials are well-known as excellent adsorbents for pollutants removal from wastewater.



**Fig. 3:** Adsorption of aquatic micropollutants using modified CNTs [123]

Amongst carbon-based nanomaterials, CNTs have been observed to have higher adsorption capacity for organic compounds because of their characteristic morphology, which offers durable interaction of CNTs with organic compound by non-covalent forces, that include  $\pi$ - $\pi$  stacking, van der Waals forces, hydrophobic interactions, hydrogen bonding, and electrostatic forces [124]. Their mechanisms are based on the features of the compound of

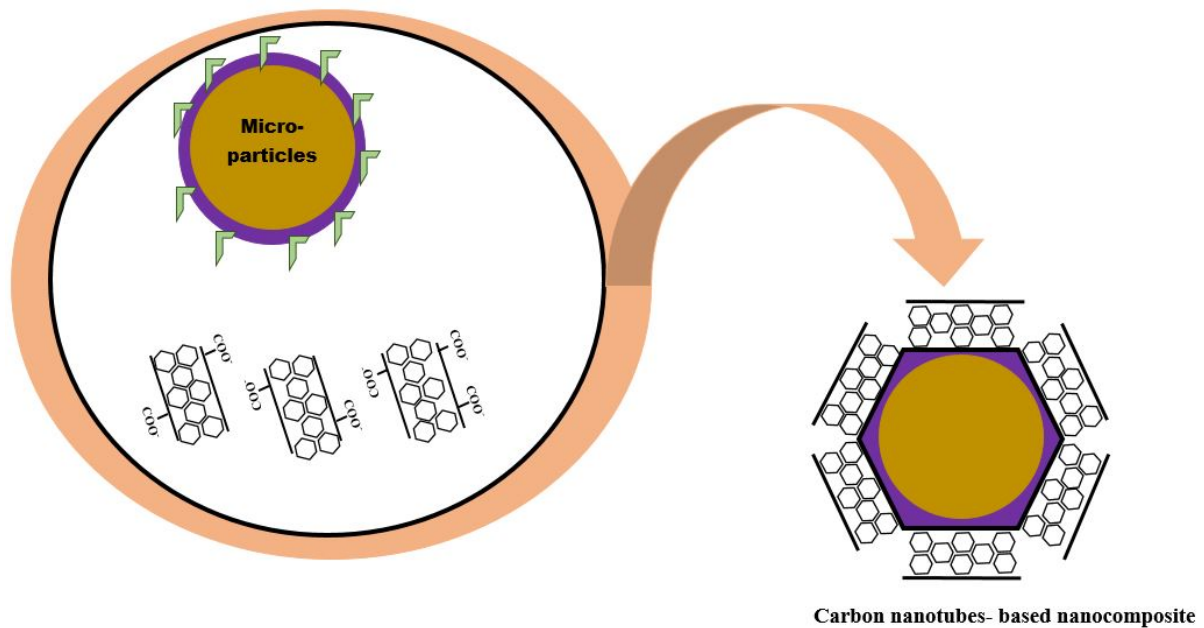
interest. The prognosticate of adsorption of organic contaminants on CNTs is not upfront since it depends upon the nature of interaction among pollutants and CNTs [125]. Features such as surface area, functional groups, purity, and adsorption sites play a crucial part in the adsorption of organic contaminants through CNTs (Fig.3). CNTs consist of high surface active sites and controlled pore size, result in tremendous sorption efficiency [126].



**Fig. 4:** Representation of the interaction of carbon nanotube with pharmaceutical micropollutants

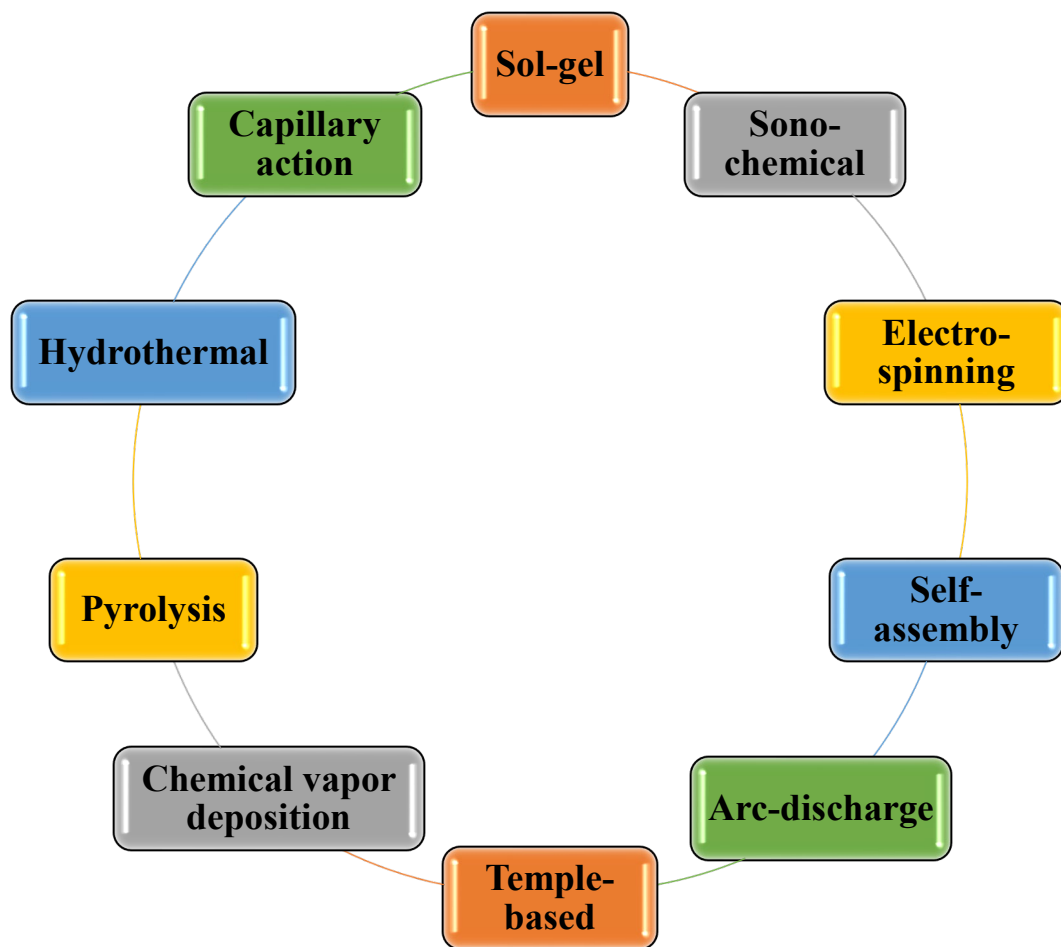
Besides, CNTs tend to aggregate in an aqueous phase after the growth of several interstitial grooves and space, which result in high adsorption sites and assist in an elevation in adsorption capabilities of organic contaminants [127]. Recently, single-walled CNTs have been observed to have great adsorption features of organic contaminants because of their large micropore volume and surface area. The factor that determines the cost-effectiveness of CNTs

is regeneration. It is recommended that CNTs can be restored by decreasing the pH of the solution employing an acid, for instance, nitric acid ( $\text{HNO}_3$ ) [128], [129].



**Fig. 5:** Graphic representation of CNT- based nanocomposite

The popularity of CNT-based nanomaterials have rapidly increased in the scientific society due to numerous aspects such as controlled nano-size and shaped, mass production, economical, and potential to be employed for various application [130]. Fabrication of these nanocomposites through suitable techniques will dictate its efficiency. Various studies have been performed to discover effective fabrication routes to attain the finest, highly stable, and shape-controlled carbon nanotube-based nanocomposites, for instance, filling, hydrothermal, arc-discharge, chemical vapor deposition, and pyrolysis methods. In our previous work [131], a comprehensive discussion of different routes through which carbon nanotube-based nanocomposites can be developed along with their merits and demerits has been presented. Fig. 6 illustrates various fabrication approaches for the synthesis of carbon nanotube-based composites.



**Fig. 6:** Fabrication routes for carbon nanotubes-based composites [132]

Several research works have shown that the CNTs' adsorption capacities can also be elevated by modifying these carbon-based nanomaterials, increasing the adsorption sites. Oxidized CNTs can be further functionalized via esterification of oxidized-CNTs with pentaerythritol (PER) stated by Yang and co-associates, to form oxidized-CNTs-PER, which was used for organic dyes removal (alizarin red S), and the result displayed good adsorption capacity, i.e., 257.73 mg/g [133]. Doping hetero-atoms in CNT is an effective technique to improve CNTs' exterior electronic polarization, which can be advantageous for adsorptive interaction of organic pollutants [134]. Yie and co-associates successfully fabricated nitrogen-doped CNTs to adsorb tylosin, tetracycline, and bisphenol-A. In contrast to non-doped CNTs, nitrogen-doped CNTs possess significantly higher adsorption capacity, credited to their electron-exhaustion and remarkably uniform  $\pi$ - electron acceptor sites. Moreover, many

studies have been conducted on the adsorption of the binary system. The antagonistic and synergistic adsorption effects would be noticed in the concurrent removal of rhodamine B and crystal violet [135]. Since numerous pollutants exist in natural wastewater, interaction among various pollutants must be studied in-depth in multi-component systems. Table 4 shows the recent research studies on CNTs for the removal of micropollutants from various water sources.



**Table 4:** Publications on pristine and surface modified CNTs for the treatment of micropollutants

	Optimum condition	Target micropollutant	Removal percentage (%)	Adsorption capacity/efficiency	Remarks	References
Pristine SWCNTs	pH=7.2 Temperature= 298 K Initial conc.= 220 mgL <sup>-1</sup>	Carbamazepine	80	130 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Freundlich isotherm model was well fit.</li> <li>Increasing pH may have an adverse effect.</li> </ul>	[136]
	Temperature= 298 K Initial conc.= 13.3 mgL <sup>-1</sup>	Atrazine	n/a	33.43 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Thermodynamic parameters observed that the reaction was exothermic.</li> <li>Desorption studies noticed that no significant desorption hysteresis happened.</li> </ul>	[137]
	pH=7.5 Temperature= 315 K Initial conc.= 1 μM Contact time= 72 hrs.	17β- estradiol	99	26.7 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Calculated data from the model revealed that the Pseudo-second-order kinetic model was the best fit.</li> </ul>	[138]
	pH=6 Temperature= 298 K SSA=652 m <sup>2</sup> .g <sup>-1</sup>	Tetracycline	96.2	100 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Lower adsorption reversibility was observed.</li> <li>Specific surface area elevated from 410.7 to 652.8 m<sup>2</sup>.g<sup>-1</sup>; moreover, extensive pore volume was developed during activation.</li> <li>It was improved in adsorption up to 2-3 times.</li> </ul>	[139]
		Sulfamethoxazole	94	10 <sup>3</sup> mg.g <sup>-1</sup>		
		Tylosin	98	10 <sup>4</sup> mg.g <sup>-1</sup>		
	pH= 7 Initial conc.=50 μgL <sup>-1</sup> Temperature= 293 K	Ibuprofen	99	231 μg.mg <sup>-1</sup>	<ul style="list-style-type: none"> <li>Polanyi-Manes model was the best-fitted isotherm model.</li> <li>Stronger sorption was observed due to the high specific surface area.</li> <li>Sorption was directly affected by the electrostatic repulsive interactions among the SWCNT surface and compound.</li> </ul>	[140]
	pH= 5 Initial conc.= 50 mgL <sup>-1</sup> Contact time= 4 hrs.	17α-ethinyl estradiol	99	120 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Experimental studies observed that both Freundlich and Langmuir models are suitable</li> <li>Variation in pH did not affect the adsorption capacity</li> <li>Observed higher log K<sub>ow</sub> value, i.e., ~10.5</li> </ul>	[141]
	pH=6.7~7 Temperature= 298 K Initial conc.= 50 mgL <sup>-1</sup> Contact time= 60 min.	Oxytetracycline	98.4	554 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>An increase in adsorption capacity was noticed at pH ranges from 3 to 7.</li> <li>Brouers-Sotolongo was considered the best adsorption model.</li> </ul>	[142]
		Ciprofloxacin	97.3	724 mg.g <sup>-1</sup>		
		98.5	475 mg.g <sup>-1</sup>			
Temperature= 298 K Initial conc.= 90 mgL <sup>-1</sup> Contact time= 4 min.	Olaquinox	99.7	133.16 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Adsorption kinetics of olaquinox was extremely fast, reached at equilibrium within 2 min.</li> <li>Langmuir isotherm model display maximum adsorption capacity of olaquinox on pristine MWCNTs</li> </ul>	[143]	

Pristine MWCNTs	Initial conc.= 10 mgL <sup>-1</sup> Temperature= 303 K Contact time= 72 hrs.	Tetracycline	90.2	192.7 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Pseudo-second and Langmuir isotherm model was the best-fitted system</li> <li>Desorption efficiencies were reasonable</li> </ul>	[144]
	pH=7 Temperature= 298 K Initial conc.= 5 mgL <sup>-1</sup>	Oxytetracycline	96.5	391 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>The temperature effect causes a slight variation in adsorption capacity</li> <li>The removal efficiency began to decline after pH 7</li> </ul>	[142]
	pH= 2 Initial conc.= 100 mgL <sup>-1</sup> Temperature= 303 K Time= 80 hrs.	ASulfapyridine	80	10 <sup>3</sup> mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>The pollutant possesses low hydrophobicity but is still strongly adsorbed to MWCNTs.</li> <li>The pH effect on adsorption was almost insignificant.</li> <li>The pollutant possesses low hydrophobicity but is still strongly adsorbed to MWCNTs.</li> <li>The pH effect on adsorption was almost insignificant.</li> <li>The experimental studies concluded that MWCNTs are an appropriate candidate for removing given micropollutants from the aqueous phase.</li> </ul>	[145]
		Sulfadimethoxine	85 90	600 mg.g <sup>-1</sup> 1300 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Pseudo-second-order kinetic model explained the kinetic data, and the Langmuir isotherm offered the best fit for all experimental data.</li> </ul>	[146]
		Tylosin	98	300 mg.g <sup>-1</sup>		
	pH= 6 Initial conc.= 500 µgL <sup>-1</sup> Time= 12 hrs.	Atrazine	n/a	36.1 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Experimental data was well-described by the dual Langmuir model for low concentration; hence, the Polanyi-Manes model is suitable for the lowest concentration.</li> <li>Atrazine sorption stayed unchanged from pH 3 to 9, whereas, after pH-6, no decrease in sorption was observed.</li> </ul>	[147]
	pH= 7 Initial conc.=500 µgL <sup>-1</sup> Temperature= 298 K pKa= 4.9	Ibuprofen	n/a	81 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>The experimental result analyzed that the adsorption capability of SWCNTs is comparatively higher than MWCNTs, whereas, in comparison to acid-treated MWCNTs, MWCNTs display higher adsorption capacity.</li> <li>Experimental data was well- described by the Polanyi-Manes model.</li> </ul>	[140]
	pH= 7.8 Temperature= 303 K	Diclofenac	96	41.4 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Based on the isotherm model, it can be reflected that a temperature rise will lower the adsorption capacity.</li> <li>The Freundlich model well- presented experimental data</li> <li>Efficient enough to be used for other emerging pollutants, such as caffeine, Isoproturon, and atenolol.</li> </ul>	[148]

Initial conc.= 8 ppm Contact time= 200 min.	Ciprofloxacin	88	1.745 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Research studies concluded that the adsorption capacity inclined with the increasing time.</li> <li>Studies revealed that adsorption of ciprofloxacin on MWCNTs. is a chemisorption process</li> <li>Pseudo-second model and Freundlich isotherm were favorable.</li> </ul>	[149]
pH= 8 Contact time=200 hrs. Temperature= 293 K	Carbamazepine	95	105 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>62.7 to 90.6 % of initially adsorbed carbamazepine on MWCNTs.</li> <li>Desorption rate depends on the pH as well as the quantity of initially adsorbed carbamazepine.</li> <li>Polanyi-Manes model well-described the experimental data.</li> <li>Desorption was lower from 5 to 6.</li> </ul>	[150]
pH= 6 Initial conc.=600 mgL <sup>-1</sup> Contact time= 24 hrs.	Diuron	>97	50.3 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Polanyi-Manes model well-described the experimental data.</li> <li>The adsorption of micropollutant was directly correlated with the SSA and micropore volume of MWCNTs.</li> </ul>	[151]
pH= 6 Initial conc.= 5 mgL <sup>-1</sup> Contact time=120 min. Temperature= 298 K	17 $\alpha$ -ethinyl estradiol	93.4	0.472 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>A high amount of MWCNTs was used in this study, i.e., 100 mg.</li> <li>A Pseudo-second model was suggested</li> <li>Thermodynamics studies revealed that the removal process is enthalpy-driven.</li> <li>The removal rate was inclined with the rising amount of MWCNTs used.</li> <li>Adsorption capacity decreased at higher solution temperature, observed through kinetic studies.</li> </ul>	[152]
	Estrone	85.6	0.423 mg.g <sup>-1</sup>		
	17 $\beta$ - estradiol	93.3	0.472 mg.g <sup>-1</sup>		
pH= 7 Initial conc.=50 $\mu$ gL <sup>-1</sup> Temperature= 293 K	Triclosan	n/a	435 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Polanyi-Manes model was well-fit to represent the kinetic model.</li> <li>Stronger sorption of triclosan was observed due to high specific surface area.</li> <li>Sorption was directly affected by the electrostatic repulsive interactions among the MWCNT surface and compound</li> </ul>	[140]
pH= 5 Temperature= 303 K	Isoproturon	>96	16.3 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>The adsorption capacity of the micropollutant decreased in the multi-pollutant solution.</li> <li>Experimental data were the best fit by Freundlich isotherm; however, equilibrium adsorption data demonstrated that Langmuir data was well-represented.</li> </ul>	[148]

(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> - H <sub>2</sub> SO <sub>4</sub> - SWCNTs	pH=7.5 Temperature= 280 K Initial conc.= 1 μM Contact time= 72 hrs.	17β- estradiol	99	26.9 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Temperature influenced the adsorption process with MWCNTs</li> <li>There is a slight elevate in SWCNTs diameter after acid treatment, noticed through Raman spectroscopy.</li> <li>The pseudo-second-order kinetic model was the best fit, noticed from the R<sup>2</sup> value.</li> </ul>	[138]
COOH- SWCNTs	pH=7 Temperature= 298 K Initial conc.= 50 mgL <sup>-1</sup> Contact time= 12 hrs.	Ethidium bromide	38.42	200 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Pseudo-second order kinetic model well-defined the kinetic model study</li> <li>Isotherm's study observed that Langmuir better-defined adsorption.</li> </ul>	[153]
COOH- MWCNTs	pH=7.2 Temperature= 298 K pKa=13.9 Initial conc.=90 mgL <sup>-1</sup>	Carbamazepine	93	13.9 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Freundlich isotherm model well-defined experimental data.</li> <li>The pseudo-second-order kinetic model represented the kinetic data successfully.</li> </ul>	[136]
	pH=7±0.5 Initial conc.= 20 mgL <sup>-1</sup> Temperature= 298 K Contact time= 72 hrs.	Alkylphenoletoxilates	94	18.49 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Freundlich isotherm model well-described experimental data.</li> <li>COOH-MWCNTs show extremely -ve surface charge at the operation parameters.</li> </ul>	[154]
Hydroxylated- MWCNTs	pH= 7.5 Temperature= 310 K Initial conc.=15 mgL <sup>-1</sup>	Norfloxacin	>94	72.04 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Freundlich isotherm well-presented the experimental data.</li> <li>The higher temperature is more likely favorable for the micropollutant sorption.</li> <li>The sorption process was thermodynamically favorable, predicted by noticing the -ve value of ΔG°</li> </ul>	[155]
O-MWCNTs	pH= 7 Initial conc.=50 μgL <sup>-1</sup> Temperature= 293 K	Triclosan	n/a	106 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Polanyi-Manes model was well-fit to represent the kinetic model.</li> <li>Sorption isotherm analysis with O-MWCNTs revealed that the chemical features of triclosan, MWCNTs' surface chemistry, and aqueous solution chemistry play a vital role in triclosan adsorption onto O-MWCNTs</li> </ul>	[140]
NH <sub>2</sub> -MWCNTs	pH=7±0.5 Initial conc.= 20 mgL <sup>-1</sup> Temperature= 298 K Contact time= 72 hrs.	Quinolone	93	163.9 mg.g <sup>-1</sup>	<ul style="list-style-type: none"> <li>Freundlich isotherm model described the experimental data well.</li> <li>The highest adsorption was noticed, compared to other pollutants used in the research.</li> </ul>	[154]

To better segregate the solution's adsorption materials, CNTs incorporated with magnetic materials such as  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_3\text{O}_4$ , iron metal-organic framework, and  $\gamma\text{-Fe}_3\text{O}_4$  [156], [157]. Duman and co-associates compared the morphology and surface features of magnetic oxidized multi-walled CNTs/ $\text{Fe}_3\text{O}_4$  and non-magnetic oxidized multi-walled CNTs [158]. The study demonstrated that non-magnetic oxidized multi-walled CNTs displayed better adsorption capacity than magnetic oxidized multi-walled CNTs/ $\text{Fe}_3\text{O}_4$ . The primary advantage of CNT reinforced magnetic materials is that they can conveniently be separated from the aqueous phase via magnetism. Donghai and associates prepared magnetic ferrite ( $\text{Fe}_2\text{O}_4$ ) modified CNTs materials that can be utilised to remove organic toxins from wastewater [159]. While introducing  $\text{Fe}_2\text{O}_4$  with CNTs was not very helpful for bezafibrate adsorption, it could be conveniently isolated magnetically and regenerate. Besides, multi-walled CNTs embedded in the iron metal-organic framework have displayed adequate adsorption capacity, particularly for tetracycline antibiotics [160]. These research works reflected that CNT-based adsorption materials could remove organic pollutants from different water sources efficiently. Table 5 reviews selected publications on CNT- based magnetic nanomaterials for the treatment of micropollutants:

**Table 5:** Publications on various CNTs-based magnetic nanomaterials for the treatment of aquatic micropollutants

CNT-based nanomaterial	Target micropollutant	Adsorption model	Max. adsorption capacity/ efficiency	Removal efficiency (%)	References
f-MWCNTs/ FeCl	Bisphenol-A Ketoprofen	Langmuir	26.53 $\mu\text{g}\cdot\text{mg}^{-1}$	>92	[161]
f-MWCNTs/ $(\text{NH}_4)_2\cdot\text{FeSO}_4\cdot 6\text{H}_2\text{O}$	Nitrofurazone Furaltadone				
f-CNTs/ $\text{Fe}^{2+}$ / $\text{SrTiO}_3$	Ethinyl estradiol	-	250~750 $\text{ng}\cdot\text{L}^{-1}$	74.4	[163]
	17 $\beta$ - estradiol			63.25	
	Progesterone			97.19	
f-MWCNTs/ $\text{FeCl}_3\cdot 4\text{H}_2\text{O}$	Ibuprofen	Langmuir	1.15~11.8 $\text{mg}\cdot\text{g}^{-1}$	>93	[164]
f-MWCNTs/ $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$	Nicosulfuron	-	-	87.3	[165]
	Metsulfuron methyl			97.7	
	Chlorimuron ethyl			96	
f-MWCNTs/ $\text{FeCl}_2$	Carbamazepine	Redlich-Peterson	65 $\text{mg}\cdot\text{g}^{-1}$	80	[166]
f-MWCNTs/ $\text{CoFe}_2\text{O}_4$	Sulfamethoxazole	Freundlich	7.39 $\text{mg}\cdot\text{g}^{-1}$	>95	[167]
	17 $\beta$ - estradiol			18.9 $\text{mg}\cdot\text{g}^{-1}$	
f-MWCNTs/ $\text{FeCl}_3$	Tonalide	Langmuir	26 to 28.55 $\mu\text{g}\cdot\text{mg}^{-1}$	>94	[161]
f-SWCNTs/ $\text{Fe}^{2+}$ or $\text{Fe}^{3+}$	17 $\beta$ - estradiol	-	-	>94	[163]
	Progesterone				
O-MWCNTs/ PDMS	Norfloxacin	-	18.8 $\text{mg}\cdot\text{g}^{-1}$	83.8	[168]
	Enrofloxacin			94.1	
	Ofloxacin			81.5	
	Ciprofloxacin			93.6	
f-MWCNTs/ $(\text{NH}_4)_2\cdot\text{FeSO}_4\cdot 12\text{H}_2\text{O}$	Diclofenac	Langmuir	33.37 $\text{mg}\cdot\text{g}^{-1}$	91	[169]
f-MWCNTs/ $\text{TiO}_2$	Tetracycline	-	10 $\text{mg}\cdot\text{g}^{-1}$	83	[170]
f-MWCNTs/ $\text{SiO}_2$	Diazinon	-	-	79	[171]
f-MWCNTs/ PAN/ $\text{TiO}_2/\text{NH}_2$	Naproxen	-	-	99	[172]
	Cetirizine			96	
f-MWCNTs/ PTFE	Diclofenac sodium	-	-	-	[173]
f-MWCNTs/ Co	Flurbiprofen	Freundlich	1176.5 $\text{mg}\cdot\text{g}^{-1}$	86.74	[174]
	Ketoprofen			1226.5 $\text{mg}\cdot\text{g}^{-1}$	
COOH-SWCNTs/ $\text{Fe}_3\text{O}_4$	Paraquat	-	2.82 $\mu\text{g}\cdot\text{L}^{-1}$	92.89	[175]

### **3.2 Membrane technology**

Membrane technology is a broadly explored approach for separating and filtrating several chemicals, commercially and domestically. In the late 1960s, the membrane processes entered industrial applications as feasible alternatives to more conventional processes such as extraction, evaporation, or distillation. Several membrane processes have been discovered, for instance, pressure-driven membrane processes that include ultra-filtration, nanofiltration, microfiltration, and reverse osmosis. All mentioned pressure-driven membrane processes are vital components of water remediation and purification globally. Generally, the membrane systems' operating cost is linked with the high pressure required to take off dissolved pollutants, such as minor organic molecules [176]. To remove organic solutes and dissolved ions, reverse osmosis and nanofiltration are mostly recommended; hence, high pressure is needed to operate these membranes, i.e., 600~7000 kPa. On the other hand, micro and ultra-filtration can be operated at much lower pressure, i.e., 34~400 kPa [177]. Such approaches are currently an established part of many industrial processes. The use of membrane processes includes nanofiltration and reverse osmosis for water purification and desalination, hemodialysis for artificial kidneys, and electro-dialysis in a caustic chlorine cell. Ultra-filtration use in the food sector for separation of protein from milk whey, genetic engineering, pervaporation for dehydration of ethanol, etc. [178].

Globally, access to clean and hygienic water has become apparent as the most serious issue of this era. Nanotechnology has enormous potential for offering environmentally and efficient, suitable solutions for upgrading water quality and elevating the amount of potable water accessible [179]. Nanomaterials have several vital physiochemical features that allow them very attractive as separation media for water cleaning and remediation. In terms of mass prospect, they have vast surface areas compared to bulk materials. Consequently, they are suitable for producing high-capacity sorbents that can be modified to improve their selectivity

and affinity. Nanomaterials can provide high capacity and reusable ligands for anions, cations, organic compounds, and radionuclides [180]. They offer excellent prospects for introducing more effective redox-active media and water cleaning catalysts because of their size, shape, and larger surface area.

### **3.2.1 Carbon nanotube-based membranes**

CNTs play an essential role in membrane technology, especially for water purification, supporting low energy explanations for water treatment. CNT-based membranes offer near-frictionless or frictionless water transports via them to retain a range of water pollutants such as dyes, desalination, heavy metal ions, and micropollutants [181]. Their high aspect ratio and even hydrophobic walls let ultra-effective transport of water molecules. CNT-based membranes can improve or change the membrane performance of reverse/ forward osmosis, micro-filtration, and nano-filtration in water cleaning and remediation [182]. It permits the CNT-based membranes to swap both ultra-filtration and reverse osmosis with low energy consumption. One of the essential benefits of CNT-based membranes is that it does not require any pre or post-treatment when employed for water-related applications. A brief comparison between CNT-based membranes and conventional membranes is presented in Table 6.



**Table 6:** Comparison of CNT-based membranes with other membranes based on various aspects

Membrane	Description	Materials	Pore-sizes/ types	Thickness ( $\mu\text{m}$ )	Operating Pressure (bar)	Permeability ( $\text{m.Pa}^{-1}.\text{s}^{-1}$ )	Advantages	References
CNT-based	An open tip single hollow structure or polymer composite settled perpendicularly with resistant filler matrices.	CNTs, ceramics, or polymers	0.8–100nm/ micro, or meso, or macro	Depend on type	Varied with application	$\sim 7 \times 10^{-7}$	<ul style="list-style-type: none"> <li>• Low consumption of energy</li> <li>• Operate in challenging environmental situations</li> <li>• Cost-effective</li> <li>• Resistance to fouling</li> <li>• High performance and durability</li> </ul>	[183]
Nanofiltration	Segregate particles and dissolved macro-molecules < 2nm	Organic polymers	<2nm / micropores	–0.05	20 to 40	$\sim 40 \times 10^{-12}$	<ul style="list-style-type: none"> <li>• Low resistance to the problematic environmental situation</li> <li>• Low durability</li> <li>• Fouling susceptible</li> <li>• Not cost-saving as CNT-based membranes.</li> <li>• Good performance</li> <li>• High consumption of energy</li> </ul>	[184]
Microfiltration	Help to eliminate solutes from solvent, >100nm	Polysulfone, polypropylene, polyurethane and so forth	50-500nm/ macropores	50-100	<1	–	<ul style="list-style-type: none"> <li>• Energy usage is moderate</li> <li>• Low performance and durability</li> <li>• Resistance is less to the severe environmental situation</li> <li>• Fouling susceptible</li> <li>• Cost is comparatively higher than CNT-based membranes</li> </ul>	[185]
Reverse osmosis	Uses trans-membranes pressure to cause selective transport of solvent against osmotic pressure difference	Organic polymer, for instance, polyether sulfone	Non-porous	–0.1 to 0.2	30 to 60	$\sim 3 \times 10^{-12}$	<ul style="list-style-type: none"> <li>• Energy consumption is relatively higher</li> <li>• Good performance and low durability</li> <li>• Operate in serve environmental situation is same as micro and nano-filtration membrane</li> <li>• Fouling susceptible</li> <li>• Not economical as CNT-based membranes</li> </ul>	[186]
Ultrafiltration	Suitable to eliminate solutes of > 1 to 100nm	Cellulose, acrylic, Polysulfone, and so forth.	2 to 50/ mesopores	150 to 300	1 to 10	$\sim 0.5 \times 10^{-10}$	<ul style="list-style-type: none"> <li>• Energy consumption is moderate</li> <li>• Operate in serve environmental situation is low</li> <li>• Fouling susceptible</li> <li>• Performance is moderate</li> <li>• Durability is the same as micro, nano, and reverse osmosis filtration</li> <li>• Not cost-effective as CNT-based membranes</li> </ul>	[187]

### 3.2.1.1 Types of CNT-based membranes

Carbon nanotube-based membranes are generally categorized according to the development approach; however, two known classes based on literature are mixed matrix and free-standing CNT membranes. Two primary types of free-standing CNT-based membranes which are broadly employed for water-related applications are vertically aligned CNT and buckypaper membranes. The vertically aligned CNT membranes (VA-CNT) are distinct micro-structures of well-assembled cylindrical pores from open CNTs arrays on a non-permeable substance that develops a well-disciplined anisotropic structure to be employed in a range of applications. Since 1998 when aligned CNTs were fabricated using the CVD approach, VA-CNT membranes have been investigated. These membranes have captivated an interest because of steady mesoporous morphology, allowing them to be utilized in various filtration membrane applications.

Conversely, buckypaper membranes hold macroscopic morphology made of CNTs with pristine thermal, physiochemical, and electrical strengths. The strength of BP-CNT membranes is provided by  $\pi$ - $\pi$  interaction and Van der Waals forces among the attached nanotubes. BP-CNT membranes provide an extremely porous 3-D framework created by interstitial gaps among the nanotubes, making it promising catalysis and adsorption in addition to separation applications.

The mixed matrix CNT membranes possess a morphology analogous to that of the fine-film composite reverse osmosis membranes, where the upper layer is mixed polymer and CNT. All mentioned types of CNT-based membranes have their own merits and demerits. For instance, fabrication techniques of BP-CNT and mixed matrix CNT is simple in comparison to VA-CNT membrane.

### 3.2.1.1 Fabrication of carbon nanotube-based membranes

Due to their popularity, several techniques have been introduced to fabricate CNT-based membranes at laboratory and commercial scales. These techniques vary based on the type of CNT membrane; for instance, a CNT-based BP membrane can be developed using shear pressing, pushing, domino, vacuum filtration, and so forth. This section describes the fabrication paths to engineer the CNT-based membranes.

**VA-CNT membranes** comprise extremely assembled, individual CNTs aligned perpendicularly on a membrane support. The gaps among the aligned CNTs are generally covered with inorganic/ polymer filler to maintain the membrane morphology, then open the aligned CNTs via plasma oxidation/ etching approaches [188], [189]. VA-CNT membranes features depend on the fabrication techniques, which can lead to a range of future applications. In 2004, Hindus and co-associates were the first research team who developed the VA-CNT membranes [190]. A summary of the discoveries and developments of VA- CNT membranes is presented in Table 7:

**Table 7:** Discoveries and developments of VA-CNT membrane

Year	Discovery	References
1996	Initially, Li and co-associates used a chemical vapor deposition (CVD) approach to synthesize a vertically aligned CNT membrane; however, the growth direction was not very straight.	[191]
1998	Very straight aligned MWCNTs on Ni-coated glass were produced employing a plasma-enhanced hot-filament CVD approach by Ren and co-associates in 1998.	[192]
1999	Initially, Fan and co-associate fabricate vertically aligned CNT membrane was conducted using CVD, known as the engineering field's key achievement.	[193]
2004	Hata and co-associates performed the production of superdense vertically aligned CNT.	[194]
2006	The friction coefficient of oriented vertically aligned MWCNTs-based on the temperature of specimen and chemical group on the surface by Dickrell and co-associates.	[195]
	First contaminants release measurement of vertically aligned CNTs.	[196]
2009	Lai and co-associates introduced nitration plasma treatment on vertically aligned CNTs.	[197]
2010	Post-treatment via oxygen pulsed direct current plasma can enhance the wettability of vertically aligned CNTs, researched by Ramos and co-associates.	[198]

2011	Bittencourt and co-associates reported Oxygen-based modification of vertically aligned CNTs via plasma techniques.	[199]
	Zhu and co-associates produced a hybrid material using vertically aligned SWCNTs.	[200]
2012	Hussain and co-associates introduced water-plasma on vertically aligned CNTs.	[201]
	Detailed life cycle assessment for vertically aligned CNTs	[202]
2013	In France, Boulanger and co-associates reported the production of large-scale vertically aligned CNT.	[203]
2019	Chen and co-associates performed large-scale principle calculations of electric transport on vertically aligned SWCNTs.	[204]

**Buckypaper CNT membranes** are randomly organized CNTs in thin mat form, arranged by Van der Waals forces. Van der Waals interactions are accountable for the powerful aggregation of CNTs producing the cohesive BP morphology. This membrane has tremendous advantages, for instance, an extensive porous 3D network and specific surface area. Several techniques are introduced to develop BP CNTs membranes, a few of them mentioned above [205]. One of the essential stages in developing BP CNT membranes is removing impurities from CNTs, which is usually done through the oxidative route. Nevertheless, the impurity removal stage damages and shortens the CNTs length, but it allows functionalizing the CNTs with hydroxyl and carboxyl groups, transforming their hydrophobic nature into hydrophilic that improves the CNTs dispersion in polar solvents, for instance, water [206], [207]. Table 8 lists the various methods that have been employed for the synthesis of BP CNT membranes along with their advantages and disadvantages:

**Table 8:** Advantages and disadvantages of BP CNT membranes preparation approaches

<b>Preparation Approaches</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>References</b>
Domino Pushing	Adequate and convenient approach, high electrical and thermal properties	Time-consuming, high pressure required	[208]
Shear Pressing	Time-saving, satisfactory volume fraction, stiffness, strength, and degree of alignment	Unpredicted thickness, high pressure required	[209]
CNT Drawing	Lengthy sheet, display density, and thickness of 0.5g/cm <sup>3</sup> and 50nm, respectively	Inappropriate for CNT forest, can form bundles	[210]
Drop Casting	Fast and straightforward approach, cost-effective, large-scale production	Low solubility and CNTs' properties, difficulty to control the thickness, and no uniform coating	[211]
Electrophoretic	Display satisfactory macroscopic homogeneity, economical and straightforward approach	Low yield, a specific range of particles are required for good deposition, display more cracks<0.06nm	[212]
Rod-coating	Economical, thickness adjustable, simple approach	Coating viscosity is an issue; optimal speed needs to attain membrane	[213]
Tape-casting	Range of membrane geometry, foldable and mass-scale production, adequate thickness, and density	Required mechanical pressing, limited application due to the width	[214]
Ink-jet Printing	Fast production, dimensions can be adjusted	Employ for specific CNTs' diameter, restricted to commercial applications, low mechanical strength	[215]
Vacuum Filtration	Wettability can be controlled, the potential to produce the thinnest membrane	Lengthy fabrication procedure, limited to lab-scale, low thickness, high pressure required	[216]
Air Spraying	Can produce long and thickness membrane, potential to be used for large range devices	Surfactant and high temperature is must, surfactant challenging to extract	[217]
Vapor Deposition	Fabricate at room temperature, adequate gap-filling, leakage free	Not suitable for mass-scale production, high cost	[218]
Non-filling	Filter nano-scale poliovirus and bacteria, high porosity, simple approach	Low mechanical stability, suitable for specific applications only	[219]
Polymer Injection	Simple approach, mechanical durability, produces a thin membrane	Interstitial filler required may cause air bubbles between CNTs	[220]
Densification	High pore density, classified as capillary and mechanical compression densification	Not suitable with smaller CNT diameters, difficult to separate the substrate, difficult to manipulate	[221]

**Mixed matrix CNT membranes** have become the center of attention in scientific society; therefore, many researchers have emphasized discovering their novel fabrication approaches. Functionalized CNTs are embedded in polymeric membranes via phase inversion or interfacial polymerization to synthesize mixed matrix CNT membranes. This type of CNTs membrane is suitable for ultra-filtration, forward/ reverse osmosis applications [222]. Zheng and co-associates [223] developed sulfonated multi-walled CNTs membrane by using interfacial polymerization techniques and salt removal. The results concluded that the prepared membrane displayed a great tendency to disperse in the solvent, particularly water, and a removal rate of 96.8%. Furthermore, a layer of polyamide membrane has free amine and carboxyl groups, and a range of -ve charged functional groups, which work as a binding site for embedding CNTs in polyamide membranes.

On The Other hand, the development of mixed matrix CNT membranes is readily realized by incorporating raw or modified CNTs in the support layer of polymeric membranes that have already been developed. A primary issue linked with such a technique is the CNTs dispersion in the substrate membrane matrix, which can be resolved using modified CNTs [224]. Table 9 lists the different research work that has been published based on CNT-based membranes synthesis, physical and chemical properties:

**Table 9:** Few of the recent publications on CNT-based membranes for various applications

Carbon nanotube membranes	Membrane matrix	Carbon nanotubes	Synthesis route	Functionalization technique	Application	Remarks	References
	Polystyrene	MWCNTs	CVD+ spin coating+ plasma treatment	Biotin	Chemical sensing and separations	<ul style="list-style-type: none"> <li>The flux was determined by Knudsen diffusion, and it showed micro-morphology</li> <li>The aligned CNT membrane morphology provide the transport of <math>\text{Ru}(\text{NH}_3)_6^{3+}</math> ions in the aqueous phase</li> </ul>	[220]
	Polyacrylic	SWCNTs	Encapsulation+ plasma etching	Carboxyl groups	CO <sub>2</sub> separation	<ul style="list-style-type: none"> <li>The prepared membrane approach has the potential to be commercialized</li> <li>Displayed gas permeability with purified SWCNTs greater than pristine SWCNTs</li> </ul>	[225]
Vertically aligned carbon nanotube membrane	Epoxy (EPON 828)	as-MWCNTs	CVD+ polymer infiltration	-	Water contamination	<ul style="list-style-type: none"> <li>The research results concluded that water flux is 3 times more significant on the developed membrane than the ultra-filtration membrane; moreover, water transport is 70000 times higher.</li> <li>The rejection property is the same as ultra-filtration membranes.</li> <li>Good bio-fouling resistance i.e. 15% less permeate flux drop.</li> </ul>	[226]
	Parylene	SWCNTs	CVD+ vapor phase infiltration	Air plasma	Protective fabrics for both domestic and military settings	<ul style="list-style-type: none"> <li>Allow elimination of <math>\geq 5\text{nm}</math> analyte via size exclusion.</li> <li>Study results confirmed that the membrane offers adequate safeguard from the biological threat.</li> </ul>	[227]
Buckypaper CNT membrane	-	as-MWCNTs	Domino pushing	-	Supercapacitor electrodes	<ul style="list-style-type: none"> <li>The result concluded that the CNTs in the BP tend to control the straight structure</li> <li>Can be employed as supercapacitor electrodes</li> <li>The thermal and electrical conductivity is higher than the previously studied</li> </ul>	[208]

						works, i.e., 331 W.m <sup>-1</sup> .K <sup>-1</sup> and 2x108 μ.S.cm <sup>-1</sup> , respectively.	
	-	as-MWCNTs	Shear pressing	-	Sensors, filters or bio-scaffolds	<ul style="list-style-type: none"> <li>Tensile analysis showed good tensile and mechanical strengths, &gt;400 MPa.</li> <li>Produced millimeter-long CNT film with high CNT alignment.</li> </ul>	[209]
	-	MWCNTs	Vacuum filtration	Nitric acid-treated	Structural material for developing high volume fraction nanocomposites	<ul style="list-style-type: none"> <li>The study results revealed that the BP CNT membrane's mechanical strength increased by improving the power of oxidation agents.</li> <li>The porosity of the membrane is affected by increasing the density of polar functional groups.</li> </ul>	[228]
	-	MWCNTs	Vacuum filtration	Carboxyl groups	Organic pollutant removal	<ul style="list-style-type: none"> <li>The prepared film was employed for the removal of organic pollutants from the aqueous phase, and it showed the removal of 93% of humic acid.</li> <li>The attachment of functional support the hydrophilicity aspect of CNT</li> </ul>	[207]
		MWCNTs	Vacuum filtration	Propan-2-ol	Salt removal	<ul style="list-style-type: none"> <li>The prepared film is exceptionally hydrophobic (113<sup>0</sup>) and porous (90%)</li> <li>The film displayed a 99% salt removal, and flux rate of approximately 12 kg.m<sup>-2</sup>.h<sup>-1</sup>.</li> </ul>	[229]
Mixed matrix CNT membrane	Polyimide siloxane	SWCNTs	Blending	Carboxyl groups	Ideal additive and suitable for gas separation	<ul style="list-style-type: none"> <li>The SEM analysis revealed that the CNTs were purified and dispersed in polyimide siloxane</li> </ul>	[230]
	Polysulfone	MWCNTs	Phase inversion	Carboxyl groups	Water removal pollutants	<ul style="list-style-type: none"> <li>Displayed good hydrophilic aspect</li> <li>The pore size of the membrane increased up to 1.5% wt. content of MWCNT, and declined after 4% wt. content of MWCNT</li> <li>The membrane displayed high flux demonstrates low rejection, and vice versa</li> </ul>	[231]



Polyethersulfone	MWCNTs	Phase inversion through immersion precipitation	Carboxyl groups	Organic removal	pollutants	<ul style="list-style-type: none"> <li>• The result showed improved anti-fouling properties [232]</li> <li>• Adequate egg albumin (protein) removal from the aqueous phase, i.e., 88%</li> <li>• Hydrophilicity properties enhanced due to the use of modified MWCNTs.</li> <li>• Permeability based on the wt. content (%) of modified MWCNTs</li> </ul>
Polypropylene	MWCNTs	Interfacial polymerization	Carboxyl groups	Salt removal		<ul style="list-style-type: none"> <li>• The analysis result showed a 51.5% higher flux rate in comparison to raw MWCNTs/ PP film [233]</li> <li>• An incline in the mass transfer coefficient, i.e. 1.5 times higher</li> <li>• Obtained high salt removal rate, i.e., 99.9%</li> </ul>
Poly tetrafluoroethylene	MWCNTs	Blending	Carboxyl groups	Salt removal		<ul style="list-style-type: none"> <li>• The result showed an increase of 54% in permeate flux and salt removal of 99.9% [234]</li> <li>• Mass transfer coefficient is comparatively higher pristine MWCNTs/ PTFE film</li> <li>• Also displayed good stability without wetting and anti-fouling problems</li> </ul>

### 3.2.1.2 Carbon nanotube-based membrane for micropollutants removal

The primary aim of water treatment is to get rid of undesired components. Membranes offer a physical obstacle for such components in their size, allowing them to employ unconventional water sources. As the vital part of water cleaning and purification, they deliver superior-level automation, reduce the use of chemicals and land, and modular structure gives flexible design [235].

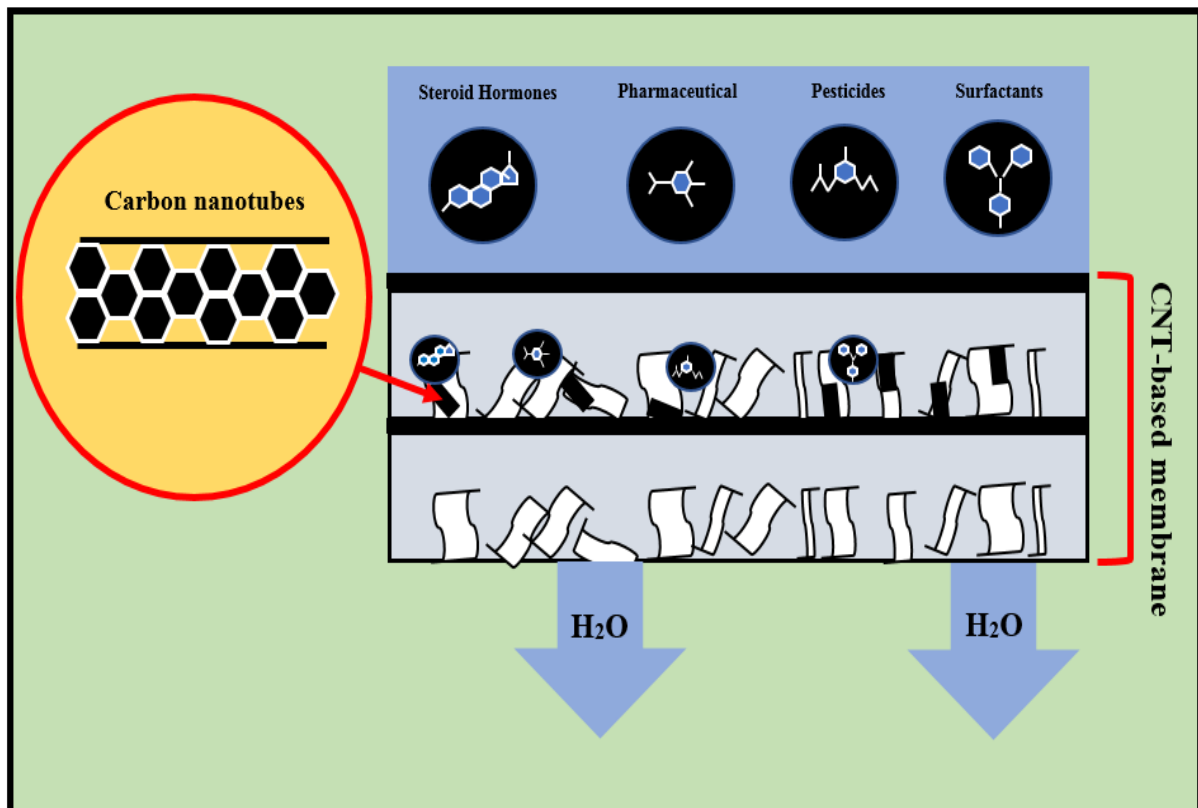


Fig. 7: Adsorption mechanism of CNT-based membrane

A significant barrier of membrane technology is the fundamental trade-off between membrane permeability and selectivity. The consumption of excess energy is an imperative barrier to the wide-spectrum applications of pressure-driven membrane processes. Membrane fouling combines the energy utilization and difficulty of the process design and operation. Moreover, it declines the membranes' modules and lifespan [236]. The efficiency of the membrane system is mainly decided by the material used for the membrane. Reinforcement in functional nanomaterials into membranes raises a great potential to enhance its fouling

resistance, permeability, thermal and mechanical strength, moreover, render modern functions for pollutant degradation and self-cleaning.

Recently, there is an immediate concern in developing novel materials for water cleaning and remediation, desalination, and many other membrane technology applications. They have received considerable attention from the scientific community regarding pollutant-free safe, clean water, CNTs, and CNT-based membrane [237]. Notably, the application of CNT-based membrane was acknowledged a long time ago, but its use as filtration has been introduced lately. Several research types have been performed on the feasibility and potential of CNT-based membranes for wastewater treatment due to their exclusive features, such as a high range of water flux and fouling resistance [238]. CNT-based membranes have been employed in membrane distillation, capacitive deionization, and pressure-driven filtration for water purification. Moreover, CNT-based membranes, particularly BP membranes, have been recommended as self-heating and supercapacitor materials for de-icing applications [239]. The schematic representation of the adsorption mechanism of CNT-based membrane is illustrated in Fig.7

Micropollutants, organic pollutants, are generally referred to as endocrine-disrupting chemicals that have been typically found in water and wastewater. Most CNT-based membranes with water and wastewater treatments are emphasized on salt rejection, heavy metal ions, and dye removal [240]. Table 10 lists removal information by CNT-based membranes technology on selected micropollutants based on literature studies.

**Table 10:** CNT-based membranes employed for micropollutants removal

CNT-based membrane	Target micropollutants	Removal efficiencies	Remarks	References
Polyvinylidene fluoride/ f-MWCNTs/ laccase	Diclofenac	95	<ul style="list-style-type: none"> <li>The highest removal efficiency was received within 4 hrs.</li> <li>The results displayed adequate operational and thermal strength due to the immobilized laccase.</li> <li>The findings suggested that the fabricated PVDF/ f-MWCNT/ laccase membrane is appropriate for water and wastewater treatment applications.</li> <li>Self-cleaning and re-coating presenting new opportunities towards sustainability and long-term applications</li> </ul>	[241]; [242]
	Bisphenol-A	85		
	Ibuprofen	63		
	Clofibric acid	52		
f-SWCNTs/ Fenton	Amoxicillin	97	<ul style="list-style-type: none"> <li>Studies displayed a high removal rate and water permeability (19.6 L/m<sup>2</sup>.h.bar).</li> <li>It can be predicted to be used for various aquatic micropollutants.</li> <li>Reliability was further observed by comparing experimental and predicted results analyzed by ORIGIN software.</li> </ul>	[243]
	Ampicillin	94		
	Florfenicol	91		
	Carbamazepine	85		
Polyethersulfone/ f-SWCNTs	17 $\beta$ -estradiol	72	<ul style="list-style-type: none"> <li>Demonstrated high permeability and removal efficiency within the range of 50- 75 % from 100ng.L<sup>-1</sup> feed solution.</li> <li>Adsorption kinetics were rapid, and adsorption was independent of retention time, ranging from 0.08-7.1.</li> <li>Displayed poor adsorption, ranging from pH 11 to 12.</li> <li>The prepared membrane could not meet the European guidelines, i.e., 99% removal.</li> </ul>	[244]
	Progesterone	75		
f-MWCNTs	Caffeine	93	<ul style="list-style-type: none"> <li>Filtration of pharmaceuticals and PPCs by the prepared membrane is an essential pre-treatment approach.</li> </ul>	[245]
	Carbendazim	97		
Sodium dodecyl sulfate/f-MWCNTs/ polypropylene	Cortisone	97.1	<ul style="list-style-type: none"> <li>The fabricated membrane was reliable and effective in removing various glucocorticoids</li> <li>Linearity range from 0.2 to 100, and the limit of quantification (LOQ) from 0.065 to 0.326 ng/mL.</li> <li>Results showed high time efficiency, good reproducibility, low consumption of solvent, and high precision with RSDs of &lt;10%.</li> </ul>	[246]
	Hydrocortisone	70.7		
	Prednisolone	77.9		
	Hydrocortisone butyrate	63.9		
Nickle-Cobalt/ f-MWCNTs	Budesonide	87.8	<ul style="list-style-type: none"> <li>Removal efficiency decreased with increasing pH to 11.</li> <li>Displayed high performance and stability.</li> </ul>	[247]
	Ibuprofen	80		
Polyethersulfone/ f-SWCNTs	Bisphenol A	80	<ul style="list-style-type: none"> <li>Removal efficiency increased with an increase in the %wt. content of f-SWCNT, however, too high %wt. content of f-SWCNT leads to saturation and probably declines the removal rate.</li> <li>Fouling of membrane also showed favorable outcomes with the increase in the %wt. content of f-SWCNT</li> </ul>	[248]
	4-Nonylphenol	84		

			<ul style="list-style-type: none"> <li>• Due to the hydrophobic nature of the organic micropollutants, it can be understood that high adsorption leads to an increase of removal for increasing the %wt. content of f-SWCNT</li> </ul>	
Polyethersulfone/ nitrogen-doped SWCNTs	Carbamazepine 4-Nonylphenol Bisphenol A Galaxolide Tonalide Caffeine	88.97 99.15 98.59 99.92 98.85 87.21	<ul style="list-style-type: none"> <li>• Results show the potential to employ the prepared membrane for various organic micropollutants</li> <li>• Water flux improved with the addition of nitrogen-doped SWCNTs to raw PES</li> <li>• The prepared membrane displayed good porosity and a large specific area, i.e., <math>0.37 \pm 0.03 \text{ cm}^3 \cdot \text{g}^{-1}</math> and <math>94.3 \pm 0.06 \text{ m}^2 \cdot \text{g}^{-1}</math>, respectively.</li> <li>• Findings displayed good chemical, mechanical, and fouling resistance properties</li> </ul>	[4]
Polyethersulfone/f- SWCNTs	17 $\beta$ estradiol	>75	<ul style="list-style-type: none"> <li>• In most studies, the complete breakthrough was not attained due to the high adsorption capacity of SWCNTs</li> <li>• Results demonstrated the ambitious drink water target; however, European regulations were not met.</li> </ul>	[249]
Polyvinyl chloride/ f-MWCNTs/ Fe <sub>3</sub> O <sub>4</sub>	Norfloxacin Bisphenol A	23 65	<ul style="list-style-type: none"> <li>• Retentions for both pollutants decrease with the increase in pressure</li> <li>• Findings showed minor effects of ionic strength and initial concentration on retentions</li> </ul>	[250]
f-MWCNTs	Ciprofloxacin	>99	<ul style="list-style-type: none"> <li>• Results concluded that the prepared membrane is a promising candidate for antibiotics removal from the aqueous phase.</li> <li>• Finding also revealed that f-MWCNTs showed higher filtration efficiency compared to pristine or modified SWCNTs</li> </ul>	[206]
Polyethersulfone/ f-SWCNTs	B-endosulfan	>99	<ul style="list-style-type: none"> <li>• Results confirmed that the prepared membrane has the potential to be employed for microcontaminants</li> <li>• Pristine SWCNTs show lower adsorption efficiency than modified SWCNTs</li> </ul>	[251]
MWCNTs	Ibuprofen Bisphenol	>90	<ul style="list-style-type: none"> <li>• Satisfactory sorption performance</li> <li>• Findings revealed that cross-flow configuration display great potential in removing the organic micropollutants</li> <li>• Excellent antifouling resistance, efficient solute transport under hydrodynamic flow, and higher retention time in eliminating organic pollutants compared to previously researched work</li> </ul>	[252]
SWCNTs	17 $\beta$ estradiol	70	<ul style="list-style-type: none"> <li>• Findings discovered that the prepared membrane is a promising material.</li> <li>• High adsorption determined</li> </ul>	[253]
TiO <sub>2</sub> /MWCNTs	Carbamazepine Acetaminophen	80 24	<ul style="list-style-type: none"> <li>• Higher reusability of the membrane</li> <li>• Findings displayed that the effect of pH on adsorption of pharmaceutical micropollutants achieved the maximum loading on the sorbent at equilibrium saturation</li> </ul>	[254]

In the past, reverse osmosis and nanofiltration membranes have been utilized widely to eliminate organic pollutants from water. However, low water permeability is the primary obstacle of these membranes, which restricts the production ability and hinders their full-scale applications. Therefore, it is essential to produce innovative high-permeability CNT-based membranes to eliminate organic pollutants from water [255]. Wang and co-associates [256] employed a CNT-PVDF membrane to the removal of ibuprofen and acetaminophen, and the result showed removal of 95% for both pharmaceutical micropollutants. Several research works showed that CNT-based membranes have high adsorption capacity towards numerous micropollutants, a few mentioned in Table 10. The removal mechanism of CNT-based membranes towards micropollutants is generally occurring because of hydrogen bonding, Van der Waals interactions,  $\pi$ - $\pi$  interactions, and chemical adsorption between the micropollutants and CNT-based materials (Fig. 7).

Likewise, elimination of inorganic pollutants, the competition among various organic chemicals in water may appear on the CNT surface which effectively declines the adsorption of organic pollutants. Thus, tailoring the surface features of CNT for selective adsorption of various organic pollutants is an essential study task in the future for improved water treatment [257].

#### **4. Future research prospect**

Even though nanotechnology-supported water and wastewater treatment developments have attained significant attention in research laboratory investigations, their willingness for industrialization differs far and wide. Few are by now on the market, while others need extensive research before proceeding for large-scale applications [258], [259]. Their future commercialization and development face many obstacles, including cost-effectiveness, technical concerns, and prospective human and environmental risk.

In this context, we have observed CNT applications and their composites and CNT-based membranes, especially free-standing membranes, for various micropollutants found in different water sources [260]. A substantial amount of research studies have been performed on CNT and their composites, but limited studies have been examined for micropollutants removal using CNT-based membranes [261]. Most of the CNT-based membrane study has been performed on salt, heavy metals, and dyes rejection or for the development of various sensors. Some of the recommendations based on literature are presented below:

- The chemical modification technique is generally used to functionalize CNT, but this requires a harsh chemical environment, consequently producing chemical effluents. In addition, excessive oxidative action drops behind damages on the side and tip walls of CNTs, which affects the thermal and electrical features. In this matter, eco-friendly and economical functionalization approaches need to be explored, which brings no or minimum structural defects and environmental contamination.
- To replace different removal technology with membrane technology for water and wastewater treatment, inclusive research study should be required for free-standing membrane category, particularly CNT-based membranes:
- Despite the superior performance of CNT and its composites, novel technologies' adoption mainly depends on potential risk and cost-effectiveness. It can be resolved through comprehensive understanding and mitigating possible hazards linked with employing CNTs and their composites/ CNT-based membranes in water and wastewater treatment, whereas cost-effectiveness can be enhanced through retaining and re-using the CNT and their composites/ CNT-based membranes.
- CNT and their composites/ CNT-based membrane applications regarding water and wastewater treatment have usually been conducted on lab-made pollutants solutions.

Therefore, studies on real natural and wastewaters are required to observe the actual adsorption efficiency and reliability.

- The long-term efficacy of CNT and their composites/ CNT-based membranes is unknown as the studies are usually performed at the laboratory for a comparatively short period. Thus, a study focusing on long-term performance is essential.
- Generally, CNT-based membranes' studies are based on simulation. For better understanding, experimental studies are in great need.
- Comprehensive analysis of various pollutants' segregation mechanisms through CNT and their composites/ CNT-based membrane is vital.
- In contrast to various endocrine-disrupting chemicals, studies on micropollutants removal from water and wastewater treatment using CNT-based membrane are in great need.

## **5. Conclusion**

The pervasive use of pharmaceuticals, personal care products, insecticides, and steroids, leading to the prevalent existence of micropollutants from  $\text{ngL}^{-1}$  to  $\mu\text{gL}^{-1}$  in different water sources, is a threat to the global terrestrial and water environment. The inadequacy of traditional water/ wastewater treatment frameworks for eliminating micropollutants from water bodies has revealed a terrific task for water management organizations and has led to the concern of the most suitable approaches to deal with these rising issues. The overview of the current studies describes that it is a challenging task to draw a common conclusion based on a comparison of the micropollutants elimination efficiency of CNT-based adsorbents and membranes due to their operation principles, parameters, and characteristics. Nevertheless, the following conclusion can be described from the detailed study provided herein:

- The growth of nanomaterials for desalination and water treatment is a rising area to fulfill the ever-growing demand for clean and fresh water globally. Among these, CNTs



have attained tremendous attention for developing composites and membranes because of their exceptional adsorption and sieving capabilities which assist in eliminating water minerals and pollutants.

- A comprehensive review of the state-of-the-art fabrication of CNT-based composites and membranes explored that innovative approaches are promising to attain the highest pollutant removal percentage via a different route, for instance, chemical surface modification of CNTs.
- The use of CNT-based composites and membranes to eliminate organic, inorganic, and microbiological pollutants in aquatic environments, such as groundwater, surface water, sewage, and wastewater treatment plants, has been broadly examined with demonstrated efficiencies. Moreover, both CNT-based adsorbents and membranes have displayed promising outcomes for micropollutant removal.
- CNT-based membranes have held higher anti-fouling resistance features attributed to the noxious effects of modified CNT and CNT-based membranes- they harm the pollutants via the creation of reactive oxygen species, and because of unique hydrophilicity, -ve charges on the surface of modified CNT, and electrical conductivity that let these membranes to reject the foulants.
- Nevertheless, several concerns require to be resolved. Regardless of the extraordinary efforts given on the structure, function, fabrication, and properties of modified CNT, there is yet a vast room for the advancement of CNT-based composites and membranes for water-related treatment purposes.

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