Review

Activated Carbon, Carbon Nanotubes and Graphene: Materials and Composites for Advanced Water Purification

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Abstract: To ensure the availability of clean water for humans into the future, efficient and cost-effective water purification technology will be required. The rapidly decreasing quality of water and the growing global demand for this scarce resource has driven the pursuit of high-performance purification materials, particularly for application as point-of-use devices. This review will introduce the main types of natural and artificial contaminants that are present in water and the challenges associated with their effective removal. The efficiency and performance of recently developed materials for water purification, with a focus on activated carbon, carbon nanotubes and graphene will be discussed. The recent advances in water purification using these materials is reviewed and their applicability as point-of-use water purification systems discussed.

Keywords: water purification; activated carbon; carbon nanotubes; graphene; water contamination; point-of-use

1. Introduction

With an increasing global usage and a growing demand for high purity, water is fast becoming one of the most important resources used by humans. Essential for the survival of life on earth, the effective management, distribution, storage, recycling and purification of water are critical to ensure the sustainable use of this resource into the future. Water is necessary for many human activities including agriculture, industrial processes, recreation and most importantly consumption.

As all water used is collected from natural sources, a proper treatment and purification process is required. Conventionally this treatment process has been applied to remove natural organic material, sediments and harmful pathogens from water prior to distribution. Recently however, the integrity of the treatment and purification process is being stressed due to widespread, human-induced

contamination of source water. Contaminant materials from industrial processes, agricultural practices and synthetic chemicals such as pharmaceuticals and cosmetics often find their way into water systems, adding to the naturally occurring impurities [1,2].

Naturally occurring contaminants in water can be either compounds derived from the breakdown of organic matter that only pose low health impact to humans, and bacteria and viruses that can have significant health implications [3,4]. Artificial contaminants, derived from human practices, may include toxic organic compounds (dyes, pesticides, pharmaceuticals), heavy metals, and by-products produced by the water treatment process itself [5]. Due to the varied chemical and physical properties of the natural and artificial contaminant species, it remains a challenge to find methods that can effectively remove all hazardous materials from water in a single process.

Water treatment processes are constantly being improved, with the aim to remove as high proportion of the contaminant species as possible. However, studies indicate that many potentially harmful compounds are still present, post treatment [6,7]. For this reason, there has been an increasing uptake of point-of-use (POU) water purification devices by individuals to deliver the cleanest possible water. In most cases POU water purification is used by individuals for home use, however larger scale water purification systems have also been integrated in industrial water treatment settings [8,9]. There is also significant interest in the use of water purification devices to deliver clean water in remote and isolated communities, where the supply of treated and purified water is limited or even non-existent. In these situations, the dual action of toxin removal and microorganism neutralization is requisite.

The most promising materials for delivering pure water are those that incorporate nanoscale features and tailorable chemical properties. Activated carbon (AC) is currently the most widely used example of this type of purification substrate and is often applied for POU devices, with many commercial systems utilizing this material for home applications. Activated carbon is a highly porous material that acts to remove contaminant species from water based primarily on surface adsorption [10]. It has been proven to be effective in removing high amounts of organic species from water and is currently the most cost-effective material for individual POU devices [11]. In recent times however there have been significant advances towards improving water purification, by applying modifications to the existing AC substrate [12]. In particular, the use of chemical treatments to improve the capture efficiency for organic and inorganic materials and through biological modifications to AC [12].

Advanced nanomaterials for high-performance water purification are also under development, with carbon nanotubes (CNTs), graphene and composite materials of each showing promising results [13]. These nanomaterials are based on the graphite-like carbon framework and commonly utilize an adsorption strategy for removing contaminant species. These materials have also shown promise as size exclusion membrane filters that allow the flow of water while blocking the flow of contaminants [14]. Certain chemical modifications or composites of the mentioned nanomaterials have also been shown as effective for the neutralization of harmful water borne pathogens [15]. The current cost of fabricating these composite graphene or CNT water purification materials make them as yet impractical for commercial sale, however many see these materials as the platform for next generation water purification, with high performance and versatility capabilities [11]. As the cost of manufacture is lowered, it is likely that these materials will become more widespread in POU water purification systems.

This review will introduce the current state of water health, identifying the major contaminant species of concern to humans and the challenges associated with the effective removal of these species. The performance of recently developed AC, CNTs and graphene materials and their composites for water purification will be explored. The properties and adsorption performance of these materials will be reviewed, including recent efforts directed at improving the performance through chemical and biological treatments. An assessment of these materials applicability for POU water purification will also be discussed.

2. Classifications of Water Contaminant Species

The health of the world's waterways and natural bodies of fresh water have been in decline for many decades. Rapidly expanding industrial practices, agricultural impacts and the effects from a growing global human population have all led to an increase in the amount of contaminant species ending up in the water system. Contamination in water is comprised of both natural and artificial components, with each species affecting human health to varying degrees. Table 1 provides an overview of the major contaminant classes and example species in each, including their current removal strategies and associated removal difficulties.

2.1. Naturally Occurring Water Contaminants

A significant proportion of contamination and impurities in water originates from naturally occurring sources [16]. Allochthonous contamination is derived from the breakdown of terrestrial plant and animal matter, which is subsequently transported into the waterways [17]. Autochthonous contamination originates from within each waterway, arising from the natural actions of the microorganisms and breakdown of aquatic vegetation [18]. Along with the myriad of individual chemical compounds that constitute the natural organic matter, the microorganisms including bacteria and viruses are also classified as natural water contaminants. While for the most part, the organic compounds are considered to be relatively benign to human health, certain microorganisms can have significant and widespread health effects [19].

2.2. Artificially Derived Water Contaminant Species

Over several decades, an increase in the concentration and variation of artificial chemical species has percolated into global waterways. The rise in industry, agriculture and the disposable nature of modern society has contributed a vast number of synthetic organic and inorganic contaminants to the water system. Industrial contaminant species include heavy metals and synthetic organic compounds such as dyes and plasticizers. Due to the considerable diversity of industrial derived contaminants, covering both organic and inorganic species, these are perhaps the most difficult to effectively remove from water [20,21]. Agriculturally derived contaminant species including pesticides and fertilizers are also commonly found in waterways, contributing to the release of phosphorous and nitrogen, with the potential to cause a rise in harmful microorganisms [22,23]. Another growing source of artificial water contamination is from pharmaceutical and cosmetic products [24]. While the release of hormonal compounds and specific therapeutics are alarming, it is the release of antibiotics that is of significant concern due to the possibility for the rise of resistant bacteria [25].

Of importance in the context of POU water purification are the contaminant species that result from the practice of sterilizing water during the treatment process. Disinfectant by-products (DBPs) are a class of species comprising small organic compounds that result from the reaction of disinfectant species (chlorine, chloramine) with the dissolved organic matter (DOM). The two main described DBPs that can form during this process are trihalomethanes (THMs) and haloacetic acids (HAAs) [26]. These species are small halogenated organic compounds that have been linked to adverse health effects in humans and are often a key target for POU water purification devices [27].

Table 1. Overview of current water contaminant species, removal methods and associated challenges.

Contaminant Class	Example Species	Removal Methods	Removal Challenges	References
Natural organic matter	Humic acids Fulvic acids Proteins	Flocculation/sedimentation Filtration Adsorption	Wide range of functionalities, sizes Different mixture of compounds for each water source, with seasonal variations Adsorption affected by environmental factors and other contaminant species (pH, temperature)	[28–30]
Microorganism	Bacteria Viruses Protozoa	Chlorine disinfection Size exclusion filtration Neutralization by nanomaterials	Chlorine disinfection leads to DBPs Neutralization must meet regulation requirements Size exclusion does not capture all microorganisms Potential release of nanoparticles/nanomaterials into ecosystem	[31–33]
Disinfectant by-products	Trihalomethanes Haloacetic acids Halonitromethanes Haloamides Nitrosamines	Adsorption	Too small for ultrafiltration Regulatory guidelines for maximum concentrations apply	[26,27,34,35]
Heavy metals	Arsenic Mercury Lead Cadmium Chromium	Ion-exchange Adsorption Filtration Reverse osmosis Flocculation/sedimentation	Both cation and anions present Range of adsorption affinities Adsorptions effected by other contaminant species	[36,37]
Synthetic organics	Dyes Plasticizers Solvents Perfluorinated compounds	Adsorption Filtration Degradation	Wide range of chemistries and molecular weights Properties can be affected by environmental factors (pH, temperature, ionic concentration)	[38]
Pharmaceuticals	Hormones Steroids Analgesics Antibiotics Cosmetics	Adsorption Filtration Degradation	Both hydrophilic and hydrophobic compounds are present Some species have low affinity to adsorbents	[39,40]
Agriculturally derived	Pesticides Fertiliser Animal waste	Adsorption Filtration Flocculation/sedimentation Reverse osmosis	Wide range of chemistries and molecular weights	[41,42]

3. Activated Carbon for Water Purification

Activated carbon is currently widely used as an adsorbent material in both water treatment plants and for POU water purification. Activated carbon is characterized as a carbonaceous material with a highly porous internal structure, which is usually derived from the pyrolysis and chemical treatment of sources including wood, coal, nutshells, bamboo and other organic materials [43]. The activation process, usually performed at high temperature by chemical or steam treatment, generates an extensive porous network within the carbonaceous material [44]. The adsorptive properties of AC towards organic contaminants have been widely recognized and studied for many years, with this material well suited for removing contaminant species from water. The majority of POU water purification devices that are currently in use are comprised of AC, as this material has the appropriate balance between performance and cost. Many AC POU devices operate under mains water pressure and flow water through a formed carbon block, where the density of packed AC particles results in maximum internal pore sizes that range from 0.5–10 μm. Other AC POU purification devices operate by a gravity mechanism, where water passes over larger AC particles to enable contaminant adsorption.

3.1. Properties of Activated Carbon Relevant to Water Purification

In general, AC is classified based on the average particle size, as either powdered or granular AC (PAC of GAC respectively). Powdered activated carbon constitutes particles <80 μm, with an average size between 10 and 50 μm, while GAC are larger particles of between 0.2 and 5 μm [43,45]. Other forms of AC include extruded AC and block AC, which are either PAC or GAC that have been compressed and held together with a thermoplastic binding agent.

Activated carbon has a highly porous internal structure with a heterogeneous range of pore diameters. Macro (>50 nm), meso (2–50 nm) and micro (<2 nm) pores are all present in the highly branched internal structure of AC [46]. The main effect of this high porosity structure is to impart a high surface area to AC, up to 2500 m^2/g [47]. Consequently, this results in a large number of binding sites for adsorbate species to interact with. The exact internal pore composition of AC is determined by the source material, activation process and any further chemical modifications.

The carbonaceous chemical structure can be loosely described as graphite like, however impurities or specific chemicals present during the activation process can lead to the incorporation of surface functional groups such as phenols, carboxylic acids and pyridines [48]. The typical elemental composition of AC is around 80% carbon, with other elements including oxygen and nitrogen accounting for the remaining material [49,50].

Both the physical and chemical properties of AC will affect the adsorption capacities to different organic and inorganic species [12,51]. The adsorption mechanism and capacity of native and modified AC will be discussed in the following sections.

3.2. Adsorption Mechanism of Activated Carbon

Due to the graphite like carbonaceous structure of AC, it is ideally suited to adsorbing organic compounds, especially species containing aromatic functionality [49,50]. Activated carbon also has a high adsorption capacity for small organic species such as DBPs and some pharmaceutical compounds [52]. Adsorption is generally through π–π interactions between the adsorbate and the AC surface, but will also occur through hydrogen bonding and Van der Waals interactions [53,54]. This material also has the capacity for cation/anion–π interactions with metal species, but this process is generally considered to be poor, especially for native AC. The adsorption of species to AC will be directly influenced by environmental factors including pH, ionic concentration, temperature and the concentration of other contaminant species, which can have both positive and negative effects depending on the adsorbate in question [30,55–57]. The physical size of compounds interacting with AC will also have an effect on the adsorption capacity and efficiency, with larger compounds likely to cause pore blockage and limit the diffusion of subsequent smaller species [58,59].

3.3. Chemical Modifications of Activated Carbon for Improved Contaminant Adsorption

As AC is such a widely used and accepted material for water purification, considerable research has been carried out into chemically modifying the surface in order to impart a higher adsorption or wider ranging capacity to the material. Chemical modification of AC can increase the selectivity of the material to certain species, usually through the introduction of acidic or basic surface functionality. This has primarily been achieved through acid or base chemical treatment procedures, which impart a more negative or positive surface charge respectively. This has implications for the adsorption of cationic and anionic compounds and also for charged organic species such as dyes [60].

For acid modification of AC, treatment with HNO_3, H_2SO_4 and HCl is commonly used, under different temperature and reaction conditions. In this case, the net effect is to increase the abundance of acidic or oxidative functional groups on the AC surface, such as carboxylic acids, alcohols and lactones [61]. When operated in aqueous media with a pH > pK_a of the acidic functional groups, the surface carries a negative charge that improves the adsorption of positively charged species [62].

Base treatment of AC with NaOH, NH_3 and KOH results in an increase in basic functionality on the AC surface through generation of amides and aromatic amines [12,63]. High temperature treatment of the AC, where oxygen species are removed from the surface can also be employed to impart a higher degree of basicity to AC [64]. Such surface chemistry will improve the adsorption of negatively charged compounds.

The main disadvantage of the acid or base treatment of AC is that depending on the chosen treatment method, the AC becomes more selective towards certain species, but loses adsorption capacity to others. This may be beneficial in the case where known quantities of a specific contaminant are present, however in the context of POU water purification highly specific selectivity would be undesirable. The development of AC for application in POU water purification devices requires the appropriate balance of selectivity, with a high adsorption capacity for a range of contaminant species.

One of the other chemical modifications to AC that is gaining interest in the impregnation of metal or metal oxide nanoparticles into the porous structure [65]. Metal impregnated AC is commonly prepared by the reduction of metal salt solutions, or by direct adsorption of pre-prepared nanoparticles [66,67]. These composite materials have shown high adsorption affinities for contaminant species including heavy metals, halides and DOM. The removal efficiency for bromide and iodide for native and silver impregnated AC was compared, with results showing a far superior removal of bromide by the silver impregnated material (95% as compared to 26% for native AC) [68]. This material also showed an improved efficiency for the removal of total dissolved organic carbon when used in conjunction with an enhanced coagulation process (77% as compared to 67%).

For heavy metal adsorption, native AC adsorption capacities for Ar(III), Ar(V), Hg(II) and Pb(II) were found to be 0.73, 0.09, 2.61 and 3.06 mg/g respectively, while adsorptions on iron impregnated AC were 4.67, 4.50, 4.57 and 4.35 mg/g respectively [65]. Activated carbons impregnated with silver nanoparticles have also been specifically investigated for their antibacterial effect and are promising materials for the treatment of contaminated water in the absence of conventional water treatment processes [69,70]. While promising, there are ongoing concerns about possible leaching of metal nanoparticles from these composites. It is for this reason that metal impregnated AC will not be used as a material in POU water purification devices until these issues have been definitely resolved.

The use of microwave heating for either the preparation or modification of AC has also been used as a viable method to prepare AC with improved adsorption capacity to certain species [71]. While not a direct chemical modification, microwave heating can result in physical and chemical alterations to AC, when compared to the conventional activation process. This can include variations in the internal surface area, altered pore size distributions and changes to the native surface chemistry [72,73]. Microwave treatment as a means to prepare AC may prove to be beneficial in terms of lower power consumption and preparation time.

The chemical and physical effects to AC, along with the targeted contaminant species and adsorption capacities for a selection of recent studies using the above mentioned chemical modification

methods are summarized in Table 2. For each modification, generally only one contaminant species was selected to assess the adsorption improvement of the AC. It would be beneficial to specifically understand AC's adsorption capacity for certain species in the presence of multiple adsorbates. Relatively few studies have considered the effect of competitive adsorption or any positive or negative effects that can arise from complex mixtures [55,59]. In the context of POU water purification, a study of this nature would be highly relevant, as a range of contaminant species at varying concentrations are likely to be present. Due to the varying composition of water contamination at different locations, the construction of tailored AC POU purification devices may prove the most effective means to deliver clean water. Tools, including chemo- and bio-sensors, for the rapid assessment of water contaminant species, may be used to direct the types of modified ACs (as discussed in this review) for the fabrication of a specific, high-performance POU water purification device. Of the carbon materials reviewed here, AC has been investigated most broadly for the removal of many different water contaminant species. The next steps for AC research in water purification should be investigations into competitive adsorption of contaminant species and a move towards location specific POU devices. In turn, investigations of this nature will lead onto determining the saturation points for certain contaminant mixtures adsorbing onto AC. The time or filtrate volume to reach saturation point will be location/water source specific, however a deeper understanding of the mechanisms and contaminant levels required to reach saturation will be beneficial in the pursuit of tailored AC POU devices.

Table 2. Chemical modifications of AC, target contaminants and adsorption capacities for specific species.

Modification Method	Modification Conditions	Carbon Source Material	Effect on Native Activated Carbon	Target Species	Adsorption Capacity (mg/g)		Ref.
					Native AC	Modified AC	
Acid treatment	HNO$_3$ + MW (130 °C, 800 W)	Rice husk	Increase oxide content Reduction in total surface area, small increase in micropore area	Pb(II)	66.23	95.24	[74]
	HNO$_3$ (120 °C, 48 h)	Not specified	Increased surface area Increased carboxylic acid groups	Cr(VI)	3.46	18.519	[75]
	(i) HNO$_3$ (60 °C, 3 h + 300 °C, 3 h) (ii) H$_2$SO$_4$ (60 °C, 3 h + 300 °C, 3 h)	Aerobic granular sludge	Increased surface acid groups Decrease in surface area (reduction in micropores)	Malachite Green	269.54	(i) 303.03 (ii) 284.90	[76]
	HNO$_3$ (120 °C, 48 h)	Not specified	Increased surface area Increased carboxylic acid groups	Cd(II)	N/A	1.98	[77]
	H$_3$PO$_4$ (110 °C, 9 h) + 380 °C	Olive stone	Narrow microporosity range High number of acidic surface groups	Amoxicillin	N/A	57.0	[78]
	H$_2$SO$_4$ + MW (450 °C, 700 W, 20 min)	Rice straw	Increased AC surface roughness Increased overall porosity	MB	N/A	62.5	[79]
	H$_2$SO$_4$/ H$_3$PO$_4$ + MW (24 h RT, 300 W, 3 min)	Cherry stone	Increase in micropore volume from 767 m^2/g to 1998 m^2/g Significantly shorter activation time	Disperse yellow 211	N/A	283.3	[80]
	Lime, ZnCl$_2$, FeCl$_3$, + MW (320 s, 1200 W)	Sapelli wood sawdust	High degree of microporosity Surface area of 914.08 m^2/g	o-cresol	N/A	239.2	[81]
Base treatment	NH$_3$ (35 °C, 12 h) MW (500 W, 8 min)	Coal	Increased basicity (higher PZC) Increased surface area and pore volume	Polyaromatic hydrocarbons (pyrene)	142.86	250.00	[82]
	1000 °C under Ar 700 °C under NH$_3$	(i) Coal (ii) Coconut shell (iii) Wood (iv) Phenolic AC fiber	Reduction of oxygen content (70%) Increased PZC (>7) Increase in surface basicity through nitrogen functionality incorporation Variations observed for different source AC	Perfluorooctane sulfonic acid	(i) 1.11 (ii) 1.72 (iii) 2.70 (iv) 3.54	(i) 2.16 (ii) 17.0 (iii) 85.2 (iv) 85.6	[64]
	NaOH (2 h) 700 °C (90 min)	Macadamia nut shells	High surface area AC Large percentage of micropores PZC > 8	Tetracycline	58.82 *	455.8	[83]
	MW (8 min) (i) 300 W (ii) 500 W (iii) 700 W	Coal	Removal of oxide groups (increased basicity) Increased surface area and pore volume	Naphthalene	111.79	(i) 125.22 (ii) 131.20 (iii) 129.05	[73]
	(i) KOH (ii) K$_2$CO$_3$	Sucrose	(i) KOH treatment leads to very high surface area (2400 m^2/g) and wide micropore distribution (ii) K$_2$CO$_3$ treatment results in 1400 m^2/g surface area and ultramicropore sizes	Ibuprofen, paracetamol, clofibric acid, caffeine, iopamidol	255 (Paracetamol) 147 (Iopamidol)	514 (Paracetamol) 1050 (Iopamidol)	[84]
	Vapor and solution-based amination	Petroleum coke	Decrease in specific surface area from both treatments Increase in PZC	2-Naphthoic acid	189	214 (vapour) 298 (solution)	[85]
	KOH + MW (12 min, 600 W)	Rambutan peel	High surface area AC Short preparation time	Acid yellow 17	133.3	215.05	[86]

Table 2. *Cont.*

Modification Method	Modification Conditions	Carbon Source Material	Effect on Native Activated Carbon	Target Species	Adsorption Capacity (mg/g)		Ref.
					Native AC	Modified AC	
Impregnation	Reduction of Cu, Pb, Zn, Ag salts	Fishtail palm seeds	Incorporation of metal nanoparticles Antibacterial effects observed	Bacteria (gram +/−)	N/A	N/A	[87]
	Mixing with AgNP	Sugarcane bagasse	Incorporation of 35 nm AgNP Retained adsorption capacity for small organics Antibacterial effects observed	*Escherichia coli*	N/A	N/A	[69]
	Calcination of metal salts (350 °C, 3 h) (i) Al_2O_3 (ii) TiO_2 (iii) Fe_2O_3	Not specified	Incorporation of metal oxide nanoparticles (Al_2O_3, TiO_2, Fe_2O_3)	Phenol	1.51	(i) 3.546 (ii) 3.153 (iii) 3.288	[88]
	O_2 plasma treatment Mixing with AgNP	Not specified	Increased hydrophilicity of AC by O_2 plasma treatment Incorporation of 28 nm AgNP Antibacterial effects observed	*E. coli*	N/A	N/A	[70]
	MW synthesis and impregnation of TiO_2 nanoparticles	Not specified	TiO_2 impregnation enabled UV photocatalyzed degradation of humic acid, resulting in higher adsorption capacity	Humic acid	6.24	9.06	[89]
	Reduction of metal salts (i) Fe (ii) Cu (iii) Al	Not specified	Decrease in specific surface area for modified ACs	Ceftazidime	N/A	(i) 161.3 (ii) 200 (iii) 172.4	[90]
	Fe_2O_3 NP impregnation via MW hydrothermal	Charcoal	Decrease in overall surface area Small increase in mesopore volume	Ar(V)	N/A	27.78	[67]
	CuS NP impregnated AC	Not specified	Composite adsorbent exhibits high surface area and high porosity	Methyl orange	N/A	122	[91]

Abbreviations: MW—Microwave, PZC—Point zero charge, NP—Nanoparticle, MB—Methylene blue, N/A—Not applicable. * Adsorption on Bio-char.

3.4. Biologically Activated Carbon for Water Purification

Research into biologically activated carbon (BAC) water purification for the improved removal of DOM and other organic contaminants has shown promising results for delivering cleaner water [92,93]. Biologically activated carbon filters are produced when specific bacteria are introduced and become entrapped within the AC porous matrix [94]. Under optimal conditions and with the appropriate organic nutrients, the bacteria can then multiply and populate the surface of the AC. When the BAC is exposed to water containing organic matter and in particular, complex macromolecular organic compounds, these species adsorb to the AC and the bacteria can biodegrade them into CO_2, water and simpler organic compounds. These degradation products can then be easily adsorbed to the AC surface and removed from the water [95]. Commonly, ozone or UV treatment is applied to the dissolved contaminants prior to BAC filtration [96]. An increased removal of THMs and HAAs of 40% and 30% respectively was observed when applying an ozone or UV pre-treatment prior to BAC filtration [92]. This process generates highly reactive species within the organic compounds increasing their bioavailability and ease of biodegradation by bacteria. Granular activated carbon inoculated with different strains of heterotrophic nitrifying bacteria showed an improved removal efficiency for ammonia, of 2.8–4 fold increase when compared to non-inoculated GAC [97]. A pilot study involving BAC filters in a water treatment plant has identified their effectiveness for the removal of THMs and HAAs, with greater that 45% and 80% removal efficiency for each respectively [98,99]. An improved removal of assimilable organic carbon has also been reported using BAC filters, which has implications for the growth of microorganisms in water [93]. The effectiveness of these materials depends on many environmental factors including temperature, pH and total DOM, which may limit their applicability in some situations.

One of the main drawbacks of BAC is the accumulation of biomass within the material, which must be periodically removed in order to maintain optimal performance. Thermal treatment and various chemical processes have been applied to regenerate the BAC, but these processes have significant drawbacks, including loss of AC structure and the use of hazardous chemicals. As a viable alternative, low frequency ultrasound has been presented as a novel method to regenerate BAC filters [100]. In this approach the regenerated BAC recovered the ability to remove dyes and ammonium from aqueous solutions.

3.5. Emerging Methods to Improve Water Purification Using Activated Carbon

The incorporation of highly specific chemical functionality onto the AC surface has afforded adsorbent materials that have a high selectivity for specific contaminant species. One such example is the grafting of cyclodextrin to AC for the selective capture of the pesticide chlordecone [101]. A host-guest complex is formed between the cyclodextrin and chlordecone and the composite material yields an adsorption capacity that is 15% higher than native AC. The development of composite particle-based adsorbents has also been demonstrated as cellulose beads combined with magnetic nanoparticles and AC. These particles have shown high adsorption performance towards copper, lead and zinc, with adsorption capacities of 45.57, 37.99 and 20.8 mg/g respectively [102]. A further advantage of this particle system is the ability to magnetically separate the particles from treated water. Another particle adsorbent system, based on a spherical Janus particle configuration (where each hemisphere is differently functionalized), combining AC and Pt functionalities has also been realized. In this case, Janus type particles that have a self-propulsion ability (due to the catalytic capacity of the Pt), have shown a high adsorption efficiency for certain heavy metals, explosives and dyes, where over 90% adsorption was observed in a 5 min timeframe [103]. While particle systems are not practical for POU water purification, they may find use in water treatment plants where their sedimentation and removal is possible.

4. Carbon Nanotube Based Water Purification Technology

4.1. Carbon Nanotube Adsorption Properties and Target Species

Since gaining intense interest in the electronics and semiconductor industries, CNTs are now finding novel applications in many other fields. The idea of using CNTs for water filtration has been postulated for over a decade with research focused on using CNTs as nano membrane filters for selective water transport [104,105]. This phenomenon is currently being widely investigated as an alternative to polymeric membranes for desalination, with CNTs materials offering the advantages of reduced size and improved water permeability [106,107]. Recently research however, into the use of CNTs and CNT composite materials as enhanced adsorbents for contaminant sequestration from water has shown promising results [108].

Carbon nanotubes have similarities to AC in the bonding structure of the carbon backbone and the relative ease of chemical modification. In the context of adsorbing contaminant species however, CNTs exhibit a high available surface area due to their nanoscale, as well as a high proportion of accessible micropores in their aggregated form [109]. There is also a large degree of scope for fabricating composite materials of CNTs, including embedded polymers, nanoparticle grafted CNTs and electrospun fibers [110–112]. The two main forms of CNTs, namely single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs), also allow further flexibility when designing water filtration and purification materials. Each of these forms has been demonstrated as effective adsorbent materials for specific chemical species [113,114].

Carbon nanotubes exhibit similar adsorption mechanisms to AC, through physical adsorption and interaction of specific chemical functionality with the graphite like carbon lattice [115]. While interaction of compounds with AC requires diffusion into the porous structure, internal diffusion is often not a limiting factor for compounds to interact with CNTs. Adsorption to the surface of CNTs, especially for larger compounds, will be the primary site of interaction. In an aggregated form, CNTs will also present internal meso and micro pore adsorption sites, suitable for smaller species to interact with [116]. The proportion of opened or closed CNTs also has a significant impact on the overall adsorption capacity of the material and is likely linked to the available surface area and chemical functional groups that are generated during CNT opening and cutting reactions [108,117].

One attractive property of CNTs for water purification is their increased capacity to remove heavy metals from solution compared to AC [118–120]. Available surface area and surface functional groups are the key determining factors that influence this improved adsorption and these parameters have been the focus of much research [121]. The use of CNTs to remove heavy metals from water is one of the most widely investigated applications in this field [122]. The filtration and removal of organic contaminants including dyes, DOM and pharmaceuticals by CNTs has also garnered increased interest in recent times [113,123–125].

4.2. Chemical Modifications and Composite Materials of Carbon Nanotubes for Enhanced Water Contaminant Removal

As with AC, chemical modifications of CNTs has been shown to improve their adsorption capacity and selectivity to various contaminant species. Recently published research on the performance of CNTs for water purification are presented in Table 3. Adsorption and purification results for modified CNTs as well as polymer composites, metal nanoparticle impregnated, membrane infused and electrospun fibres are also outlined in Table 3.

Due to the similar chemical structure between CNTs and AC, oxidative acid treatment by HNO_3 or H_2SO_4 is a common method for introducing or modifying the surface functional groups and serves two main purposes [126]. The first purpose is to open the ends of the CNTs and to shorten or cut the tubes [127]. This increases the surface area of the CNTs and can help to homogenise the CNT mixture allowing for more precise control over the physical properties. The second effect of acid treatment is to introduce oxidative functional groups (carboxylic acids, alcohols, epoxides) along the edges of the CNTs

and particularly around the openings, which enables the CNTs to be further chemically modified [128]. Shortening the tube length and addition of polar functional groups also enables the CNTs to be more easily dispersed in aqueous solutions. Acidification of CNTs and subsequent modification with an ionic liquid has enabled the adsorption of Cr(VI) from solution at 85.83 mg/g [129]. HNO_3 treatment of MWCNTs followed by combination with iron oxide nanoparticles has afforded a composite material with adsorption capacities for the dyes methylene blue, neutral red and brilliant cresyl blue of 74.23, 55.17 and 62.35 mg/g respectively [130]. There is however an optimal oxidation extent for CNTs to achieve maximum adsorption capacity, with 3.2% (oxidation) reported for optimal adsorption of the antibiotic tetracycline [131].

Introduction of specific functional groups not only has the beneficial effect of enhanced adsorption for certain species, but also allows the CNTs to be easily incorporated into composite materials. Commonly, CNTs are combined with different polymers to form water permeable composites, with the capacity for adsorbing contaminant species or filtering particulate matter. Polymers that have been used to form CNTs composites include chitosan, polyacrylamide, polysulfone and polyaniline, each of which have been tailored for specific applications and target contaminant species [132–135]. The performance of these CNT-polymer composites is summarized in Table 3.

Along with polymer composites, CNTs have been combined with solid support materials including silica, aluminum and ceramics to facilitate water filtration and purification [136–138]. The introduction of metallic nanoparticles along the CNTs has also been studied for similar applications as in AC. Various metal/metal oxide nanoparticles (Cu, Fe_3O_4, Ag) have been shown to enhance adsorption of specific species including heavy metals and dyes [139,140].

Another promising water purification method using CNTs involves vertically aligned CNT (VA-CNT) array membranes. Theoretical and practical studies have indicated high water flow through VA-CNTs membranes, with the hope to improve on current nano- and ultrafiltration materials [141]. The VA-CNT arrays are usually prepared by fabricating VA-CNTs on a solid or porous support and infiltrating a non-permeable polymer (epoxy, urethane) around the CNTs to hold them in position [142,143]. Most of the research into VA-CNT membranes has been associated with desalination, however the physical rejection of organic contaminant species has also been investigated [144,145]. The current efficiency, stability and long term performance have limited the widespread application of VA-CNT membranes, however this system may prove applicable in combination with one or more of the water purification materials discussed in this review.

Due to their conductive properties, certain CNT composites have also proven effective in the removal of some dyes and pharmaceutical compounds from water through electrochemical oxidative breakdown and adsorption [146,147]. In this process a bias is applied across the composite material, while the contaminated water is passed through the membrane. Interactions between the CNTs and contaminant species causes direct electron transfer and subsequent oxidative degradation, followed by adsorption of the breakdown products onto the CNTs. The presence of natural organic matter however has a negative effect on the removal of tetracycline, due to competitive adsorption to CNTs [148]. As discussed in the following section, this purification method has also been applied for the inactivation of viruses in contaminated water [149].

While the cost of producing and modifying CNTs has dramatically reduced in recent years, this form of carbon is not currently widely used for water filtration. Issues with the potential environmental release and toxicity of the CNTs themselves has hindered their implementation into commercial water purification devices. It is likely that POU water purification systems that utilize CNTs will be based around the types of composite materials that have been discussed here. Polymer supported CNT membranes provide the advantage of mechanical strength and desirable properties with the ability to upscale production. More work must be done to address the environmental concerns associated with CNTs and also the practical consideration such as competitive adsorption between multiple contaminant species.

4.3. Carbon Nanotube Materials for Antimicrobial and Antibiofouling Water Purification Applications

One of the promising applications of CNTs in water purification is for the neutralization of bacteria and virus or the exclusion of these species from water via nanofiltration. A further desirable property for advanced water purification materials is an antifouling capacity in order to prevent the adhesion of bacteria and biofilm formation. Various CNT composite materials have been investigated in order to achieve both neutralization and antifouling water purification platforms.

Due to the nanoscale features of CNTs, this material presents as a promising means to generate size exclusion membranes, capable of blocking the transport of certain microorganism across the membrane. Aggregated CNTs deposited onto a porous polymer membrane can effectively filter bacteria from aqueous solutions, where the amount of CNT loading also has an effect on virus filtration capacity [150]. A more elaborate example of a CNT membrane for bacteria and virus filtration has been fabricated as polymer bound, vertically aligned CNTs that enable size exclusion of sub 5 nm materials [110].

Resistance to bacterial adhesion by self-supported CNT membranes was observed, with the resistance attributed to an effect of the surface roughness at the nanoscale [143]. An epoxy entrapped vertically aligned CNT material has displayed similar antibiofouling properties with physical damage and oxidative stress to microorganisms proposed as the mechanisms of action [151]. A more direct approach to fabricate antibacterial CNT water purification membranes has been realized by the incorporation of the natural bactericide nisin, through adsorption onto the CNTs [152]. The nisin adsorbed CNTs were then coated onto a polycarbonate filter membrane where bacteria would become entrapped and then neutralized.

4.4. Point-of-Use Water Purification Devices Based on Carbon Nanotubes

Cost of synthesis and device manufacture will likely prohibit the development of standalone CNT POU water purification devices in the short to medium term, however the effectiveness of this material cannot be understated. Carbon nanotubes increased capacity for the adsorption of contaminant metal ions (over AC) and the ability to fabricate complex composite materials that impart novel and advantageous properties, highlight CNTs future in water purification. As discussed for AC, competitive adsorption analysis must be performed on these materials, however in the short term it is likely that CNT composites could be incorporated into AC POU devices for the highly targeted removal of specific water contaminant species. The material's electrical conductivity properties should also enable an enhanced removal of certain species when coupled to traditional AC POU devices. Finally, the promising antimicrobial properties that can be imparted to CNT composites will be highly beneficial in situations where access to treated water is limited. While certain questions remain to be answered, such as CNTs leaching from devices, it is clear that this material and its composites have a clear role in water purification and POU devices more specifically.

Table 3. Carbon nanotube modifications, composites and water purification properties.

CNT	Materials and Modification to CNT	Method	Target Species	Performance	Ref.
Native	MWCNT/SWCNT sponges	Flow Adsorption	Polychlorinated biphenyls	81–119% recovery from real sample	[153]
	SWCNT membrane	Batch Photodegradation induced adsorption	Rhodamine B	190 mg/g adsorption (1.3 times higher than best performing carbon materials	[154]
	MWCNTs	Batch Adsorption	THMs	Adsorption capacities of 10.98, 6.85, 6.57, and 5.95 mg/g for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ respectively	[155]
	Acid treated MWCNTs	Batch Adsorption	Tetracycline	253.38 mg/g adsorption	[156]
	(i) Pristine MWCNTs (ii) COOH-MWCNTs (iii) NH_2-MWCNTs	Batch Adsorption	1,8-Dichlorooctane, quinolone, alkylphenoletoxilate	Adsorption of target species affected by CNT functional groups and relative hydrophobicity of each	[157]
	HNO_3 treated CNTs	Batch Adsorption	Cd(II)	Acid treated CNTs showed higher adsorption capacity than acid treated AC, carbon nanofibers and fly ash Greater than 95% removal of Cd(II) by CNTs	[77]
Polymer composite	Acid treated MWCNTs + chitosan	Electrosorption	Aniline	26.4 mg/g adsorption	[132]
	Hydroxylated MWCNTs + PANI + PES	Flow Size exclusion Adsorption	Humic acid	80% removal of humic acid High water flux	[135]
	SWCNTs + parylene membrane	Flow Size exclusion	Direct Blue 71, AuNP, Dengue virus	High water flux Rejection of $\geq$5 nm species	[110]
	SWCNTs + Kevlar nanofibers	Batch Adsorption	Phenylic compounds, heavy metals, dyes	Composite material displayed higher adsorption capacity for all compounds, when compared to polyethersulfone and polysulfone adsorbents	[158]
	CNT/silica nanoparticle sponges	Batch Adsorption	Oils, organic solvents	High adsorption capacity to oils and solvents, up to 1885 weight %	[136]
	MWCNT/TiO_2/polysulfone	Flow Adsorption Exclusion	Humic acid	Composite outperformed native polysulfone material in terms of both adsorption/rejection of humic acid and water permeability Composite was flexible for different concentrations of humic acid	[133]

Table 3. *Cont.*

CNT	Materials and Modification to CNT	Method	Target Species	Performance	Ref.
Metal nanoparticle composite	Acid activated MWCNTs + TiO_2 nanoparticles	Batch Photocatalyzed degradation	4-Chlorophenol	Two fold increase in photocatalyzed degradation with MWCNTs	[159]
	MWCNTs + Graphene + Fe_3O_4 nanoparticles	Batch Flow Adsorption	Ar(III) and (V)	Flow outperformed batch adsorption for removal of Ar(III) and Ar(V), 100% and 74% removal respectively	[160]
	Carrageenan modified acid treated MWCNTs + Fe_3O_4 nanoparticles	Batch Adsorption	Methylene blue	Carrageenan modified MWCNT composites outperformed non-carrageenan Composite could be magnetically separated	[139]
Filter membrane infused	PVDF membrane + (i) Native MWCNTs (ii) Hydroxylated MWCNTs (iii) Animated MWCNTs (iv) Large inner diameter MWCNTs	Flow Adsorption	Triclosan, prometryn, 4-acetylamino-antipyrine, carbendazim, caffeine, ibuprofen, acetaminophen	Highest adsorption performance observed for hydroxylated MWCNTs High specific surface area improved performance	[113]
	PTFE membrane + (i) Pristine MWCNTs (ii) COOH-MWCNTs	Flow Electrochemical degradation Adsorption	Ibuprofen	Near 100% removal of target with 2 V bias Higher adsorption performance by COOH-MWCNT membrane, due to increased surface area and hydrophilic chemistry	[161]
	PVB fiber + oxidized MWCNTs	Flow Ultrafiltration	BSA Humic acid	Improved filtration performance by MWCNT embedded fibers	[162]
	Porous alumina + CNTs	Flow Adsorption	Humic acid	High initial water flux capacity Strong adsorption of humic acid, led to decline in flux	[145]
	MWCNT network supported on PTFE membrane	Flow Electrochemical degradation Adsorption	Tetracycline	High degradation and removal efficiency of MWCNT electrochemical filter Performance was negatively effected by the presence of natural organic matter	[148]
Electrospun fiber	Carbon nanofiber of polyacrylonitrile + MWCNTs	Flow Adsorption	Atrazine, sulfmethoxazole	Comparable adsorption capacity to AC, faster adsorption kinetics	[163]

Abbreviations: PVDF—polyvinylidene fluoride, PANI—polyaniline, PES—polyethersulfone, AuNP—gold nanoparticle, PVB—poly(vinyl butyral), BSA—bovine serum albumin, PTFE—Polytetrafluoroethylene.

5. Graphene-Based Materials for Water Purification

5.1. Properties of Graphene and Graphene Oxide

Graphene is considered a two dimensional material and exists as sheets of a single layer of graphitically bonded carbon atoms [164]. Like CNTs, this material has received attention from the electronics industry due to attractive conductivity and thermal resistance properties, with application in circuitry, solar cells and batteries under investigated [165,166].

In the context of water purification, graphene presents as an interesting carbon material that offers certain advantages over AC and CNTs. The high available surface area for contaminant species to adsorb to, as well as the potential for exotic chemical modifications and composite fabrication make graphene an attractive material to use for water purification [167]. Much like CNTs, a considerable amount of research on graphene for water purification has focused on nano-perforated graphene sheets as size exclusion filtration membranes [168]. Graphene adsorbents and antibacterial materials have recently been explored as more advanced alternatives to AC for water purification [169,170].

For water purification applications, graphene is usually converted into graphene oxide (GO) via an acid treatment process, namely the Hummers or improved Hummers methods [14]. This conversion to GO introduces a high number of hydrophilic oxygen containing groups across the graphene sheet, including hydroxyls and epoxides [171]. The most profound effect of the chemical modification is to markedly increase water flow through GO materials due to an increase in hydrophilicity, enabling the formation of membranes with high water permeability and flux [172]. The water permeability effect has been exploited by the fabrication of laminar structures from GO, which act as selective or exclusion membranes without the need for controlled nano-perforation of the graphene sheets [173]. Water purification applications using this platform are currently being investigated, with results demonstrating that these structures are capable of filtering organic compounds of various sizes. Filtration of dyes has been achieved, where acid brilliant blue, chrome blue-black and methyl orange were rejected by the filter at 98.2%, 95.2% and 73.4% respectively [174]. A chemically cross-linked analogue of the graphene laminar structure has also shown up to 34.3% rejection of dissolved organic carbon [175]. Such laminar structures also have the capacity for graphene to act as an adsorbent material and antibacterial agent, which is of particular interest in water purification, with the material performing to a high capacity in both applications [176,177].

5.2. Water Purification Mechanisms Using Graphene and Specific Targeted Species

The purification mechanisms of graphene and GO composite materials can be separated based on the type of material or composite. There are adsorbent graphene materials that rely on a similar mechanism for adsorbing contaminant species as AC and CNTs. Electrostatic, hydrogen bonding and π–π interactions between contaminant species and the graphene material all contribute to the material's excellent adsorption capacity [178]. Further to the chemical properties, the high specific surface area (over 1000 m^2/g) of this 2D material facilitates excellent adsorption capacity [179]. Secondly are the nano-filtration GO membranes that rely on exclusion of contaminants to deliver purified water, including the laminar structures and nano-perforated membranes previously mentioned. Molecular dynamic studies have been performed to assess the ability of nanoporous graphene to purify water of trihalomethanes [180]. Recent research has extended the idea of the laminar structure by confining the hydration related swelling of the layered graphene and flowing a solution parallel through the laminar structure [181]. This system has been specifically designed for the rejection of ions and desalination purposes however control over the pore diameter introduces the possibility for the filtration of different contaminant species. Finally, graphene materials and composites for neutralizing microorganisms function through different mechanisms, with the graphene effecting or disrupting the biological function of these species and inactivating them. The hypothesized antibacterial mechanisms of action include penetration and compromization of the bacteria membrane, generation of reactive oxygen species (ROS) and envelopment of microorganisms [177,182,183]. Composites of silver nanoparticle decorated GO deposited onto cellulose acetate membranes have also proven effective

as antibacterial agents, where inhibition of bacterial growth and prevention of biofilm formation has been observed [184].

5.3. Emerging Composite Graphene Materials for Enhanced Water Purification

Due to the scale and current high cost of producing graphene, composite materials are often fabricated that contain a percentage of graphene or GO. These composites provide a high filtration ability and appropriate physicochemical properties (i.e., mechanical strength, magnetism, hydrophilicity, etc). Similar to CNTs, graphene has been combined with metal nanoparticles such as silver, iron oxides and TiO_2 to impart antibacterial, heavy metal ion and organics affinity respectively. An iron oxide/non-oxidative graphene/CNT composite gave a maximum adsorption capacity for As(III) and As(V) as 9.11 and 5.21 mg/g respectively [160]. The removal of over 98% humic acid from water was achieved using a novel TiO_2 nanowire/iron oxide nanoparticle/GO composite, where the iron oxide facilitated humic acid adsorption and the combination of TiO_2 nanowires and GO allowed photocatalytic degradation of the species [185]. The combination of silver nanoparticles and GO sheets has enabled the fabrication of a highly effective antibacterial material [186].

The combination of graphene with various polymers or the deposition of graphene sheets onto solid micro or ultra-filtration membrane supports has also allowed the development of promising materials for water filtration and purification applications. Chitosan has been used with GO to prepare adsorbent hydrogel materials that have affinities for both cationic and anionic dyes, as well as heavy metals. The adsorption capacities of the dyes methylene blue and Eosin Y were reported as greater than 300 mg/g, while the adsorption of Cu(II) and Pb(II) were found to be 70 and 90 mg/g respectively [187]. A more complex material for the adsorption of Pb(II) has been realized by the combination of magnetic chitosan and GO that was imprinted with Pb(II) ions. Removal of the imprint ion and subsequent re-adsorption from solution gave a maximum adsorption capacity of 79 mg/g [188]. The inclusion of magnetic properties in this material also allowed the adsorbate to be easily separated from aqueous solution. The application of a polydopamine/GO hydrogel composite has afforded adsorption capacities for Pb(II) and Cd(II) of 336.32 and 145.48 mg/g respectively, while also facilitating the adsorption of the dye species Rhodamine B (207.06 mg/g) and *p*-nitrophenol (260.38 mg/g) [189]. A one-step hydrothermally assembled aerogel graphene and CNT composite has also been used for removal of the dye methylene blue from aqueous solution, with 97% of the dye captured by the material [190].

The deposition of GO or nitrogen doped GO onto a TiO_2/ZrO_2 ceramic membrane has demonstrated the effect of the GO thickness on water flux and also shown the nitrogen doped GO as a potential materials for the preparation of an electrodegradation membrane [191]. Another application of supported GO membranes has been shown, where polydopamine coated polysulfone was used as the solid support to fabricate a cross-linked GO network. This membrane provided a moderate rejection of the dye methylene blue (46–66%) and a high rejection of the dye Rhodamine WT (93–95%) [172]. In each case, these graphene composites have generally been investigated for the removal or adsorption of one target species, or multiple targets analysed individually. One study however has investigated the simultaneous adsorption of heavy metals and inactivation of bacteria using a multi-component composite material of GO, CNTs and the antimicrobial peptide PGLa. Results indicated a near 100% removal of bacteria and over 95% removal of As(III) and Pb(II) [192]. The adsorption performance of the above mentioned graphene composite materials are summarized in Table 4.

Further to the two or three component graphene composites, more complex materials are being developed. Aerogels of graphene coated, chemically modified silica diatoms, impregnated with iron nanoparticles have shown a high affinity towards mercury ions, with an adsorption capacity of >500 mg/g [193]. The fabrication of GO-microbots, consisting of layers of GO, nickel and platinum have been used as environmental clean-up agents for the removal of lead from water, where depending on the GO-microbot dose, up to 95% removal of lead was observed [194]. In this case, the GO can capture lead from solution, while the platinum allows added hydrogen peroxide to be converted to $H_{2(g)}$ and $O_{2(g)}$ that act as propellants and the nickel facilitates magnetic control of the microbots.

Table 4. Target species and performance of graphene-based water filtration materials.

Target Class	Specific Compound(s)	Graphene Material Properties	Adsorption Capacity (mg/g)	Ref.
Heavy metals	(i) Cu (ii) Pb (iii) Cd	Sulfydryal modified GO/chitosan composite	(i) 425 (ii) 447 (iii) 177	[110]
	(i) Cu (ii) Mn	Surfactant modified graphene	(i) 369.16 (ii) 223.67	[195]
	Pb	GO and manganese oxide NPs	553	[196]
	(i) Ni (ii) Pb (iii) Zn	Cross-linked GO on porous ceramic support	>95% rejection	[197]
	(i) As(III) (ii) As(V)	Fe_3O_4/non-oxidative graphene/CNT composite	(i) 9.11 (ii) 5.21	[160]
	(i) Cu(II) (ii) Pb(II)	GO/chitosan hydrogel	(i) 70 (ii) 90	[187]
	Pb(II)	Magnetic chitosan/GO composite, imprinted with Pb(II)	79	[188]
	(i) Pb(II) (ii) Cd(II)	Polydopamine/GO hydrogel	(i) 336.32 (ii) 145.48	[189]
Dyes	(i) MB (ii) Rhodamine B	GO hydrogel	(i) 7.85 (ii) 29.44	[198]
	(i) MB (ii) Eosin Y	GO/chitosan hydrogel	>300	[187]
	(i) Rhodamine B (ii) p-nitrophenol	Polydopamine/GO hydrogel	(i) 207.06 (ii) 260.38	[189]
	MB	Graphene/CNT aerogel	81.97	[190]
Pharmaceuticals	Ibuprofen	Ethylene diamine modified GO	95.2	[199]
DOM	Humic acid	TiO_2 nanowire/Fe_2O_3 nanoparticle/GO composite	>98% rejection	[185]

Abbreviations: GO—graphene oxide, MB—methylene blue, NPs—nanoparticles.

5.4. Graphene and Graphene Composites for Point-of-Use Devices

As the most recently discovered of the carbon materials discussed here, many of the graphene materials and composites that have been developed for water purification applications are still in the early research phase, however these materials show significant future potential. The application of graphene in water filtration devices will likely be through integration of the material into existing supports or membranes to enhance the filtration performance. The higher cost of fabrication will limit the production of homogeneous graphene-based filter systems in the short term, with composite materials the likely avenue to commercial devices. Graphene POU devices also face limitations in the short term, related to water flux, membrane stability and robustness. For use in POU water purification devices the potential leaching and health effects of the graphene must also be taken into consideration prior to commercial development.

6. Conclusions and Future Perspectives

Carbon-based materials are currently dominating the water filtration research field with adsorbent, size exclusion membrane and antimicrobial systems all described. Correlation between the recent explosion in research output of water purification materials utilizing these carbon frameworks and the increasing level and range of water contaminant species is no coincidence. There is now global recognition that the health of waterways is in decline, with much effort applied to maintaining the effectiveness of water treatment facilities. Ultimately however, individuals will still be exposed to water contaminants that escape (or result from) the treatment process. This will undoubtedly lead to an increased uptake of POU water purification devices. Many of the composite materials that are described in this review will be well suited for small scale filtration systems, which fits for in-home POU water purification applications.

Activated carbon, due to its current cost of manufacture, will remain the most prominent carbon-based water filtration material for the time being, with chemical modifications to improve capture capacity and efficiency maintaining its relevance. As the cost of fabricating CNTs and graphene are reduced, it is highly likely that these carbon nanomaterials will be developed into advanced filtration devices or as additional components to broad spectrum AC POU devices, to capture specific contaminants. For POU water purification, the ability to regenerate the filter is highly advantageous to extend working life and maintain performance. Graphene and CNT materials offer significant advantages over AC for regeneration and this capacity will likely influence the next generation of water purification devices. Effective neutralization of microorganism by CNT and graphene devices also provides advantage over AC and will be directly applicable in situations where access to treated water is limited.

One of the promising aspects of CNT and graphene-based materials for water purification is the relatively low quantity of material required to achieve high adsorption or filtration capacity. In the short term, the combination of existing carbon materials (ACs) with other, emerging nanomaterials or chemistries will be highly relevant in developing the next generation of water filtration and purification materials and devices.

Conflicts of Interest: The authors declare no conflict of interest.

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