Research article

A critical review on organic micropollutants contamination in wastewater and removal through carbon nanotubes

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ABSTRACT

The prevalence of organic micropollutants (OMPs) in various environmental compartments is posing a serious health risks to all kinds of lives on the planet. The levels of OMPs such as polyaromatic hydrocarbons, antibiotics, pesticides, contraceptive medicines, and personal care products in water bodies are increasing with each passing day. It is an urgent need of time to limit the release of OMPs into the environment, and to remove the prevailing OMPs for sustainable environmental management. The majority of the conventional means of water decontamination are either inefficient or expensive. However, due to nanosize, high surface area, and hollow and layered structure, carbon nanotubes (CNTs) serve as excellent sorbents for the removal of a diverse range of OMPs. The occurrence of emerging OMPs and their detrimental effects on human and animal health are collected and discussed in this review. The characteristics and efficacy of various CNTs (pristine and modified) for the efficient removal of different OMPs, and the removal mechanisms have been reviewed and discussed. The literature demonstrated that adsorption of OMPs onto CNTs is very complicated and rely on multiple factors including the properties of adsorbent and the adsorbate as well as solution chemistry. It was found that H–bonding, electrostatic interactions, van der Waals forces, hydrophobic interactions, H-π bongs, and π-π interactions were the major mechanisms responsible for the adsorption of OMPs onto various kinds of CNTs. Despite of higher affinities for OMPs, hydrophobicity and higher costs restrain the practical application of CNTs for wastewater treatment on large scale. However, continuous production may lead to the development of cost-effective, efficient and eco-friendly CTNs technology for wastewater treatments in future.

1. Organic micropollutants: an emerging environmental concern

Rapid urbanization and industrialization have disrupted the natural balance of the ecosystem by contaminating almost all the environmental compartments with a range of pollutants. As a result, the availability of high quality drinking water has been diminished drastically. Environmental, economic and social factors have led to minimal supply of clean water, especially to the poor (Mara, 2003). About 200 million people die every year due to water borne and non-fatal infections (Leonard et al., 2003). More than one billion people do not have access to safe water sources which has resulted in major health problems worldwide. Agricultural, poultry and dairy farms, as well as industrial, household and municipal waste generations are polluting the

world water resources drastically and reducing the availability of clean water exponentially. Among various pollutants which are posing a serious threat to the global ecosystem health, organic micropollutants (OMPs) are considered as an emerging problem worldwide (Ye et al., 2017a; Lapworth et al., 2012). The OMPs include a range of natural and anthropogenic chemical species occurring along with other persistent pollutants (Loos et al., 2010). Surfactants, solvents, personal-care products, phthalate asters, pesticides and endocrine–disrupting compounds (Gimeno et al., 2004), polycyclic aromatic hydrocarbons (PAHs) (Valavanidis et al., 2008), bisphenol A (BPA) (Fromme et al., 2002), organochlorine pesticides (OCPs), alkyl phenols (APs) (Sánchez-Avila et al., 2010), polychlorinated biphenyls (PCBs), polybromodiphenyl ethers (PBDEs) (Pérez-Carrera et al., 2007), pharmaceutical products,

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and microcystins (Liu et al., 2013) are considered as the most commonly occurring OMPs. Despite the adverse effects and toxicities, the levels of OMPs have been estimated to be increased in the future due to rapidly growing world population, dependency on chemicals and non-biodegradability of the most of the OMPs (Wanda et al., 2017). Additionally, there are a huge number of anthropogenic activities such as shipping, motorboats and port activities (Mestres et al., 2010), oil spillages (Soriano et al., 2007), ballast water discharges (European Environment Agency, 1995), and industrial, municipal and untreated wastewater discharges (European Environment Agency, 1995), which are introducing a range of synthetic OMPs on daily basis to the water bodies (Sánchez-Avila et al., 2010). Majority of these OMPs are persistent and therefore posing potential adverse health impacts on ecosystem (Choi et al., 2013).

The presence of OMPs in drinking water in extreme low levels such as part per billion (ppb) or even in part per trillion (ppt) can potentially affect the human or animal health drastically (Westerhoff et al., 2005; Suárez et al., 2008; Huerta-Fontela et al., 2011). However, as the wastewater is a complex mixture of various pollutants such as metals, pesticides, pharmaceuticals products, personal care products, industrial compounds, and their intermediates, the conventional analytical techniques have been found insufficient to quantify all chemical compounds in waters (Neale et al., 2015). Thus, researchers have successfully developed more reliable methods to quantify the targeted compound with higher accuracy. The quantification of OMPs in water with advanced analytical detection methodologies has identified the presence of both the natural and synthetic OMPs in water bodies around the globe.

2. Sources of organic micropollutants

Up to 1997, approximately 6 million chemical compounds have been made, about 1000 new chemicals were being fabricated annually and above 60,000–95,000 chemicals were in commercial use (Alloway and Ayres, 1997). While in 2008, the situation has been changed drastically. According to CAS (Chemical Abstracts Service) registry, about 33 million organic and inorganic substances has been synthesized from 1907 to 2008, and about 4000 new compounds were being added to the list on daily basis (Binetti et al., 2008). Many of these chemicals such as pesticides, medicines (antibiotics), hormones, and personal care products are being used in our routine lives, consequently affecting the human and animal's health chronically. For instance, pesticides alone are responsible for killing more than 220,000 people annually (Richter, 2002).

The sources of OMPs introduction into wastewater, surface water, ground water and drinking water resources are of diverse nature and include both point and non-point sources. The major sources and their pathways to introduce OMPs into the environment are represented in Fig. 1. It has been reported that agricultural and certain land use

activities release complex mixtures of various OMPs into the water bodies, thus making it hard to determine the source of a particular OMP. These activities are responsible for the transport of OMPs through soil surface runoff, preferential flow, interflow, atmospheric depositions, and leaching, and therefore are considered as the nonpoint sources of OMPs contamination of water, while the effluents of wastewater treatment plants (WWTPs), industrialization, household wastewater, and combined sewer overflows (CSO) serve as point sources of OMPs (Skelton et al., 2014; Müller et al., 2002). However, there is very limited data available for quantification of the loads from either sources of pollution.

Among the most problematic OMPs, pesticides (insecticides, herbicides, insecticides and fungicides) are of significant importance as about 4.6 million tons of pesticides are being sprayed annually, containing highly poisonous chemicals such as mercury, lead and arsenic (Richter, 2002). About 99% of these pesticides are being exposed to non-target media through domestic effluents and runoff from lawns and gardens. A huge quantity of pesticides finds its way to water bodies from agricultural lands serving as non-point source. The steroid hormones and pharmaceuticals such as antibiotics, anticonvulsants, lipid regulator, β-blockers, and stimulants enter into the environment through domestic and hospital effluents, as well as through runoff from livestock and aquaculture activities (Luo et al., 2014). Zimmerman (2005) has reported thirteen organic waste compounds including three pharmaceuticals and six organophosphates in eight wastewater
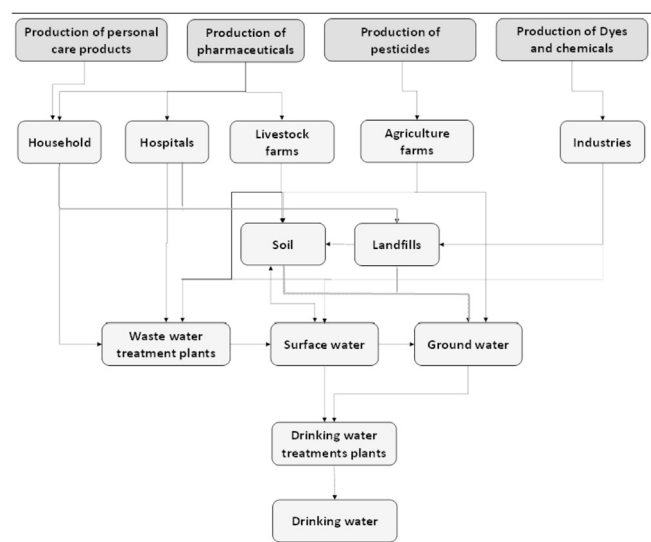

Fig. 1. The sources and pathways for the release of organic micropollutants (OMPs) into various environment compartments.

impacted drinking water wells. The personal care products (PCPs), fragrances, UV filters and disinfectants release through bathing, shaving, spraying, and swimming activities. The surfactants, plasticizers, and fire retardants release through domestic and industrial wastewater effluents (Luo et al., 2014). Besides the aforementioned OMPs, the natural and by-products of chemical reactions among natural products and oxidizing agents used in the treatment of drinking and wastewater are the other major sources of water pollution. For instance, all natural waters contain significant amounts of organic acids such as humic or fulvic acids as organic by-products of decomposition, tannins, terpenes, amino acids and protein (Oliver et al., 1983). The occurrence of these organic acids results in water acidification (pH 3.0–3.4), dystrophication and coloring (Oliver et al., 1983). Moreover, the fulvic and humic acids possess higher affinity to bind with hydrophobic OMPs such as PAHs and PCBs, resulting in water deterioration and contamination (De Paolis and Kukkonen, 1997). Organic polymers such as epoxy resins used as lining material can spill out through small holes in pipe and contaminate nearby environment (Kekki et al., 2007). Various materials (plastics, polymers, ceramics etc.) are used in the composition of the pipes which are being used in drinking water distribution systems. The water has to reside within these pipes for several days, which results in corrosion and leaching of these compounds from pipes subsequently affecting the water quality (Kekki et al., 2007). Various investigations have demonstrated that perfluoroalkyl acids (Post et al., 2013; Schaider et al., 2014), pharmaceuticals, organophosphate flame retardants (Schaider et al., 2014), and OCPs also occur in low quantities in water (Schwarzenbach et al., 2006) and contaminate the ecosystem. Therefore, the domestic, hospital, and industrial wastewater effluents as well as runoff from agricultural lands are adversely contaminating the aquatic environments (Tijani et al., 2013). Investigation about quantity, distribution, type, sources and composition of these pollutants is of critical importance to formulate efficient and sustainable remediation technologies.

3. Emerging organic micropollutants

The occurrence of OMPs in the aquatic environment is posing a serious environmental threat to the whole world. The emerging OMPs are consisting of vast array of natural and anthropogenic substances which are generally categorized into six groups i.e., pharmaceuticals, pesticides, PAHs, PCPs, surfactants and endocrine disrupting compounds (EDCs).

3.1. Pharmaceutical products

The utilization of pharmaceutical products is increasing exponentially worldwide. The occurrence of more than 200 different pharmaceutical compounds in river waters have been reported worldwide (Hughes et al., 2012). The anti-depressants, β-blockers, non-steroidal anti-inflammatory drugs (NSAIDs) and the antiepileptic carbamazepine are among the most studied and commonly occurring pharmaceuticals (Petrie et al., 2015). Additionally, antibiotics, anti-inflammatory drugs, and X-ray contrast media are the most commonly used pharmaceutical products. The occurrence of pharmaceutical residues in the water makes it chronically toxic for the human and animals. The prevalence of antibiotics in the environment is of critical importance. Antibiotics are being used as a treatment for the bacterial infections in human beings and animals, as well as for meat production in livestock industry. About $40 billion are being consumed for the production of antibiotics each year (O'Neill, 2015). Over 250 types of antibiotics are currently in use in human and veterinary medicines and 63,151 tons of antibiotics are being used annually (Ashfaq et al., 2016). It has been estimated that ~70% of antibiotic is neither metabolized nor absorbed in human or animal body and excreted into the environment via faeces (Ahmad et al., 2019). The extensive utilization of antibiotics in human and animals is resulting in elevated levels of these

compounds in various environmental compartments. The antibiotics may release into the environment through manufacturing plants, human beings, patients, sewerage lines and improper handling of these antibiotics. Antibiotics can also be entered to the ground water through the fertilizer application and leaching (Kümmerer, 2009). Antibiotics affect the prokaryotic cells by incontinence of cell envelope, protein synthesis and nucleic acid (DNA/RNA). The exposure of antibiotics to the microorganisms (bacteria) may develop resistance to these drugs. The range of antibiotics in the soil and water is from few nanograms to the hundreds of nanograms per kg and per liter of soil or water, respectively. This concentration may raise several folds in soil or water adjacent to the hospital or animal production farms (Verlicchi et al., 2015; Patrolecco et al., 2015). However, some of the antibiotics i.e., penicillin may undergo some degradation, while others such as tetracycline remain in the environment for longer periods of time and cause more environmental effects (Blackwell et al., 2005). The prevalence of pharmaceutical products into the environment is increasing with each passing day due to their continuous release into the environment and persistency in the environment.

3.2. Polyaromatic hydrocarbons

The PAHs represent a group of semi-volatile, ringed and toxic OMPs widely distributed in various environmental compartments. The majority of the PAHs has been found carcinogenic, teratogenic and mutagenic (Fouillet et al., 1991). The PAHs with 4–7 ringed structures are considered as highly carcinogenic and mutagenic, while with 2–3 rings are mutagenic (Fernandes et al., 1997). For these reasons, understanding the behavior, transport, fate, environmental risk, and ecological impacts of PAHs is very important. It has been reported that PAHs can potentially alter the contents of water soluble organic carbon and humic contents consequently affecting the transformation and speciation of other coexisting contaminants (Ye et al., 2019).

The PAHs enter into the environment through anthropogenic activities, as well as petrogenic and pyrolytic sources. The PAHs can be produced via waste incineration, petroleum cracking, production of coke, coal gasification and liquification processes, emissions from vehicle exhausts, unvented radiant, asphalt pavements, heating appliances, pyrolytic processes, smoking, incomplete combustion of organic charcoal broiled and biomass and fossils fuel and enter into the waters through industrial and municipal effluents, atmospheric precipitation, sewage outfalls, maritime transport, runoff and rain waters (Countway et al., 2003; WHO, 2001). It has been reported that the anthropogenic activities including industrial, urban, or petroleum transportation, and petroleum hydrocarbons production are responsible for the introduction of the majority of the PAHs into the environment (Soclo et al., 2000). More than 100 PAHs have been recognized yet, of which 16 (naphthalene, dibenz[α,h]anthracene, acenaphthylene, anthracene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, benzo[α] anthracene, chrysene, dibenz[α,h]anthracene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, benzo[α]pyrene, and indeno[1,2,3-cd]pyrene) are claimed human carcinogens and have been listed as priority pollutants by the Environmental Protection Agency of the USA (Manoli et al., 2000). The PAHs may get mixed with the foods stuff through curing, drying, roasting, grilling and food processing (SCF, 2002).

3.3. Pesticides

Pesticides can be defined as any substance which is used to protect the plant from the attack of pests. Pesticides include insecticides, herbicides, fungicides, molluscicides, rodenticides, and nematocides. The pesticides can also be used as plant regulator or plant growth promotor (USEPA, 2014). According to the World Health Organization (WHO), approximately 3,000,000 cases of pesticides poisoning and 220,000 cases of death are reported every year. Hence, the extensive use of

pesticide has resulted in accumulation of higher levels of pesticides residues in world water resources. The organochlorine and organophosphorous are among the most important classes of pesticides.

The applied pesticides affect the non-target species as well, subsequently causing many harmful effects on the human beings, animals and other terrestrial organisms. It has been reported that about 80–90% of the applied pesticides convert into vapor forms and damage the plants and other non-target organisms (Straathoff, 1986). The pesticides can enter into the environment through agricultural activities, industrial waste, storage tank leakage, landfills leaching, sewer and septic leakage, and many other sources (Agrawal et al., 2010). The pesticides are highly toxic to the human and animals and can potentially affect by disrupting the function of sex hormones and reproductive system. The pesticides are often termed as xenohormones because of their interference with endocrine processes (Agrawal et al., 2010). The excessive use of weedicide, fungicide and pesticide is reducing the density of plants and shrubs and causing deforestation.

3.4. Personal care products

The residues, metabolites and transformation of PCPs such as fragrances, UV filters, disinfectants, lotions, shampoos, creams, soaps, sunscreens, toothpaste and other cosmetics are being released into water and consequently causing many serious health hazards worldwide (Liu et al., 2013).

The sewage treatment plants, fertilization, landfill leachate, and livestock breeding have been found as the main sources for the infusion of PCPs into water bodies (Liu et al., 2013). Moreover, several volatile compounds such as terpenes, emitted from PCPs act as primary pollutants, which react with the ozone and create the secondary pollutants like formaldehyde and acetaldehyde (Nazaroff and Weschler, 2004). The continuous exposure to PCPs such as powder, mascara, eyeliner, eyeshadow, nail polish and many types of creams results in various chronic disorders (Reed, 2007).

3.5. Surfactants

The extensive industrial and household utilization of surfactants resulted in their accumulation in various environmental compartments. It has been reported that the annual production of synthetic surfactants exceeded 12.5 million tons per year (Edser, 2006). Depending upon the charge on head groups, the surfactants are categorized as cationic, anionic, nonionic and amphoteric. The class of surfactant molecule describes its physicochemical properties and application. The surfactants and their residues can either enter directly into the surface water or can enter into groundwater through sewage system resulting in adverse environmental impacts (Ivanković and Hrenović, 2010). The occurrence of surfactants may cause physiological, pathological and biochemical impacts on human, animals and aquatic life (Önder et al., 2007).

3.6. Endocrine disrupting compounds

The EDCs include a diverse group of chemicals which could potentially interfere with the functioning of the human and animal endocrine systems. The EDCs could antagonize the impacts of endogenous hormones and disrupt the metabolism of endogenous hormones. The prevalence of natural (estrone (E1), 17β-estradiol (E2) and estriol (E3)) and synthetic estrogens (17α-ethinylestradiol (EE2)) has been reported in the wastewater (Racz and Goel, 2010). The natural (excreted from human and animals) as well the synthetic steroid hormones enter into the environment via sewage discharge and animal wastes. The natural and synthetic EDCs are responsible for various disorders in human beings including declined sperm count in males, breast cancer in females and impairments to the reproductive systems.

4. OMPs associated health risks

The rising global pollution due to contamination from OMPs is posing a serious risk to environmental sustainability and human health, subsequently disrupting the natural ecosystem. The environmental risk assessment (ERA) to investigate the effects of OMPs on human health, plants (phytotoxicity), surface/groundwater quality, and aquatic/terrestrial organisms demonstrated a wide range of disorders induced by the exposure of OMPs (Garland et al., 2000; van Wezel and Jager, 2002; Eriksson et al., 2006). The presence of these chemical compounds in drinking water may lead to serious chronic effects (Kidd et al., 2007; Santos et al., 2010) and bring irreversible mutations in both wildlife and human beings (Daughton and Ternes, 1999; Jjemba, 2006).

The organic compounds found in aquatic systems are causing reproductive systems impairments in fish and other fresh water organisms (Brian et al., 2007; Barnes et al., 2008). Aromatic OMPs react with free chlorine to produce chlorinated byproducts which are more persistent, poisonous and have adverse effects on living organisms (Chan et al., 2003). It has been reported that the OMPs formed during chlorination and several other compounds found in raw water are very carcinogenic in nature (Chan et al., 2003). The triclosan (an antibacterial and antifungal agent used in manufacturing of PCPs) interferes with hormonal functions, changes the metabolism, and disturbs the reproductive systems and growth in human beings (Jackson and Sutton, 2008). Some of the EDCs result in birth abnormalities and feminization in fish, birds, frogs and some mammals (EPA, SA, 2008). Similarly, the pesticides enter the human body through direct contact via handling of pesticides, inhalation, ingestion and penetration through skin (Spear, 1991). Although human body have an immunity system for the excretion of toxins, but the pesticides are absorbed in the circulatory system immediately (Jabbar and Mallick, 1994). The acute affects include swindling of eyes and skin, throat and nose vexation, skin concupiscence, rashes in the skin, vertiginous, belly pain, nausea and vomiting, eyesight weakness and rarely death. Chronic effects of the pesticides include the memory loss and eyesight weakness. It damages the immune system and also causes the asthma and allergy. The pesticides residues have been reported in the blood cells of the cancer patients. Leukemia, brain cancer, breast cancer, birth defects, instinctive abortion, infertility, liver damage, kidney failure and lungs damage happen due to the toxic effects of the pesticides. Hypersensitivity to light, sound and touch, vomiting, nausea, confusion, nervousness and tremors are caused by the inhalation of organochlorines. Exposure to pesticides is also linked with Parkinson's disease and Alzheimer's disease (Casida and Durkin, 2013). 2,4-Dichlorophenoxyacetic (a herbicide) changes the shell development of the bivalve *Anodonta cygnea*, and is also responsible for chronic toxicity in human beings (Buerge et al., 2009). Dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs) are very toxic compounded and their exposure can cause thinning of eggshell and abnormal gonadal growth in birds (WHO, 2002). Diethylstilbestrol (DES) treatment results in ovarian cancers in adult females and undescended testis in adult males in humans. Likewise, the exposure to PAHs causes much serious harm to the children. One of the common disorders found in the children due to PAHs toxicity is attention-deficit hyperactivity disorder (ADHD). The common symptoms of this disorder include failure in focus to a task, obsessional imperturbable behavior, quiescent inattention, which lead to impairment in family, school and social life (Barkley, 2002). The PAHs cause synaptic plasticity and neuronal activity because they enter into the blood brain barrier (Chepelev et al., 2015; Dutta et al., 2010). The health risks associated with the PCPs are headaches, contact dermatitis, mucosal problems, respiratory disorders and asthma (Kelman, 2004). In a survey in 2002–3 and 2005–6, it was reported that 17.5% and 20.5% of the US population was suffering with the problems of breathing and headaches when exposed to air fresheners and deodorizers, respectively (Caress and Steinemann, 2009). The PCPs also contain numerous heavy metals such as lead, nickel, cadmium and zinc.

Exposure to cadmium causes kidney dysfunction and if exposure prolongs, death may also be occurred. Exposure to zinc causes stomach cramps, vomiting, skin irritation, nausea and anemia. Other health risks which are contributed by the zinc, copper and cadmium include pneumonia, gastro intestinal disorder, diarrhea, convulsion, stomatitis, tremor, paralysis, ataxia vomiting and depression (Mayildurai et al., 2015). Nickel causes kidney problems, pulmonary fibrosis and skin dermatitis (Borba et al., 2006). However, the impacts of most of these OMPs on human health are still not well understood, and therefore need to be explored further.

5. Solution to the problem

The occurrence of OMPs even in very low concentrations is considered as potentially harmful, while the advancements in analytical technologies have revealed the prevalence of pharmaceuticals, EDCs and PCPs in environments in higher quantities (Heberer, 2002; Snyder et al., 2004; Cunningham et al., 2006). A range of physical, chemical and biological treatments have been employed for the removal of OMPs from wastewater effluents. However, majority of the conventional wastewater treatment technologies are either inefficient, expensive or

Table 1
Selected prominent characteristics of carbon nanotubes (SWCNTs: single walled carbon nanotubes, DWCNTs: double walled carbon nanotubes, MWCNTs: Multi-walled carbon nanotubes, C: carbon, H: hydrogen, O: oxygen).

Type	Modification	Micropore volume ($cm^{-3} g^{-1}$)	Mesopore volume ($cm^{-3} g^{-1}$)	pore volume ($cm^{-3} g^{-1}$)	Surface area ($m^{-2} g^{-1}$)	C (%)	H (%)	O (%)	Reference
MWCNT 10	Pristine	0.142	0.951	–	357	96	0	0	Lin and Lin (2007)
MWCNT 100	Pristine	0.023	0.114	–	58	98	0	–	
CNT	Methane	–	–	0.28	122	–	–	–	Li et al. (2003a, 2003b)
CNTs	H_2O_2 oxidized	–	–	0.32	130	–	–	–	
CNTs	$KMnO_4$ oxidized	–	–	0.36	128	–	–	–	
CNTs	HNO_3 oxidized	–	–	0.58	154	–	–	–	
SWCNTs	Catalytic chemical vapor deposition	0.0249	0.093	–	576.67	–	–	–	Ncibi and Sillanpaa (2015)
DWCNTs	Catalytic chemical vapor deposition	0.149	0.098	–	382.24	–	–	–	
MWCNTs	Catalytic chemical vapor deposition	0.061	0.042	–	158.15	–	–	–	
MWCNTs	Pristine	0.029	0.58	–	258.6	–	–	–	Deng et al. (2012)
MWCNTs	Oxidized	0.041	0.89	–	427.5	–	–	–	Deng et al. (2012)
SWCNTs	Pristine	–	–	–	625	–	–	–	Ding et al. (2016)
SWCNTs	Hydroxylated	–	–	–	526	–	–	–	
SWCNTs	Carboxylated	–	–	–	552	–	–	–	
MWCNTs	Pristine	–	–	–	148	95	1	–	Ji et al. (2009a, 2009b)
MWCNTs-2O	Sodium hypochlorite (NaClO)	–	–	0.64	471	–	–	–	Yu et al. (2016)
MWCNTs-3.2O	Sodium hypochlorite (NaClO)	–	–	0.58	318	–	–	–	
MWCNTs-4.7O	Sodium hypochlorite (NaClO)	–	–	0.58	382	–	–	–	
MWCNTs-5.9O	Sodium hypochlorite (NaClO)	–	–	0.49	327	–	–	–	
MWCNTs	Hydroxylated	–	–	–	228	94	3	3	Zhang et al. (2011a)
MWCNTs	Carboxylated	–	–	–	164	97	3	0	
MWCNTs	Graphitized				117	98	2	0	
MWCNTs	Chemical vapor deposition on alumina supported iron catalyst powders,	0		1.59	284		–	–	Carabineiro et al. (2012)
SWCNTs	Pristine	–	–	–	370	82	–	–	Ji et al. (2009b)
MWCNTs	Pristine	–	–	–	148	94	–	–	
SWCNTs	Pristine	–	–	–	541	–	–	–	Li et al. (2014)
MWCNTs	Graphitized	–	–	–	117	–	–	–	
MWCNTs	Carboxylated	–	–	–	164	–	–	–	
MWCNTs	Hydroxylated	–	–	–	228	–	–	–	
MWCNTs	Hydroxylated	–	–	–	553	94	3	3	Peng et al. (2012)
MWCNTs	Carboxylated	–	–	–	569	97	3	0	
MWCNTs	Graphitized	–	–	–	541	100	1	0	
SWCNTs	Hydroxylated	–	–	–	117	95	3	2	
SWCNTs	Carboxylated	–	–	–	164	69	1	2	
SWCNTs	Purified	–	–	–	228	96	2	2	
MWCNTs	Pristine	0.01	0.08	0.37	156	–	–	–	Strachowski and Bystrzejewski (2015)
MWCNTs	Co/SiO at 700 °C	0.76	0.003	–	411	–	–	–	Frackowiak and Beguin (2001)
MWCNTs	Co/SiO at 900 °C	0.66	0	–	396	–	–	–	
MWCNTs	Co/NaY at 600 °C	0.43	0.004	–	128	–	–	–	
MWCNTs	CVD of propylene on alumina template at 800 °C	1.04	0.014	–	311	–	–	–	
CNTs	Pristine	0.0025	0.3404	0.34	64.8	–	–	–	Niu et al. (2007)
CNTs	KOH	0.2233	1.3717	1.6	830	–	–	–	
SWCNTs	Pristine	0.28		1.55	1587	–	–	–	Cinke et al. (2003)
CNTs	Pristine	0	0.66	0.66	194.1	–	–	–	Jiang et al. (2002)
CNTs	KOH	0	0.91	0.91	510.5	–	–	–	
CNTs	Pristine	0.0784	0.371	–	231.89	–	–	–	Lu et al. (2008)
CNTs	HCl	0.0361	1.473	–	271.2	–	–	–	
CNTs	H_2SO_4	0.0367	1.971	–	237.83	–	–	–	
CNTs	HNO_3	0.0223	1.1599	–	165.24	–	–	–	
CNTs	NaOCl	0.0382	1.11	–	194.08	–	–	–	
MWCNTs	Pristine	–	–	0.08	310.75	–	–	–	Su et al. (2010)
MWCNTs	NaOCl	–	–	0.02	88.56	–	–	–	

do not remove the OMPs completely from the wastewater (Chen et al., 2018). Therefore, the risk of OMPs contamination is escalating as most of the conventional WWTPs can efficiently eliminate a range of contaminates; however, the removal of OMPs often remains inefficient (Baresel et al., 2019; Reemtsma et al., 2006; Lishman et al., 2006; Luo et al., 2014). Several studies demonstrated that the conventional wastewater treatment processes such as sedimentation, flocculation, and active sludge treatment are inefficient for the removal of pharmaceuticals and PCPs from wastewater (Liu et al., 2013; Santos et al., 2007). Likewise, the incomplete removal of EDCs by conventional wastewater treatment has also been documented by various researchers (Leech et al., 2009; Liu et al., 2009). Therefore, development of a cost-effective, sustainable and eco-friendly technology to remove OMPs from wastewater is still a challenge for the environmentalists around the world.

A range of advanced wastewater treatment technologies such as oxidation, catalytic degradation, adsorption, membrane filtration, ion exchange, solvent extraction, steam stripping, and microbial degradation have been developed for the removal of OMPs from the environment (Lin and Lin, 2007; Smith et al., 2004; Zinovyev et al., 2005; Braass et al., 2003; Lopez-Montilla et al., 2005). However, majority of these technologies require higher electricity and resources consumption and may result in the production of more toxic metabolites (Varga et al., 2019; Foteinis et al., 2018). The existing studies demonstrated that ozonation is very effective technique for the removal of OMPs from wastewater; however, it is expensive, requires high energy and is inefficient for removal some of the substances even with higher ozone application (Baresel et al., 2019; Chen et al., 2012). Additionally, the OMPs could be transformed into more toxic metabolites which need an extra treatment (Baresel et al., 2019; Magdeburg et al., 2012, 2014; Stalter et al., 2011). Likewise, the use of activated carbon (AC) is a widespread and the most commonly used technique for wastewater treatment; however, the production and regeneration of AC require enormous energy and resources (Baresel et al., 2019). Granulated activated carbon (GAC) based filters have been used by researchers to enhance the biological activity within the filter system to improve the filter performance. Nevertheless, the clogging problems induced by biological activities significantly reduced the performance of GAC-filter systems (Baresel et al., 2019). Similarly, chlorination is an effective wastewater treatment technology, however, may yield some detrimental chlorinated disinfection by-products (DBPs) (Chen et al., 2012). Due to simplicity and feasibility, adsorption is a widely accepted technique, however sorbent (with high adsorption capacity, high porosity and large surface area) selection and operating cost is very critical to be considered. Most commonly used sorbents include carbon, clay minerals, biochar, metal oxides and powder activated carbon (Meinel et al., 2015). However, for the complete removal, an adequate contact time and mixing is needed which requires an extra reactor (Mailler et al., 2015), and separation of sorbent after saturation requires an additional filter which increases the cost of this technology. Moreover, the application of an individual remediation technology could not attain the desired results due to the presence of multiple contaminants in the wastewater (Ye et al., 2017b). Therefore, researches are focusing on the application of joint-remediation technology for the complete and efficient decontamination of wastewater. A joint application of sorbents and microbial processes can be applied for combined benefits, nevertheless sorbents coating by biofilms results in reduced efficacy (Widjaja et al., 2004).

These flaws make the majority of these conventional wastewater treatments inefficient in removing most of the OMPs, especially from real wastewater streams (Ruel et al., 2012; Mailler et al., 2014). Due to the inefficiency of these technologies, effluents from WWTPs, due to presence of OMPs, are considered as major point source of OMPs in the environment (Snyder et al., 2001). Therefore, it is the devastating need of the time to develop cost-effective, environment friendly and sustainable technologies to limit the release of OMPs from the wastewater streams prior to their disposal into the environment, and for the complete removal of prevailing OMPs from various environment matrices.

6. Carbon nanotubes: as remediation technology for OMPs

6.1. Introduction to carbon nanotubes

The carbon nanotubes (CNTs) have come up recently as efficient sorbents for water purification because of their remarkable wastewater treatment capabilities and their suitability for the removal of organic, inorganic and biological water pollutants (Upadhyayula et al., 2009). Tunable physical, chemical, electrical and structural properties, large specific surface area as well as small, hollow and layered structure make the CNTs as very efficient adsorbent for a range of OMPs.

The CNTs are derived from graphite and composed of many sheets of a single atom in a hexagonal structure in honeycomb crystal lattice called as graphene. These graphene structures can be folded into cylindrical shape to give rise to single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and/or multi-walled CNTs (MWCNTs). The SWCNTs are composed of tubular shaped graphene sheets which bound together and look similar to the benzene rings of carbon atoms. It usually contains ten atoms around their circumference having the thickness of about one atom. The DWCNTs and MWCNTs are larger in size and contain two and several SWCNTs, respectively, stacked inside one another. All kind of CNTs consist of hollow structures having a diameter of 0.4–3.0 nm. The MWCNTs can further be categorized into two main groups i.e., (i) parchments like structure and (ii) Russion doll model, while SWCNTs can be classified further into (i) zigzag pattern, (ii) helical, (iii) armchair and (iv) chiral structures.

6.2. Properties of CNTs

The CNTs possess exclusive electrical and structural characteristics which make them potential candidates for a number of applications. Some prominent properties of CNTs are presented in Table 1. As in SP^2 hybridization, the elemental carbon makes variety of shapes, therefore apart from graphite, carbon can also make closed and open cages. Thus, due to SP^2 hybridization, the CNTs are stiff and possess a higher axial strength (Robertson et al., 1992). From various carbon cages, Iijima (1991) observed nanoscale tubular carbon structure first time in 1991. These nanoscale tubular structures were made up of several tens of graphitic shells therefore were termed as MWCNTs. The CNTs are allotropes of carbon and explained as graphene sheet rolled into a tube. Physical properties of CNTs such as higher mechanical strength, low electrical resistivity and higher thermal conductivity are due to unique structure of CNTs (Iijima, 1991). The results of theoretical calculations and experimental demonstrations explained that CNTs are extremely flexible with a high young modulus (Li et al., 2014). The structural properties of CNTs revealed that CNTs are either metallic or semiconductors (Mintmire et al., 1992; Saito et al., 1992). The CNTs exhibit higher electrical conductivity, structural integrity, chemical stability and lower threshold electric field, aggregated pores (formed by CNTs due to van der Waals forces of attraction), large external surface area, hollow interiors of nanotubes, interstitial pore spaces between the tubes bundles, and grove at the boundary (Agnihotri et al., 2005; Donaldson et al., 2006; Yan et al., 2008).

Functional properties of CNTs include shape recovery, dry adhesion, high damping, tetra hertz polarization, large stroke actuation, near ideal black body absorption and thermosacoustic sound emission (Cao et al., 2005; Qu et al., 2008; Xu et al., 2010; Ren et al., 2009; Aliev et al., 2009; Lima et al., 2012; Mizuno et al., 2009). The chemical compatibility with DNA and proteins made the CNTs as components of biosensors and medical devices. The CNTs meshes in portable filters and purify the contaminated water by removing bacteria, viruses and electrochemically oxidized organic contaminant (Gao and Vecitis, 2011; Rahaman et al., 2012). Some of the CNTs possess hydrophilic

nature; therefore, due to their higher dissolvability in water, their adsorption capacity for OMPs from wastewater improves significantly (Huang et al., 2004).

The performance of the CNTs depends on their characteristics, which can be tuned during its fabrication through activation and modifications to achieve higher efficiency. Several activation approaches have been employed to modify the surface and structural properties of CNTs for particular application. However, generally the CNTs can be functionalized by either covalent or noncovalent approaches (Spitalsky et al., 2010). The covalent functionalization of the CNTs can be performed via oxidizing with acid to create carboxylic or hydroxyl groups (Cha et al., 2016). Trojanowicz (2006) reported that the fullerene-like tips were more reactive than the walls, therefore the functional groups (–COOH, –OH and –C═O) can be generated on CNTs via end functionalization. The surface of CNTs can also be functionalized with amino groups to enhance its capability to sense organophosphorus pesticides (Yu et al., 2015a). In the noncovalent functionalization, various biochemically active molecules can be attached to the CNTs through non-covalent sidewalls via H–bonding, van der Waals forces, π-π stacking, hydrophobic interactions or electrostatic forces (Chen et al., 2001). The noncovalent functionalization is considered more attractive as it maintains the structural characteristics of pristine CNTs (Cha et al., 2016). The CNTs can also be functionalized with ultrasonication, dilute acid treatment, irradiation, acid oxidation and microwave acid digestion to produce pure CNTs without the impurities of graphite particles, amorphous carbon and metal catalysts (Karimifard and Moghaddam, 2016).

6.3. CNTs as sorbents for OMPs

The CNTs have attracted a great deal of attention of the researchers for the removal of emerging pollutants from the aqueous streams in recent times. The CNTs have been found as efficient sorbents for the removal of a diverse number of emerging pollutants including chemical, biological, organic and inorganic contaminants (Patiño et al., 2015). The unique chemical structure, one-dimensional macromolecules, large specific surface area, small pore size, and layered structure induce the exceptional sorption properties into CNTs making them potential candidate for the removal of OMPs (Karimifard and Moghaddam, 2016). Thus, due to their exceptional properties, and chemical as well as thermal stability, CNTs possess higher binding affinity and capacity for the elimination of OMPs from water (Gupta and Saleh, 2013; Khani et al., 2010; Gupta et al., 2015). The specific textural properties including surface area, pore volume and pore diameter are the prominent factors which are considered very effective for the higher adsorption capacity of CNTs. Presence of micro and mesopores, specific functional groups and net positive charge on the surfaces are the prominent factors responsible for higher adsorption of OMPs onto CNTs (Cheng et al., 2005; Dastgheib et al., 2004). The adsorption capacity of CNTs is many folds compared to the common adsorbents as it is influenced by highly reactive surface sites on the matrix of CNTs (Gupta and Saleh, 2013; Ren et al., 2011). Unlike other commonly used sorbents, the CNTs are pathogen sensors and adsorb bacteria as well by their adsorption capacity for bacteria (Upadhyayula et al., 2009). The CNTs are used as nano-membrane filters for selective water transport due to its reduced size and improved water permeability in comparison to polymeric membrane (Weber, 2002). The adsorption phenomenon of CNTs can be changed when CNTs are in cluster due to the generation of the new adsorption sites (Serp et al., 2003; Ren et al., 2011).

The CNTs particles may also work as size exclusion membrane filters that allow the flow of water while block the flow of contaminants (Han et al., 2013). The CNTs have a strong affinity towards organic chemicals, especially to non-polar organic compounds such as naphthalene (Gotovac et al., 2007a, 2007b), phenanthrene and pyrene (Yang et al., 2006). Various researchers have synthesized and successfully applied numerous types of CNTs for the remediation of OMPs from wastewater.

For instance, Maphutha et al. (2013) synthesized a novel CNTs and applied for the separation of oil (organic compounds) from water for the treatment of oil contaminated wastewater. The catalytic activity toward contaminant mitigation can further be enhanced by using CNTs (Qu et al., 2013). The CNT based materials are excellent adsorbents for detergents, insecticide, herbicide, drugs, dyes and volatile organic compounds (Rao et al., 2007). The CNTs are being used in sea and brackish water desalination technologies for supplying clean water to the masses (Das et al., 2014). To enhance the efficiency and achieve the target functions, the CNTs can further be modified via chemical, physical, biological and/or mechanical treatments. Adsorption capacity of CNTs can also be increased by treating it with acids (Liao et al., 2008), bases (Chen et al., 2006; Liu et al., 2018; Niu et al., 2007), gaseous compounds (Chen et al., 2006) or thermal treatments (Lu and Su, 2007). Hence, the application of CNTs for the remediation of wastewaters may serve as a state-of-the-art technology for sustainable ecosystem.

6.4. Limitations of CNTs application as sorbents

Several studies demonstrated that CNTs are potential adsorbents for the removal of a diverse range of OMPs from wastewater streams (Upadhyayula et al., 2009). Nonetheless, certain limitations restrain the potential applicability of CNTs on large scale for the treatment of wastewater streams. Among these limitations, hydrophobicity and higher production cost are considered as the major constraints (Pan and Xing, 2008; Agboola et al., 2007). Upadhyayula et al. (2009) stated that the cost of CNTs production is a major obstacle for their application on large scale.

Another biggest challenge in practical application of CNTs is the commercial production of pure CNTs (Agboola et al., 2007). Generally, the CNTs also include some impurities of graphite particles, amorphous carbon and metal catalysts (Karimifard and Moghaddam, 2016). Moreover, the difficulties in centrifugation separation approaches reduce the industrial applications of CNTs (Fard and Barkdoll, 2018). Another major concern of CNTs application is their potential discharge into environment and subsequent exposure to the human beings. The continuous exposure to CNTs may cause detrimental health impacts on human, animals and aquatic life; however, it largely depends on the quantity of CNTs discharged into the environment (Upadhyayula et al., 2009).

Thus, the practical application of CNTs for wastewater treatment on large scale has many limitations which need to be resolved. Nonetheless, the continuous production, development of new production techniques, and functionalization approaches may result in the synthesis of CNTs with lower costs and high purity in the coming years.

6.5. Ecological effects of CNTs and treated water

The fate, transport and ecological effects of CNTs are not well understood (Petersen et al., 2011). Although, majority of the CNTs products are either sealed or bounded with polymers, hence, chances of their introduction into drinking water after filtration are fewer (Gottschalk et al., 2009; Mueller and Nowack, 2008). Therefore, it has been claimed that the presence of CNTs in water could be through tailoring, use, finishing, and degradation of CNT-containing textiles (Gottschalk et al., 2010). However, there is a concern that smaller quantities of CNTs may originate from WWTPs effluents into drinking water and pose hazardous effects on human health (Petersen et al., 2011).

The structure, aspects ratio, length and size distribution, shape, degree of dispersion, surface area, potential of agglomeration, impurities, degree of oxidation, functional groups, dose, and cellular uptake of CNTs determine their possible cytotoxic effects. The residues of CNTs in drinking water may lead to the damage of DNA and impairments of different organs in human body (Kolosniaj et al., 2007; Lam

Table 2

Efficiency of various pristine and modified carbon nanotube for the removal of different organic micropollutants from aqueous media (SWCNTS: single walled carbon nanotubes, MWCNTS: Multi-walled carbon nanotubes, K_F: Freundlich isotherm predicted sorptive affinity coefficient in L g^{-1}, Q_L: Langmuir isotherm predicted maximum sorption capacity in mg g^{-1}).

Type	Modification	Target pollutant	K_F (L g^{-1})	Q_L (mg g^{-1})	Conditions	Mechanism	Reference
MWCNTs	Pristine	Sulfamethazine	6.73	38.13	Temp.298 K and pH 5	π-π interaction	Yang et al. (2006)
MWCNTs	Hexadecyltrimethylammonium bromide	Sulfamethazine	2.99	27.29	Temp. 298 K, and pH 5	π-π interaction	
MWCNTs	Amino groups and Co(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O	Sulfamethoxazole	5517	17826	Temp. 298 K and pH 5.7	π-π and hydrophobic interactions	Wang et al. (2015)
MWCNTs	Amino groups and Co(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O	17β-estradiol	169.8	31.8	Temp. 298 K and pH 5.7	π-π and hydrophobic interactions	
MWCNTs	Carboxylic groups, Co(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O	Sulfamethoxazole	5.48	354	Temp. 298 K and pH 5.7	π-π and hydrophobic interactions	
MWCNTs	Carboxylic groups, Co(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O	17β-estradiol	52.27	29.1	Temp. 298 K and pH 5.7	π-π and hydrophobic interactions	
MWCNTs	Pristine	Sulfamethoxazole	9.17	21.37	Temp. 298 K, pH 5.5	Electrostatic attraction and surface area	Chen et al. (2018)
MWCNTs	SiO$_2$	Sulfamethoxazole	3.608	172.4	Temp. 298 K, pH 5.5	Electrostatic attraction and surface area	
MWCNTs	Al$_2$O$_3$	Sulfamethoxazole	6.02	28.74	Temp. 298 K and pH 5.5	Electrostatic attraction and surface area	
MWCNTs	Carboxylic	17β-estradiol	41.8	34.1	Temp. 298 K and pH 3-11	Electrostatic attraction and surface area	Shen et al. (2017)
MWCNTs	Fe$_2$O$_3$ NPs	17β-estradiol	92.4	76.6	Temp. 298 K and pH 3-11	Electrostatic attraction and surface area	
MWCNTs	ZnO NPs	17β-estradiol	36.4	22	Temp. 298 K and pH 3-11	Electrostatic attraction and surface area	
MWCNTs	Pristine	Sulfamethoxazole	24.7	28.88	Temp. 298 K and pH 7	Ion-dipole and π-π interactions	Tonucci et al. (2015)
SWCNTs	Catalytic chemical vapor deposition	Oxytetracycline	107.5	737.5	Temp. 288.15–318.15 K and pH 3-11	Macrodispersion and surface sites	Ncibi and Sillanpaa (2015)
DWCNTs	Catalytic chemical vapor deposition	Oxytetracycline	72.1	688.2	Temp. 288.15–318.15 K and pH 3-11	Macrodispersion and surface sites	
MWCNTs	Catalytic chemical vapor deposition	Oxytetracycline	59.2	355.1	Temp. 288.15–318.15 K and pH 3-11	Macrodispersion and surface sites	
SWCNTs	Catalytic chemical vapor deposition	Ciprofloxacin	148.8	933.8	Temp. 288.15–318.15 K and pH 3-11	Macrodispersion and surface sites	
DWCNTs	Catalytic chemical vapor deposition	Ciprofloxacin	98.08	901.2	Temp. 288.15–318.15 K and pH 3-11	Macrodispersion and surface sites	
MWCNTs	Catalytic chemical vapor deposition	Ciprofloxacin	36.34	651.4	Temp. 288.15–318.15 K and pH 3-11	Macrodispersion and surface sites	
MWCNTs	Pristine	Diuron	31.83	39.69	Temp. 298 K and pH 7	Surface area and the pore volume,	Deng et al. (2012)
MWCNTs	Oxidized	Diuron	44.32	48.6	Temp. 299 K and pH 7	Surface area and the pore volume,	Deng et al. (2012)
SWCNTs	Pristine	2-Chlorophenol	24.95	24.9	Temp. 298.15 K and pH 4-10	π-π interaction, cation-π interaction, and surface area	Ding et al. (2016)
SWCNTs	Pristine	4-chlorophenol	24.92	29	Temp. 298.15 K and pH 4-10	π-π interaction, cation-π interaction, and surface area	
SWCNTs	Pristine	2,4-dichlorophenol	54.85	59	Temp. 298.15 K and pH 4-10	π-π interaction, cation-π interaction, and surface area	
SWCNTs	Pristine	2,6-dichlorophenol	45.61	55.3	Temp. 298.15 K and pH 4-10	π-π interaction, cation-π interaction, and surface area	
SWCNTs	Pristine	2,4,5-trichlorophenol	102	107.7	Temp. 298.15 K and pH 4-10	π-π interaction, cation-π interaction, and surface area	
SWCNTs	Pristine	2,4,6-trichlorophenol	122.9	166.8	Temp. 298.15 K and pH 4-10	π-π interaction, cation-π interaction, and surface area	
MWCNTs	Pristine	Sulfapyridine	350		Temp. 298.15 K and pH 4-6	π-π interaction	Ji et al. (2009a, 2009b)
MWCNTs	Pristine	Sulfamethoxazole	510		Temp. 298.15 K and pH 4-6	π-π interaction	
MWCNTs-2O	Sodium hypochlorite (NaClO)	Ciprofloxacin	90.9	150.6	Temp. 298 K	π-π interaction	Yu et al. (2016)
MWCNTs-3.2O	Sodium hypochlorite (NaClO)	Ciprofloxacin	97.51	178.9	Temp. 298 K	π-π interaction	
MWCNTs-4.7O	Sodium hypochlorite (NaClO)	Ciprofloxacin	119.7	206	Temp. 298 K	π-π interaction	
MWCNTs-5.9O	sodium hypochlorite (NaClO)	Ciprofloxacin	116.8	181.2	Temp. 298 K	π-π interaction	
MWCNTs	Pristine	Tetracycline	148.2	234.7	Temp. 273 K and pH 4.5-7	Non-electrostatic – dispersion and hydrophobic interaction	Zhang et al. (2011b)
MWCNTs	Pristine	Tetracycline	159.9	269.5	Temp. 293 K and pH 4.5-7	Non-electrostatic – dispersion and hydrophobic interaction	
MWCNTs	Pristine	Tetracycline	172.9	309.6	Temp. 333 K and pH 4.5-7	Non-electrostatic – dispersion and hydrophobic interaction	

Table 2 (*continued*)

Type	Modification	Target pollutant	K_F (L g^{-1})	Q_L (mg g^{-1})	Conditions	Mechanism	Reference
MWCNTs	Chemical vapor deposition on alumina supported iron catalyst powders,	Ciprofloxacin	86	135	Temp. 298 K and pH 5	Electron–donor capacity, and surface area	Carabineiro et al. (2012)
SWCNTs	Pristine	Ciprofloxacin	70.6	100	Temp. 298 K and pH 7	π-π interaction	Li et al. (2014)
MWCNTs	Graphitized	Ciprofloxacin	24.41	30.86	298 K and pH 7	π-π interaction	
MWCNTs	Carboxylated	Ciprofloxacin	24.8	30.3	Temp. 298 K and pH 7	π-π interaction	
MWCNTs	Hydroxylated	Ciprofloxacin	23.83	42.37	Temp. 298 K and pH 7	π-π interaction	
MWCNTs	Pristine	Toluene	1.823	23.28	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	Yu et al. (2016b)
MWCNTs	KOH	Toluene	11.98	53.44	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	Pristine	Ethylbenzene	3.098	92.71	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	KOH	Ethylbenzene	12.7	213.8	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	Pristine	p-Xylene	1.921	44.15	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	KOH	p-Xylene	7.328	98.19	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	Pristine	m-Xylene	3.972	70.58	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	KOH	m-Xylene	15.19	196.6	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	Pristine	o-Xylene	2.656	44.18	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	KOH	o-Xylene	12.51	127.5	Temp. 293 K and pH 6	Micro-/nano-pore structures and surface area	
MWCNTs	Oxidized	1-Naphthylamine	53.48	217.4	Temp. 293.5 K and pH 3–11.3	π-π and hydrophobic interaction	Hu et al. (2011)
MWCNTs	Iron oxide	1-Naphthylamine	25.14	153.8	Temp. 293.5 K and pH 3–11.3	π-π and hydrophobic interaction	
MWCNTs	Iron oxide and β-cyclodextrin (β-CD)	1-Naphthylamine	28	200	Temp. 293.5 K and pH 3–11.3	π-π and hydrophobic interaction	
MWCNTs	Iron oxide and β-cyclodextrin (β-CD)	1-Naphthylamine	41.35	243.9	Temp. 313.15 K and pH 3–11.3	π-π and hydrophobic interaction	
MWCNTs	Iron oxide and β-cyclodextrin (β-CD)	1-Naphthylamine	55.75	294.1	Temp. 333.15 K and pH 3–11.3	π-π and hydrophobic interaction	
MWCNTs	Pristine	Nalidixic acid	111.7	196.1	Temp. 298 K and pH 7	π-π interaction	Patiño et al. (2015)
MWCNTs	COOH	Nalidixic acid	79.28	149.3	Temp. 298 K and pH 7	π-π interaction	
MWCNTs	NH$_2$	Nalidixic acid	98.09	163.9	Temp. 298 K and pH 7	π-π interaction	
MWCNTs	Fe/SiO$_2$ catalyst from acetonitrile	Nalidixic acid	107.7	169.5	Temp. 298 K and pH 7	π-π interaction	
MWCNTs	Pristine	2-(4-methylphenoxy) ethanol	10.55	172.4	Temp. 298 K and pH 7	π-π interaction	
MWCNTs	COOH	2-(4-methylphenoxy) ethanol	18.49	769.2	Temp. 298 K, pH 7	π-π interaction	
MWCNTs	NH$_2$	2-(4-methylphenoxy) ethanol	19.94	909.1	Temp. 298 K and pH 7	π-π interaction	
MWCNTs	Fe/SiO$_2$ catalyst from acetonitrile	2-(4-methylphenoxy) ethanol	33.27	909.1	Temp. 298 K and pH 7	π-π interaction	
MWCNTs	Pristine	Phenol		23.6	Temp. 295 K and pH 6	Munlti-layer sorption	Strachowski and Bystrzejewski (2015)
MWCNTs	Pristine	2-Chlorophenol		86.1	Temp. 295 K and pH 6	Munlti-layer sorption	
MWCNTs	Pristine	4-Chlorophenol		51.5	Temp. 295 K and pH 6	Munlti-layer sorption	

et al., 2006). Patlolla et al. (2010) reported substantial increase in genotoxicity, cytotoxicity and apoptosis in human being under MWCNTs exposure; however, no carcinogenic affects have been seen (Simate et al., 2012). The cytotoxic effects of CNTs on bacterial community in WWTPs have also been reported. The physical interaction of CNTs and bacteria, as well as presence of extracellular polymeric substances in WWTPs may result in cytotoxicity. Kang et al. (2009) reported cell inactivation in bacteria in the presence of SWCNTs and MWCNTs in water. Likewise, Luongo and Zhang (2010) reported that MWCNTs resulted in bacterial respiration inhibition. The adverse effects of CNTs on aquatic organisms and mammalian cell systems have also been reported (Cheng et al., 2007; Lam et al., 2004; Warheit et al., 2004; Upadhyayula et al., 2009).

The removal of loaded CNTs after wastewater treatments varies with the properties of CNTs and the aqueous media. Gottschalk et al. (2009 and 10) reported that about 96.3–99.7% CNTs can be removed from wastewater after treatment, while according to Holbrook et al. (2010) the removal of MWCNTs was in range of 10–85%. Thus, before the application of CNTs as adsorbents for wastewater treatment, the possibility of loaded CNTs removal from water, effects of CNTs on microbial communities and potential toxic ecological risks of CNTs must be investigated.

7. Mechanisms of OMPs removal using CNTs

The mechanism of contaminants adsorption onto CNTs is controlled by the characteristics of the CNTs and the adsorbate (whether it is a polar or a non-polar compound). Likewise, the maximum adsorption capacity of a particular CNT for specific contaminant depends on the characteristics of the adsorbent and adsorbate, as well as the sorption conditions. Table 2 represents the adsorption efficiencies of various types of CNTs for a particular OMP containment, the effects of activation/modification on adsorption efficiency, the effect of sorption conditions, and dominant adsorption mechanisms. The mechanism of the adsorption of OMPs onto CNTs is complex as it could be physical adsorption, chemical adsorption, interaparticle diffusion, interactions with specific functional groups, or a combination of these mechanisms (Chen et al., 2009).

The surface of CNTs act as adsorption sites for the larger compounds while meso– and micropores on the matrix of the CNTs may also serve as active sites for the adsorption of smaller species (Czech and Oleszczuk, 2016). Generally, two steps are involved in the adsorption of a contaminant onto CNTs. In the first step, the pollutants diffuse from mass into the mesopore region, while in the second step, the adsorbed pollutants interact with the surface and the pores of CNTs (Ye et al., 2007). Hence, the removal of OMPs by CNTS depends upon the functional groups and external appearances of pollutants as well as physiochemical properties of CNTs including surface area, solution chemistry (pH and ionic strength) surface charge and hydrophobicity (Fasfous et al., 2010; Li et al., 2003a). Therefore, considering all these factors, the prediction of mechanism of OMPs removal by CNTs is very complicated and varies with the type of CNTs and the contaminant (Pan and Xing, 2008).

7.1. Multiple removal mechanisms

Due to diverse characteristics of CNTs and OMPs, multiple mechanisms including H-bonding, electrostatic interactions, van der Waals forces, hydrophobic interactions and π-π interactions may occur simultaneously for the removal of OMPs using CNTs; however, π-π interactions and H-bonding have been reported as the most commonly occurring mechanisms. A combination of hydrophobic interactions, π-π interactions, electrostatic interactions, H-bonding, and covalent interactions has been reported as the mechanism for the removal of PAHs, norfloxacin, PCPs, pesticides, pharmaceuticals, BPA and 17β-estradiol (E2) onto CNTs (Yang and Xing, 2010; Heo et al., 2012; De Martino

et al., 2012; Yang et al., 2006). Moreover, Liu et al. (2018) reported that the adsorption of organophosphorus pesticide onto CNTs was through valence-electron-driven adsorption via electrons sharing.

The molecules of perfluorinated compounds (PFCs) possess hydrophilic groups on one hand and oleophobic C-F chain and hydrophobic groups on the other hand. Therefore, the adsorption of PFCs onto CNTs is a complicated process and depends on multiple factors (Deng et al., 2012). Several mechanisms including electrostatic interaction, hydrophobic effect, H-bond, π-π ion exchange, and van der Waals force could be involved in PFCs adsorption onto CNTs (Du et al., 2014). Deng et al. (2012) studied the adsorption of 6 PFCs and found that hydrophobic interactions and electrostatic forces were responsible for their adsorption onto CNTs (Deng et al., 2012).

7.2. π-π interactions

The CNTs have been found as excellent adsorbents for the removal of emerging OMPs; however, due to differences in hydrophobicity, strengths of π-π interactions and electrostatic interactions, as well as adsorbent surface activity, the interpretation of adsorption mechanism is very complex (Deng et al., 2019). Generally, the OMPs molecules contain π-electrons which can form π-π bonds with CNTs as each carbon atom in CNTs possesses one π-electron. However, the presence of functional groups on the benzene rings of OMPs determines the strength of π-π bonds. Therefore, π-π electron donor-acceptor interactions are the most dominant mechanisms for the removal of different OMPs through CNTs. Ji et al. (2009a) and Chen et al. (2007) reported that the benzene rings and aromatic heterocyclic groups on the surface of sulfapyridine and sulfamethoxazole compounds were bounded with π-electron rich sites on aromatic rings of CNTs via π–π interactions. Moreover, the substituted benzene rings of aforementioned compounds created additional π-π stacking and resulted in higher removal of these compounds (Ji et al., 2009b). Likewise, the π–π stacking was also reported as dominant mechanism for the removal of sulfamethoxazole, tetracycline, and tylosin through CNTs (Ji et al., 2010). The protonated amino groups on tetracycline and tylosin were seen making strong cation–π interaction with π–electrons on the surface of CNTs resulting in higher removal (Ji et al., 2010). Similarly, Deng et al. (2019) reported that π-π electron donor-acceptor interactions were controlling the adsorption of carbamazepine onto CNTs.

The π−π electron-donor–acceptor interactions and π-electron coupling have also been found responsible for the removal of PAHs through CNTs in various studies (Wang et al., 2010; Chen et al., 2007). Gotovac et al. (2007a, 2007b) studied the adsorption of phenanthrene and tetracene and reported that π−π interactions were the dominant removal mechanism. However, the mechanism of PAHs adsorption onto CNTs is poorly understood, as it is greatly influenced by the hydrophobicity of PAHs compounds (Wang et al., 2010).

Pan et al. (2008) studied the adsorption behavior of benzene containing EDCs onto CNTs and stated that π-π electron donor-acceptor interactions were the dominant removal mechanism. The similar findings have also been reported by Jung et al. (2015) stating that π–π bonds were responsible for EDCs removal through CNTs. In another study, Joseph et al. (2011) investigated the adsorption of BPA and 17α-ethinyl estradiol (EE2) onto SWCNTs and found that π-π electron donor-acceptor interactions were the potential adsorption mechanisms. Jung et al. (2015) reported that higher adsorption of triclosan (TCS) resulted due to the formation of π–π bonds of the C=C double bonds with CNTs (Jung et al., 2015).

7.3. H-bonding

The oxygen containing functional groups on the surface of CNTs interact with –OH, –NH and –NH$_2$ via H-bonding subsequently resulting in the adsorption of OMPs onto CNTs (Zhao et al., 2016). Yu et al. (2014) reported that H-bonding was the major mechanism for diuron

and dichlobenil adsorption onto CNTs. In another study, Sun et al. (2012) showed that the hydrophobic interaction, H-bonding and O-containing functional groups of SWCNTs were responsible for the adsorption of diuron, fluridone and norflurazon. However, the metal ions present within the pesticides may get complexed with O-containing functional groups resulting in the interference for the pesticides removal (Lu and Liu, 2006; Li et al., 2003b). The higher removal of TCS was obtained due to the presence of OH– groups which resulted in the formation of H-bonding between OH–containing groups and O–containing groups (Chen et al., 2007; Zhou et al., 2013). Fang and Chen (2012) reported that H-bonding was the dominant mechanism for perchlorate adsorption onto CNTs. The surface charge and specific surface area were the main factors responsible for perchlorate adsorption onto CNTs. Likewise, few previous studies showed H-bonding as mechanism for the adsorption of PAHs onto CNTs; however, direct evidences for this mechanism are scarce (Wang et al., 2010; Franz et al., 2000).

7.4. Electrostatic interactions

The occurrence of positive or negative charges on the surface of CNTs due to the variations from pH at point of zero charges creates electrostatic forces on the surfaces. Likewise, the surfaces of OMPs become charged due to protonation or deprotonation at different pH levels. These electrostatic forces on the surface of both OMPs and CNTs result in the adsorption due to electrostatic interactions. The strength of electrostatic forces changes with protonation/deprotonation of functional groups (Cho et al., 2011). Wang et al. (2015) reported that removal of TCS and ibuprofen by CNTs was due to electrostatic interactions between them. Similar results were also reported by Shen et al. (2017) stating that electrostatic interactions were responsible for the removal of diethyl phthalate and oxytetracycline on CNT-based adsorbents.

7.5. Hydrophobic interactions

Hydrophobic interaction is also responsible for the removal of a range of hydrophobic OMPs by CNTs (Nam et al., 2014; Pyrzynska et al., 2007). At zero net charge density of CNTs and molecular state of OMPs, the strongest hydrophobic interactions are created resulting in highest adsorption (Lu et al., 2006). Yu et al. (2015b) reported that hydrophobic interactions were the dominant adsorption mechanism for the removal of sulfonamides.

8. Conclusion

Organic micropollutants (OMPs) are deteriorating the global water resources due to their continuous and ever increasing release into the environment. It is devastating need of time to formulate sustainable, efficient and eco-friendly technologies to remove the OMPs from water for a sustainable environmental management. Contamination due to the presence of OMPs in the water is causing a lot of health risks not only to the human beings but to plants, animals and aquatic life. Many technologies have been proposed to decontaminate wastewater; however, majority of these cannot be adopted due to higher costs and complexity in use. The application of carbon nanotubes (CNTs) as adsorbent has been employed for environment management for a range of contaminants. Due to their nanosize, large surface area, hollow structure and other chemical and physical properties, CNTs can efficiently be used for the removal of OMPs. The CNTs are easy to use and are being considered as potential candidates for the removal of OMPs from wastewater streams. However, impurity, higher production costs, hydrophobicity and release of CNTs into the environment are major obstacles for applicability of CNTs on large scale. The removal of a particular OMP is highly dependent on the characteristics of CNTs, nature of pollutant and the sorption conditions. The mechanism and efficiency

of OMPs removal from water by using CNTs varies with pollutant type and properties of CNTs. Therefore, the properties and structure of the CNTs can be tuned to achieve highly efficient sorbent for the removal of a particular pollutant through activation/modification with chemical, physical, biological, and/or mechanical means.

Hence, the fabrication of desired CNTs for a particular type of pollutant can serve as an efficient, cost-effective, environment friendly and sustainable technology for the decontamination of wastewater. However, future research should focus on developing new production techniques and functionalization approaches to produce CNTs with lower costs and higher purity. Moreover, the possibility of loaded CNTs removal from water, potential impacts of CNTs on microbial communities and toxic ecological risks of CNTs must be investigated prior to their application as wastewater treatment technology. The commercial CNT products must be investigated for their stability and dispersive properties in the ecosystem to avoid adverse environmental impacts. Furthermore, the potential impacts of continuous and long term exposure of human and animal to CNTs residues in drinking water must be explored in details.

Declaration of interests

None.

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