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Applications of carbon nanotubes (CNTs) for the treatment of drinking and waste water-a brief review

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Abstract

Conventional methods used for drinking and waste water treatment and purification require reevaluation and enhancement in order to improve deteriorating water quality and water issues being faced around the globe. Nanotechnology including Carbon nanotubes (CNTs) are emerging technologies that offers operational and economically feasible solutions for treatment of drinking and wastewater. This brief review covers various CNT applications for drinking and wastewater treatment. CNT filters and POU based CNT water treatment can serve as high quality adsorbents for removal of biological as well as heavy metal contaminants commonly found in water treatment plants. On the other side promising applications of CNTs for waste water treatment include membrane processes, disinfection and microbial control, detection of water borne pathogens and monitoring and sensing of wastewater. CNTs are achieving tremendous attention worldwide in water/ waste water treatment and has potential for future implications.

Keywords: nanotechnology, nano-materials, CNTs, FWCNTs, SWCNTs, MWCNTs, water and wastewater treatment, water reuse, sorption, membrane processes, disinfection, DBPs, microbial control, sensors

1. Introduction

Water is known as the most important part of our lives and the basic component on earth and it is considered as the most significance resource for development. The consistent access towards pure and reasonably price water is the most reliable goal for civilization, but it remains a great task for 21st century worldwide. The recent water supply is facing both new and old various tasks. According to statistics of WHO of the year 2012, about 780 million of people are still facing water crises of getting pure source of water. It is vital to implement the procedure for water treatment in especially developing and third world countries as soon as possible where the infrastructure for water and waste water have not existed before. Various human activities are playing a great role in order to overcome the water crises by preventing the pure water sources from contamination in both developing and industrialized countries. According to the present studies, developing countries have shown increasing non-compliance with internal recommended standards developed for various harmful contaminants being discharged in water bodies [1].

The latest water treatment system is considered unsustainable due to reliance of supplies and releasing practices on transportation and central systems. The new advancement in nanotechnology is offering major opportunities for implementing water supply systems for the coming generation by providing efficient, modular and multifunctional system in order to provide great performance, reasonable water price and solutions for treating waste water without depending on mega infrastructures and centralized systems. Nanotechnology suggest low cost substituted technology for waste water treatment. Nanotechnology includes nano scale materials that have ability to function accurately, have great specific surface area, high power of reactivity and variety of size dependent properties makes them good for use in wastewater treatment and for water purification process as efficient absorbers, catalyst or sensors. Some of the applications of nanotechnology for promising waste water treatment techniques include photo-catalysis, nano-filtration, nano-sorbents, disinfection & microbial control, sensing and monitoring [2].

The latest studies show that many natural and engineered nanomaterials have physically powerful antimicrobial properties. In contrast to conventional disinfectants, these antimicrobial nanomaterials are powerful oxidants and they are moderately motionless in water. Moreover they are not probably predicted to make harmful disinfection by-products (DBPs). Implementation of correct method will result in the possibility to restore and improve the conventional processes for water treatment. The use of antimicrobial nanomaterial is too decentralized. However, at present, the application of CNTs in water treatment system is catching attention due to increasing water crisis issues and the deteriorating water quality which are mostly linked with aging distribution network, due to which the cost of energy for transporting water will continue to increase. There is an urgent need for more water supply sources and recycling of wastewater, especially in regions which are facing water deficiency and national safety problems [3].

Carbon Nanotubes CNTs

Various studies are being conducted on CNTs since their discovery in 1991. Keeping in view the current water crisis and its pollution problems around the world, the CNTs are the most inspiring technology that readily deals with various water properties including physical, chemical or electrical and structural. Nanotechnology CNTs are used in the water treatment application of many fields including sorbents, catalyst, filters and membranes [4].

The CNTs are the graphene sheets that are rolled within the tube and are mostly capped by half fullerene. They consist of singles walled nanotubes (SWNTs) or single piped with a diameter up to 5 nanometers or multi walled nanotubes

(MWNTs) with many nested tubes, varying in length of about 100 nm. CNTs' toxic studies show that both SWNT and MWNTs are associated with causing acute pulmonary toxicity and cytotoxicity to mammalian cells. Due to dispersion difficulties of CNTs in water, less studies have been done on effects of CNTs on microorganisms including bacteria and viruses. However, some studies have suggested the use of polymers and surfactants such as triton x and sodium dodecyl benezesulfate SDBS to decrease the difficulty of dispersion of CNTs in water medium. Few studies have recognized antimicrobial activity of SWNTs towards gram positive and gram negative bacterial strains [5]. The application of CNTs in water treatment has been proven to be effective in preventing biofouling formation and microbial attachment on the filters. In order to ensure the effectiveness of microbial activity of CNTs, there is a need for extensive consideration of bioavailability and configuration of nanotubes. At present, large scale application of CNTs for water treatment material is considered as a limiting factor. However studies have shown latest developments of CNTs at economic rates which shows potential for developing large scale CNT applications for drinking and waste water treatment.

Properties of CNTs

Size, shape, surface or molecular space are the most cited properties of carbonaceous materials for environmental applications. Unique properties of individual as well as bulk carbonaceous nanomaterial configurations including electrical conductivity and adsorption offer potential for expansion of their environmental applications. Detailed characterization of properties, methods of synthesis and methods for purification of carbon nanotubes (CNTs) can help in technical and environmental advancements. Solvent chemistry and bundling state of CNTs greatly influence physical properties of carbonaceous nanomaterials that include shape, surface area and size. In addition to this, mechanical strength, physicochemical, thermal and electrical properties as well as bundling behavior of CNTs are greatly influenced by the nature of impurities such as heavy metals and biomolecules of vapors. Although most of the studies have addressed physical properties of CNTs, less literature is available on the characterization of inconsistent physicochemical properties of CNTs that are associated with the secondary structure of bundles or aggregates of carbonaceous nanomaterials [6].

This review paper covers modern developments and the application of carbon based nano technology in water and wastewater treatment. This paper also underlining the possible usage of CNTs or CNTs based membrane to report numerous encounters confronted by the present water/wastewater treatment technologies.

2. Application of CNTs in drinking water purification

Disinfection and purification of water is of significant importance to ensure clean and safe drinking water supply for everyone. The present methods used for disinfection are effective. However, these methods including chlorination are associated with formation of disinfection by-products (DBPs) that have been shown as harmful as well as some as carcinogenic in nature by studies done in the last decade that have reported over 600 DBPs in the literature [7]. Therefore, in order to ensure effective disinfection techniques and to avoid the formation of harmful DBPs, the existing and conventional water purification and disinfection methods need to be reconsidered and new techniques should be evaluated.

2.1 Drinking Water Contaminants

The major type of contaminants found in drinking water both in probability of occurrence as well as quantity in the water treatment plant consist of biological contaminants that are further classified into three types; cyanobacterial toxins, Natural Organic Matter (NOM) and microorganisms including fungi, viruses, bacteria and protozoa. The presence Natural Organic Matter (NOM) is associated with increased microbial growth as they provide carbon source. Biological toxins that mainly include cyanobacterial toxins are produced as a result of lyses of cyanobacterial cells present in the water treatment process. These toxins are not entirely removed from water due to lower efficiencies of conventional technologies for water treatment. Harmful algal bloom (HAB) is a toxic species of cyanobacteria that is responsible for producing toxins. Cyanobacterial cells form a layer of scum on the surface of water due to their buoyancy and in this way, they are easily transported to treatment plants where they undergo lyses to form toxins including commonly produced toxin named microcysteine toxins (MC) that are mainly responsible for causing taste and odor issues. These species commonly present in non-turbulent rivers and lakes and are found in all around the world with exception of Antarctica. Microorganisms mainly found in the water treatment plant include taste and odor causing bacteria, pathogenic bacteria originating from discharge of untreated sewage into the influent water, nuisance bacteria consisting of sulfur and iron reducing bacteria, microorganisms that are native to the habitat or environment [8]. Potential contaminants that consist of biothreat microorganisms that are used for bioterrorism purpose can also occur among other microorganisms in treatment systems [9]. In addition to biological contaminants, many studies have shown effectiveness of CNTs in removal of heavy metal ions including that of nickel, lead, silver and cadmium from drinking water by using multi-walled carbon nanotubes.

In contrast to conventional technologies for water purification, carbon nanotubes (CNTs) provide better media for adsorption and removal of a range of biological contaminants and heavy metals. This is due to the unique functional, physical and structural properties of CNTs.

2.2 Use of CNTs as Absorbent Media for Removal of Drinking Water Contaminants

CNTs have shown improved and higher efficiencies for adsorption of bacteria and other microorganisms than other adsorbents such as granulated activated carbon (GAC) and powdered activated carbon (PAC) commonly used in the water treatment processes that have large surface areas but the surface area of the micropores is not accessible by them that in turn contributes to lower adsorption capacities. In addition to this, studies have shown that the fibrous structure of CNT filters result in simultaneous capture and deactivation and removal of pathogenic microorganisms as compared to carbon based filters that only capture but do not deactivate the pathogens [10].

Adsorption of microorganisms on CNTs

CNTs offer higher efficiency adsorption of various microorganism as compared to other adsorbents. Many studies have shown that single-walled nanotubes (SWNTs) show higher adsorption capacities for many bacteria than other available adsorbents mainly due to the fibrous structure and external surface accessibility. A study showed that adsorption of a bacterial strain, Bacillus subtilis in SWNT is up to 37 times greater than in other adsorbents such as Nanocream and activated carbon. Another distinguishing feature of CNTs is that these adsorbents offer selective adsorption of bacterial species. Studies have shown selective adsorption and concentration of one bacterial species over another [11]. In addition to this, CNTs show instantaneous adsorption kinetics of bacteria which can extend their use as sensors of pathogens for rapid concentration of desired pathogenic strain. A study showed that SWNT adsorbed approximately 95% of the bacteria present in a solution within half an hour. In this way, CNTs can be used in point of use (POU) water treatment systems for adsorption of a variety of microorganism [12].

Adsorption of natural organic matter (NOM)

Carbon adsorbents provide efficient removal of a variety of NOM from raw water. At present, powdered activated carbon, granulated activated carbon and biological activated carbon are commonly used carbon-based adsorbents for adsorption of NOM in water treatment processes. Factors such as chemical composition and size of NOM found in water, physical characteristics of carbon surface, use of mesopores or microporeses in the carbon surface, type of functional group present on the surface affect the sorption efficiency of NOM [13, 14]. In most cases the size of the mesopores is 1 nm whereas the NOM have size in the range of 0.5-5nm which leads to lowered efficiencies of sorption on carbon based surfaces. In addition to this, different sections of NOM interact differently with the surface of adsorbents which also effects the sorption capacity for NOM. Adsorption of NOM on CNTs is superior to adsorption of NOM on microporous adsorbents due to factors such as comparable less surface charge of CNT adsorbents and large mesoporous volumes of aggregated pores [15]. CNTs not only offer high sorption capacity of NOM but also offers effective removal of microorganisms due to the colloidal stability of CNTs which is enhanced by the presence of NOM in water. Studies have also shown faster and higher desorption of NOM than in granulated activated carbon mainly because dissolved organic carbon (DOC) is caught in the aggregated pores whereas in case of GAC, DOC is trapped in the interior region which results in slower and less efficient desorption [16]. In addition to this, CNTs in contrast to microporous adsorbents, offer efficient and unaffected removal of NOM in the presence of other competitive adsorbates including micropollutants due to the large surface area that can remove a variety of contaminants adsorbents.

Adsorption of cyanobacterial toxins

Conventional processes of water purification such as coagulation and flocculation offer inefficient removal of cyanobacterial toxins including MC's that commonly occur in raw waters [17]. Due to the sensitivity towards the changes of temperature and pH conditions, the use of strong oxidizers (ozone, chlorine, hydrogen peroxide and potassium permanganate) also proved to be ineffective for the deactivation of MC toxins. Activated carbon is shown as effective adsorbent media for the removal of cyanobacterial toxins as compared to clay adsorbents [18]. Granular based activated carbon shows the highest adsorption efficiency as compared to coconut based powdered and wood based activated carbon adsorbents. However, CNTs prove to be even better adsorbents as compared to activated carbon and shows four times higher adsorption efficiency than clay minerals. A study was conducted to test the adsorption efficiency of CNTs for the deactivation and removal of two types of cyanobacterial toxins including MC-RR and MC-LR. Many studies have found various factors that are associated with higher adsorption capacities of CNTs for the removal of MC's. These include symmetrical structure and external diameter of CNTs, large volume of mesopores [19], increased surface area of adsorbent [20], surface defects on CNTs. On the other hand, the studies done in the past show that the cytotoxic property of CNTs prevents bioremediation cyanobacterial toxins. However recent studies show that bio-compatible CNTs allow bacterial growth on these CNTs that leads to efficient bioremediation of MC's. A study showed that growth of a plant based bacteria named Ralstonia solanacearum on bio-compatible which was also non-toxic resulted in considererable removal of MC's from water. The efficiency of this simultaneous existence of selected pathogen and CNTs higher than the removal efficiencies achieved by the CNTs and this plant based pathogen separately [21].

Adsorption of heavy metals

Many studies have shown that pH level plays an important role in removing heavy metals through CNTs [22]. A study indicated that efficiency of removal of lead from water can be increased by optimizing the pH level. It was also seen that maintaining the pH higher than 4 can result in efficient removal of chromium. This study concluded that CNTs can serve as effective adsorbents for removal of heavy metals increases by increasing the pH that results in decrease in the protonation of the surface that in turn increases the adsorption capacity of CNTs [23].

2.3 Practical Considerations for the use of CNTs and POU Filters

According to many studies, the application of CNTs and point of use (POU) filters cannot be applied on large scale mainly due to economic non-feasibility. However, many present studies showed that CNTs can be used on a large-scale purpose for the purification of drinking water [24]. A study showed that large scale CNTs can be constructed at an economically feasible rate at lab scale by using a well-established technique that involves use of chemical catalytic vapour depositor (CCVD) for the decomposition of hydrocarbons [25]. Another study suggested that point of use (POU) water treatment system can be combined with CNT based membranes and filters to construct a large-scale drinking water purification system [26]. Many studies confirm the operational feasibility of CNTs. CNT filters can be cleaned more easily than granulated activated carbon filters due to prevention of biofilm formation of the surface of the films owing to the cytotoxic characteristics of the CNT filters. CNT filters also offer high rate of water permeability than polycarbonate membranes [27]. CNT filters also offer high level of virus and bacterial removal. A study showed that CNT filters succeeded in subsequent adsorption and deactivation of bacterial concentration up to 106 CFU /ml. Spray pyrolysis method can be used to prepare CNT filters that have been prove for effective removal of MS2 viral strain [28]. In addition to high adsorption performance and operational feasibility, CNT filters have proven usability which is mainly due to the mechanical properties and their ability to carry out thermal regeneration techniques which are absent in most of the available water purification filters.

3. Application of CNTs for Waste Water Treatment

Wastewater produced from two major sources one is residential source other is non-residential source. The water that is mostly diluted and produced from public dwellings is termed as sewage. Residential waste water is also known as sewage. Sewage comprises of 99.8% of water and 0.11% of suspended solids, inorganic solids, metals, decomposable organic compounds, and pathogenic micro-organisms. Nutrients like nitrogen & phosphorous also present in sewage which are contaminants and should be removed in order to avoid toxicity. The water that is produced from agriculture fields, industries and commercial actions is termed as Non-residential wastewater. Rain water obtained from streets is comprises of both organic & inorganic contaminants is also a form of non-residential waste water. Present technologies of waste water requires large areas for installing plant, high operating cost, high maintenance cost & high energy demand. Nanotechnology suggest low cost substituted technology for waste water treatment. Carbon-based nanotechnology involves carbon-based nanomaterials like carbon nanotubes for the treatment of wastewater contaminants. Other various nanomaterials like metal oxides, metal nanoparticles, and zeolite are also used in these techniques [30, 33].

3.1 CNT based membranes and membrane processes

Nano-filtration (NF) is defined as a membrane separation technique that require low energy consumption. As nanofiltration technique involves unique filtration process and due to the presence of different kinds of membranes, so this technique is more appropriate to filter out all organic & inorganic pollutants from waste water. Type of membrane material decide the working of nanofiltration membrane systems. Efficient membrane permeability, mechanical & thermal strength, fouling resistance, and pollutant decomposition can be obtained by incorporating nanmaterials into membranes**.** Because of easy preparation, high powered strength and best rejection ability carbon base nanomaterials are mostly used for membrane production. CNT membrane comprises of open end single empty structure which is settled upright with resistant filter media. These CNT membranes are considered as a model water distillation tool. One of the CNT based membrane advantage is these membranes are tough like ceramic membrane & elastic or soft like polymeric membranes. The second major advantage is CNT membrane allow fast infiltration of water. Graphenes membrane produced more accurate results then CNTs membranes. Graphenes membrane shows same chemical & thermal strength with best elasticity. These membrane show high rejection of organic dye in water. As compared to other membranes CNTs membrane show high innovative performances and in coming future has the ability to be feasible commercially. The marketable accessibility of the CNT membranes must follow definite criterions such as desalination ability, toughness, water penetrability, solute discrimination, antifouling, energy funds, material costs, and compatibility with industrialized sites. By adding nanomaterials in to active layer of TFN composite membrane through doping in casting solution better performance of membrane is achieved. TFN membrane show better anti-bacterial characteristics. TFN membrane kills 61% bacteria in almost one hour interaction time. These membrane minimize membrane bio-fouling. Unaligned CNTs because of their anti-microbial activities covalently bonded single walled nanotubes to a TFC membrane surface for reducing microbes [30-32].

3.2 CNTs for Disinfection & Microbial Control

Now a days, for water industry, development of harmful (DBPs) & their current disinfection shows a great challenge. DBPs are formed by conservative disinfectants which includes ozone & chlorine disinfectants. Nano-materials have low ability to form DBPs and without strong oxidation show anti-microbial properties. Such nano-materials includes nano-ZnO, nano-Ag, nano-TiO2 and CNTs. By disrupting particular microbial process, and by causing physical discomposure of cell membrane, CNTs remove bacteria. Graphene which is another carbon based membrane also show anti-microbial properties with same process. Physiochemical properties determine cytotoxicity of CNTs. CNTs consisting of small diameter are more harmful. Membrane bio-fouling can also be reduced by antimicrobial nanomaterials (nanoAg and CNTs). Through direct contact CNTs deactivate bacteria. By using polyvinyl-N-carbazole-SWNT, almost 91% bacterial inactivation has been attained. No replacement is required as CNTs are not absorbed as well as are not soluble in water. Long time filtration experiments are required to define the effect of fouling on the antimicrobial activity of CNTs, as direct contact is required for inactivation [29, 33, 35].

3.3 CNTs for sensing and monitoring of wastewater

Due to the tremendously low quantity of some pollutants present in water, the high difficulty of the wastewater mediums and the deficiency of pathogen detection water quality is an important challenge for water industry now a days. Advanced sensors that consist of high discrimination & sensitivity, with fast reaction are required for sensing contaminants detection in waste water [34, 36].

3.4 CNTs for detection of pathogens in wastewater

In waste water presence of pathogen detection is of great importance as these pathogens are directly related to public health and environment. Regular indicator like Coliform bacteria are regular indicators and are fail to sense the presence of pathogens in water. For pathogen detection mostly used nanomaterials are Quantum dots (QDs), magnetic nanoparticles, noble metals, and CNTs. For sample concentration & purification, magnetic nanoparticles and CNTs are used on large scale. CNTs considered as best electrode material due to its high conductivity. Subsequently, by enhancing electron transfer & electrode analysis contact, CNTs can enable electrochemical detection. Detection sensitivity can also be enhanced through the adsorption ability of CNTs. Heterogeneity of CNTs is a great challenge for CNT based sensors. For environmental analysis of trace metal, CNTs have huge capability as CNTs have best recovery rate, great adsorption ability and rapid kinetics [36, 37].

4. Current hurdles and future challenges

Following are the five present hurdles which are as follows:

- First complication is the difficult process which involves the breakdown of CNTs with even pore size and distribution. Present CVD process failed to breakdown such controlled-pores with even distribution. Bottom up approach which is expensive & time consuming could be used for breakdown of these controlled-pores [31].
- Second hurdle involves minimization of diameter of CNT membrane & pore size. Good desalination properties can be obtained only with single walled carbon nano tubes (SWCNTs). Large pore diameter nano tubes have minimum ion rejection efficiencies as compared to small pore diameter nano tubes which have high ion rejection efficiencies [31, 35].
- Third complication may be growth of CNT with appropriate alignment. Toxic effects on water path & salt rejection was seen due to the abnormalities in membrane shape [31].
- Fourth complication involves at CNT tips addition of suitable useful groups. In order to allow efficient water flow closed tip ends of CNTs must be opened by suitable wet chemical treatments. Adding new functions or properties which is termed as functionalization is considered as a limiting step. This should be handle properly to adjust CNT membrane penetrability to solutes & water molecules [31].
- Fifth complication is cost that is a major limiting factor as single walled carbon nano tubes (SWCNTs) are not cost effective. With sub-nanometer pore diameter, MWCNTs cannot be used to breakdown CNT membranes. As compared to SWCNTs and MWCNTs Few walled carbon nano tubes for 1 nm pore diameter membrane are proved very cost effective [31, 35].

5. Conclusion

Carbon based nanotechnology for water/wastewater treatment is gaining tremendous attention worldwide. The innovative properties of carbon based nano tubes membranes have notable endeavors regarding purification capacity, water penetrability, energy funds, solute discernment, toughness & anti-fouling. From the point of generation (POG) to the point of use (POU) treatments, CNT-membranes could be used at all stages. These CNTs have opened a new road to create initial point separation of contaminants in water/waste water purification technology. Therefore, it is proved that CNT membrane is best option for contaminants removal that are present in water/waste water and is a cost effective technology as well and because of the high capability to give filtered water instantaneously, CNTs is considered as a future generation water filter.

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