



A Review of the Performance of Carbon Nanotubes in Reducing Environmental Pollution

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ABSTRACT

Introduction: In recent times, one of the most important purposes of sustainable development has been defined as the protection of environmental health. Using appropriate and innovative infrastructures such as nanotechnology is a solution to walk along the path of sustainable development and solves many environmental problems. The purpose of this study is to review the application of carbon nanotubes in the removal of environmental pollutants, based on conducted studies.

Materials and Methods: All scientific data related to the issue were collected from scientific databases of Google Scholar, Scopus, Elsevier, and SID to evaluate and conduct the study. Keywords such as carbon nanotubes, environmental pollutant, sustainable development, and environmental health were used. 85 articles were also used in this review research (1993–2016).

Results: Based on the evaluated studies, the results indicated that common methods of sewage treatment are not enough to remove the mentioned environmental pollutants completely. In the mentioned methods, despite high decomposition, the amount of mineralization has been reduced and the toxicity of wastewaters has remained unchanged or has increased. Adsorption has been propounded due to its simplicity and lower energy consumption compared with other methods. Carbon nanotubes (CNTs) are unique one-dimensional macromolecules which have high thermal resistance and chemical stability. Adsorption through CNT as the adsorbent in the treatment of drinking water and sewage polluted with pharmaceutical, petroleum, heavy metal, and leachate pollutants has been studied widely.

Conclusion: This study indicated CNT as effective adsorbents that have high potential to protect the environment and promote sustainable development.

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Introduction

Developments in science and engineering at the nano scale have shown that many of today's problems related to environmental pollutants can be solved or improved greatly through nano

adsorbents, nano catalysts, bioactive nanoparticles, nanostructured catalytic membranes, and nanoparticles improving filtration, among other products and processes derived from nanotechnology. Using new technologies to

remove environmental pollutants is one of the important purposes of sustainable development. For example, innovation in developing the new technologies to desalinate water has been hopeful. Nanotechnology has also been able to reduce the concentration of toxic compounds below specified ppb levels in order to achieve higher standards in health and quality of water. Some new developments have been conducted in the processes and materials at the nano scale to treat surface water, groundwater, and industrial wastewater polluted by toxic metal ions, radionuclides, organic and inorganic minerals, bacteria, and viruses. Innovative use of nanoparticles in order to treat industrial wastewaters is one of the potentially useful and beneficial applications. Many factors are involved in the production of high amounts of wastewater. Removal of pollutants and recycling of treated water lead to considerable reduction in costs, time, and labor in industry that result in improvements in environment protection¹.

Carbon nanotubes (CNTs), as new members of the carbon family, have been one of the important parts in nanotechnology in recent years. These nanotubes were first discovered by Iijima in 1991². Later they were considered for research because of their physicochemical characteristics. CNTs have high thermal resistance and chemical stability³. They have a needle-shaped structure, created as single lamella tubes because of locating graphite; in this mode they make single-walled CNTs and if a large number of single tubes with various diameters around an axis are formed, they make multi-walled CNTs. The size range of single-walled CNTs is 0.4–3 nm and that of multi-walled CNTs is 1.4–100 nm⁴. Because of placing them as graphite lamellae, high absorption power is one of the factors of their application in environmental activities⁴. These nano substances have a lot of layers of carbon atoms due to their fullerene structure (ball-like). Their surfaces have a strong tendency to react with other molecules and atoms⁵. Adsorption in CNTs occurs on four sites. These are:

1. Adsorption in internal part of cavities of nanotubes in cases when their ends are open.
2. Adsorption by surfaces between pores created within a network, which is made between nanotubes.
3. Adsorption by external surfaces of nanotubes.
4. Adsorption on branches existing in the border of tubes⁶.

CNTs due to their large special surface, surface functional group, and hydrophobicity⁷, are used as a kind of adsorbent to remove organic pollutants such as dioxins and volatile organic compounds from the gas phase of aqueous solutions⁸. The adsorption method through CNTs as adsorbent in order to remove organic (phenol) pollutants in low concentrations by creating strong connection between organic molecules and CNT, has been studied⁹. Recent studies have indicated that CNTs have high adsorption capacity for organic and nonorganic pollutants¹⁰. Many industries such as pharmaceuticals, textile, paper, plastic, etc. consume considerable amounts of water. The purpose of this study has been a review of CNTs in the removal of environmental pollutants such as pharmaceutical, dye, petroleum, and heavy metal pollutants based on conducted studies.

Materials and Methods

This review research has been written on the basis of the evaluation of several studies that have focused on using CNTs in the removal of various environmental pollutants. All scientific data related to the issue were collected from scientific databases of Google Scholar, Scopus, Elsevier, Web of Science, and SID, while 85 articles have been used in this research (1993–2016).

Results

Application of Carbon Nanotubes in Removal of Pharmaceutical Pollutants

Documents of recent researches have shown that both production and treatment of pharmaceutical compounds are different in various countries. The increase of population age and improvements in the quality of life across the world will also lead to increases in the consumption of pharmaceuticals in future years¹¹.

During the 1990s, various drugs such as lipid regulators, analgesics, antibiotics, disinfectants, hormones, chemotherapy drugs, and beta-blocker drugs have been identified in wastewaters, rivers, and groundwater resources in European countries¹². Drugs are very important for life and are used to treat diseases in humans and animals. The existence of this group of pollutants in the environment is one of the basic problems in the world today. Recently, some developed countries such as the United States of America, England, Germany, and Italy evaluated the effects and dangers caused by these pollutants in the environment.

In recent years, several studies have been conducted about the effect of these drugs, which have entered the environment widely and with thousand points of release and about their impact on living beings and the environment¹³. Very high solubility of drugs in water has led to their adsorption in target cells in humans, animals, and plants. Drugs are very resistant to biodegradability and that has led to their non-degradability under normal conditions. As a result, they need specific reactions under certain conditions for degradation¹⁴. In the 1990s, some wide scientific researches were conducted on the presence of drugs in local rivers and sewage treatment systems. In some of them more than 60 pharmaceutical compositions have been reported till 2002. Furthermore, several researches were conducted about some specific drugs as pharmaceutical pollutants in various countries and they confirmed the results of each other¹⁴. The entrance of these pollutants into the food cycle and drug resistances have been the main reasons for evaluating and controlling this pollutant in the environment, which has a lot of effects environmentally and medically. One of their potential effects is the presence of antibiotics in water resources and urban sewage, which causes microbial resistance and increase of drug resistance in humans and in the population of pathogenic microbes in the environment (water, soil, and air)¹⁵. A significant correlation has been reported between pharmaceutical pollutants and microbial resistance by Goldman in 1996¹⁶.

According to reports, each year thousands of tons of active pharmaceutical ingredients enter the environment; all unconsumed drugs and more than 90 percent of drugs that are consumed are discharged in the environment unchanged, and they are converted to active ingredients again during metabolism processes, which are conducted by microorganisms, especially bacteria¹⁷. As a result, urban sewage is polluted by pharmaceutical pollutants that change with differences in time, location, and type of pharmaceutical pollutants. Outbreak of certain diseases, climate, and topography of a region lead to the entrance of drugs in water resources which directly (drinking water) or indirectly (plants and animal products) enter the food cycle. Besides, pharmaceutical industrial activities generate considerable amounts of these compounds in the environment, while water, soil, air, wind direction, topography, and precipitation perform basic roles in the distribution of pharmaceutical pollutants¹⁸. Studies conducted in European countries have confirmed this issue, and even their high standards of conventional water treatment have not able to remove pharmaceutical pollutants^{19, 20}. Castiglione reported that pharmaceutical pollutants in the scale of gram per liter or milligram per liter are observable in most of the surface waters (river, lake, and sea). Eating, drinking, breathing, and skin absorption are some of the ways that pharmaceutical pollutants enter the body. Drinking water is one of the most important direct ways for pollutants to enter the human body¹⁴. Another important effect of drugs on the environment is the impact on wildlife and lives of living beings and birds. Real examples of this impact are the cases of ethinyl estradiol compound, a derivative of estrogen that led to sexual changes in male fishes; and the death of many vultures in Asia who fed on carcasses of cats that had received diclofenac as an anti-inflammatory drug¹⁵. Therefore, efforts in the way of an efficient and logical pharmaceutical system is considered an important goal for all healthcare centers in the world, and improving

methods of drug consumption and trying to make society safe with rational, and quality consumption of drugs are considered the basis of the measures and recommendations of the World Health Organization (WHO)²¹.

Unsuitable technology of urban wastewater treatment systems to remove this group of pollutants has not been effective mostly²². Traditional methods such as activated sludge are not enough to remove pharmaceuticals and other sewage compounds completely. As a result, advanced oxidation²³, membrane filtration²⁴, reverse osmosis²⁵, and activated carbon^{26, 27} have been used as complementary treatment methods²⁸. Adsorption is a very effective method to remove pollutants from water and wastewater even in low concentrations (lower than one milligram per liter), besides being cheap and executable compared with other simple methods²⁹. In 2015, Hu et al. used CNTs in order to remove diclofenac and achieved a removal efficiency equal to 93 percent³⁰. In another study in 2015, antiviral pharmaceutical removal with an efficiency higher than 90 percent by nanotubes was conducted³¹. Efficiency of these nanoparticles in the removal of triamine with efficiency between 80 percent and 95 percent was evaluated in 2016³². Some studies were conducted by Samadi et al. which indicate high efficiency of nanotubes in removal of amoxicillin³³. The removal of atenolol with efficiency equal to 94.8 percent was reported in 2016 which demonstrated the high efficiency of this nanoparticle³⁴.

The Application of Carbon Nanotubes in Treatment of Leachate

After precipitation and entrance of waters in landfill sites, various organic compounds and minerals are produced during biological, physical, and chemical processes which are considered the basis of producing leachate. The beginning of the leachate production process is after exploitation of landfill sites³⁵. The quality and quantity of leachate is affected by several factors such as disposal methods and the compaction degree of wastes, moisture, the amount of precipitation and evaporation,

vegetation of the area, topography of landfill site, and the quantity of waste materials³⁶. Leachate includes 200 types of organic compounds which have been placed in groups of cyclic hydrocarbons, aromatics, alcohols and ethers, ketones, acids, esters, nitrogen, phosphorus, sulfur, and other compounds, toluene, ethyl benzene, naphthalene, 3-phenyl ester, dichlorobenzene, etc. that can be mentioned as examples of its basic pollutants³⁷. Therefore, due to the mentioned cases, leachate is considered as a dangerous pollutant for the environment. Its entrance into the soil and then into ground water is very dangerous especially because of hydrocarbon compounds and heavy metals, and the improper exit of these from landfill sites and entry into surface waters cause various diseases in humans³⁸. Treatment onsite by recycling and physicochemical treatment and biological treatment in refinery can be mentioned as examples of conventional and usual methods of managing leachate. Based on the studies, due to presence of very dangerous toxic materials, the conventional treatment is not enough and using supplementary treatment methods have been suggested³⁹.

Nanoparticles are useful to treat this type of pollutants due to their small size, high cross-section and reactivity. CNTs are durable and have high thermal stability against mechanical forces; it is also easy to clean and reuse them. Membranes of the nanotubes have more current than the other porosities due to the smooth inner surfaces and these membranes can remove carious bacterial, viral, and organic pollutants, and opacity¹. Due to the growth of population and industry in the country, daily quantities of leachate being produced and discharged into the environment are increasing, which will lead to health and environmental hazards; so management and required measures to control the leachate are necessary. In 2012, Kashi Tarashi et al. used CNTs as a new study in order to remove trash leachate and obtained efficiency equal to 58.23 percent.

Application of Carbon Nanotubes in removal of Petroleum Compounds

Nowadays petroleum and its products are considered as the sources of numerous environmental pollutants. Benzene, toluene, ethyl benzene and the three isomers of ortho-, para-, and meta-xylene are generally known as benzene, toluene, ethyl benzene, and xylene (BTEX)⁴⁰. BTEX are volatile, organic, single loop, nonionic, and nonpolar compounds which exist in petroleum products. Due to relative high solubility of BTEX compounds in water these aromatic organic compounds have been used as solvents in the production of paints, thinners, adhesives, inks, and many pharmaceutical products. BTEX are pollutants that cause major concern because of their toxicity and the various methods of producing them in the environment⁴¹. Important pollution sources of waters with mono-aromatic compounds have been mentioned as storage tanks (which are distributors of petroleum products) such as stations of gas sites, airports, pipelines, paint industries, leachate of landfills, partial oxidation of fossil fuels, and chemical industries (pesticides, plastics, synthetic fibers) due to leak, improper disposal of industrial waste, and accidents during transportation in petroleum industry (petroleum refinery and petrochemical company). These compounds, especially toluene, are produced naturally by anaerobic bacterial species in anaerobic sediments of lakes due to degradation of aromatic compounds such as phenylalanine.

The United States Environmental Protection Agency (USEPA) has classified BTEX as prioritized pollutants and is trying to assert the importance of their treatment in order to protect people's health⁴². BTEX are the most common pollutants which have polluted groundwater through leaks or accidents related to petroleum materials (especially gasoline). Mono-aromatic compounds have higher solubility compared with other hydrocarbons existing in gasoline such as aliphatic hydrocarbons so that when gasoline is mixed with water approximately 50–60 percent BTEX of gasoline enters the waters⁴³. The volume

percentage of benzene, toluene, ethyl benzene, and mixture of xylenes in gasoline have also been reported as 1, 1.5, lower than 1–1.5, and 8–10 percent, respectively therefore, the presence of a low quantity of aromatic hydrocarbons in water is an indication of the presence of petroleum products. The ethanol existing in gasoline and petroleum products also increases the solubility of BTEX and simplifies its progress in water resources. BTEX form approximately 18 percent of the weight of gasoline. These compounds have high tendency to accumulate in groundwater. But in addition to groundwater they have been responsible for air and soil pollution⁴⁴. These aromatic compounds are considered as serious problems for humans due to toxicity and carcinogenicity⁴⁵. The USEPA has determined the safe levels of the pollutants in drinking water at benzene 0.005 mg/l, toluene 1 mg/l, ethyl benzene 0.7 mg/l, and isomers of xylene 10 mg/l. These compounds also cause many environmental problems, of which the most important include effect on global warming, ozone depletion in the stratosphere, production of ozone caused by chemical reactions, and creation of unpleasant odors in the environment in terms of air pollution.

Based on guidelines of WHO, the maximum allowable amounts of benzene, toluene, ethyl benzene, and xylene have been suggested as 0.01 mg/l, 0.7 mg/l, 0.3 mg/l and 0.5 mg/l respectively in drinking water⁴⁶. These organic materials are flammable, toxic, carcinogenic, and mutagenic. The presence of these compounds in water is very worrisome even in low concentrations. Therefore, the removal of these compounds from water to ensure its health is a necessary matter.

Benzene with molecular formula of C_6H_6 and molecular weight of 78.11 has been identified as one of the pollutants of air, surface waters, and groundwater⁴⁷, which is used as a starting material in the production of compounds such as styrene, phenol, cyclohexane, aniline, and alkyl benzene used in making plastics, resins, and detergents⁴⁸. Exposure to high amounts of benzene over a short time or small amounts over a long period of time can lead to leukemia⁴⁹. This substance enters

the body through breathing or skin absorption and causes damage to organs such as liver, kidney, lung, heart, brain, etc. Epidemiological studies have also confirmed the dangers of benzene for humans. So the International Agency for Research on Cancer (IARC) has classified benzene as carcinogenic for humans (group 1)⁴⁷.

Toluene has an extraordinary significance as an intermediate and solvent chemical in various industries. This substance with chemical formula of C_7H_8 or $C_6H_5-CH_3$ and with synonyms of phenyl methyl and methane benzene is a colorless and transparent liquid and it is in the group of aromatic hydrocarbons under the head of benzene. One of important pathogenic effects of toluene is the effect on the central nervous system which is in the form of numbness, irritation at feeling happy, and, associated with that, imbalance, tremor, buzzing in the ears, blurred vision, delirium, lack of power in controlling voluntary muscles and seizures, and eventually coma⁵⁰.

Ethyl benzene (C_8H_{12}) is a colorless liquid, flammable, and smelling like gas oil, which is found in natural products like coal and gasoline. This substance exists in manmade products like insecticides and paints. Chronic exposure to ethyl benzene has destructive effects on the respiratory system and the kidneys. The IARC Chas classified benzene in group 2B⁵¹.

Xylene is a transparent, colorless, flammable and hydrophobic liquid which has a pungent and burning smell that is widely used as solvent in paint, rubber, leather, typing and proliferation industries, making insecticides, and coating industries⁵².

Those methods which are usually used in order to remove these pollutants include biological treatment, membrane filters, or adsorption with activated carbon or synthetic zeolite. The adsorption method is widely used due to its simplicity, effectiveness, and easy use. Among the adsorbents used, activated carbon has been used more than others to remove organic compounds due to its high adsorption capacity.

High adsorption capacity of organic pollutants by CNTs is mainly due to its porous structure and a wide variety of surface functional groups. To treat such wastewaters, a treatment system is required, which can remove BTEX compounds and should have economic justification, too. Most of the treatment methods such as chemical oxidation, biological treatment, aeration, and adsorption are successfully used to remove BTEX from water and wastewater⁵³. Adsorption is one of the best treatment methods for there moval of these pollutants from the liquid environment due to its capability of revival of both adsorbent and adsorbate⁵⁴. It is also a process which can be used both in polluted environment and outdoor relatively simply.

Using nano substances to remove pollutants from the environment is a new method which has been considered a lot in recent years due to the special properties of the compounds. Most of the atoms placed on surfaces of these nanoparticles have not been saturated so they can bond with other atoms simply. Also, these nano substances have very high adsorption capacity. Having the two important properties has led to their easy exploitation, which has increased operation of the pollutant adsorption and velocity of their removal. Therefore, the application of these nano substances as adsorbent in controlling environmental pollutions has grown dramatically in recent years. One of the important parts of nanotechnology which has been considered by researchers in recent decades is CNTs⁷. In a research which was conducted by Pourzamani et al. in order to remove benzene by the nanotubes, efficiency obtained was at 33.3 percent⁴⁷. In Taiwan, modified CNTs were used to remove benzene, toluene, ethyl benzene, xylene, and BTEX and the respective efficiencies of removal were equal to 91.44 percent, 97.8 percent, 98.2 percent, 98.9 percent, and 98.7 percent³. These nano substances were also used in order to remove phenol⁵⁵, bisphenol A^{56,57}, trichlorethylene⁵⁸ and other organic materials with high efficiency.

Application of Carbon Nanotubes in Removal of Heavy Metals

Heavy metals such as iron, zinc, copper, and iodine are essential for human health and have a basic role in the metabolic processes, but some others such as cadmium, chromium, lead, arsenic, etc. are toxic and dangerous and do not have an effective role in the physiology of the body⁵⁹. Their increasing use during the past years and their entrance into surface waters and groundwater have caused some dangers for the environment and the health of living creatures⁶⁰. One of the important features of heavy metals is that they are not disposed from the body and accumulate in fat tissue, muscles, and bones that can cause neurological disorders and cancer. For example, one of the most important heavy metals is hexavalent chromium which enters through wastewaters of plating, tanning, or dyeing activities. Trivalent chromium is necessary for metabolic processes while hexavalent chromium is toxic and dangerous and causes lung cancer, destruction of kidney tissue, and hole and wound in the nose^{62, 63}. Cadmium as another common heavy metal that leads to damage to the kidneys, respiratory system, disorders in the absorption of calcium, and rickets⁶⁴. Conventional methods to treat this type of pollutants are chemical precipitation, ion exchange, electrical precipitation, and biological and membrane processes, which include high energies and costs, according to studies. CNTs were used to remove heavy metals such as lead⁶⁵, cadmium, cobalt¹⁰, copper and zinc^{66, 67}, and arsenic⁵⁸; the efficiencies obtained were 85 percent for lead, 94.26 percent for cadmium, and higher than 50 percent for cobalt. Also, CNTs were very effective in the removal of copper and arsenic.

Application of Carbon Nanotubes in Dye Removal

Dye is the first recognized pollutant in wastewater and the existence of very low quantities of dye in water is observable and unfavorable. Many of these dyes include aromatic

rings which are carcinogenic and mutagenic. Therefore, dye removal is very important to restore the environment. The production of dye in the world has been estimated at approximately 700,000 to one million tons^{68, 69}. Various industries use dyes, such as in the production of cosmetics, leather, paper, and textiles. Dyes are classified into azo, anthraquinone, xanthine, acridine, etc. based on chemical structures⁷⁰ and practically they are divided into reactive, acidic, direct, curved, etc.⁷¹. Azo compounds are the most important dyes which are synthesis organic and reactive is from their group due to high solubility and low degradability. The complexity of structures and the hydrophilicity of reactive dyes lead to inefficiency of biological methods in the treatment process since they reduce the dye adsorption on biomass^{72, 73}. Reduction of water clarity and light transmission, reduction of dissolved oxygen, and increase of chemical oxygen, are some disadvantages of the existence of dyes in water, which are hazardous for aquatic life; besides, they are toxic, mutagenic, and allergenic. Coagulation and flocculation, advanced oxidation, and membrane processes are conventional processes of removal but the adsorption has a faster, more efficient and more economical performance. In this regard, attention has been drawn to nanoparticles due to their capability of revival and reduction of costs^{74, 75}. CNTs used in the removal of Methyl Orange and Methyl Blue, which was conducted by Jie et al., had high adsorption capacities respectively equal to 149 and 399 mg/gr⁷⁶. Many studies have been conducted on the removal of dyes by CNTs, especially on the wastewaters of the textile industry^{77, 78}.

Conclusion

The overall impressions from the findings of this research are that as the quantity of pollutants existing in the environment increases with the growth of population and development of industry, easy, fast, high efficiency, and economical methods should be used to manage pollutants. Based on the conducted researches, CNTs have high efficiency in the removal of

various pollutants and even their modified mode can be utilized as a new method. It is also possible to reuse them and they are considered eco-friendly materials.

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Conflict of interest

the authors have no conflict of interest to declare.

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