EXISTENCE OF CARBON NANOTUBES AS SORBENTS IN WATER TREATMENT AND ITS TOXIC EFFECTS.

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ABSTRACT

Water crisis is one of the greatest concern of our time. The absence of hygienic water is a developing issue far and wide. Water request is increasing quickly as an after effect of growing population and fast urbanization. As of late nanomaterials are utilized as adsorbents for expulsion of harmful and organic pollutants from contaminated water storages. Carbon nanotubes (CNTs) owing to their tunable physical, chemical, electrical and structural properties, motivate creative advances to address the water deficiency and water contamination issues. The mechanical adaptability and robustness, thermal stability and resistance to brutal environment endow CNTs with excellent application potential in water treatment. CNTs can possible used as efficient adsorbents for both organic and inorganic contaminants from water frameworks. However these nanosorbents have not being evaluated on the basis of toxicity. Therefore it is very essential to confirm the impact of nanosorbents on environment and human health before their large scale commercialization.

Keywords: Carbon nanotubes, Pollutants, Adsorbents, Nanosorbents, Toxicity.

Introduction

Rapid industrialization of human society has forced the release of different contaminants to various water systems like metal ions, organic bacteria, viruses and so on which are very harmful to human health. The growing population, exhausting water resources and changes in climate have made drinking water as ruthless resource in many parts of the world. Water resources are polluting due to inadequate sanitation, contamination by algae blooms, detergents, increased use of fertilizers and pesticides, chemicals, heavy metals and so forth. The customary materials and advancements like Oxidation, Activated Carbon Nano-filtration and reverse osmosis are not successful to treat muddled contaminations. Biological treatment is incapable to remove large number of contaminants. Pressure driven filtration processes like micro filtration, ultra-filtration, nanofilteration and reverse osmosis are some new highly effective processes to remove huge amounts of organic micro pollutants [1-2]. So the clarion call is to develop economical and durable materials and ways to provide pure water in sufficient amount. Nanotechnology has been considered effective in solving water problems related to quantity and quality [3]. Carbon nanotubes have astounding application potential in water treatment because of their mechanical adaptability and strength, thermal stability and imperviousness to brutal environment. CNTs can possibly serve as unrivaled adsorbents for expulsion of organic and inorganic contaminants from water frameworks.

Carbon nanotubes as sorbents for removal of Organic and Inorganic pollutants.

Adsorption one of the competent method for the removal of organic and inorganic compounds in drinking water treatment. Out of various adsorbents like activated carbons (ACs), zeolites, and resins, ACs are one of the most widely used type of adsorbents in water treatment, owing to their wide-ranging removal capability toward pollutants, chemical inactivity, and thermal stability. In any case, ACs in water treatment have moderate adsorption energy and trouble for recovery. To take care of these issues, activated carbon fibers (ACFs) were created as the second era of carbonaceous adsorbents. The pores in ACFs straightforwardly open on the surface of carbon framework, because of which the diffusion distance of pollutants to adsorption sites get abbreviates. As a result, ACFs usually possess higher adsorption rates than ACs.

Table-1 Selected CNTs for removal of organic pollutants

Adsorbents	Pollutant	Function	Ref
As-grown CNTs and graphitized CNTs	1,2-dichlorobenzene (DCB)	Rough surface of As-grown CNTs made adsorption of organics easier. Graphitized CNTs became smooth and the adsorption of organics decreased.	Peng,X.J, et al.[4]
HNO_3 and H_2SO_4 mixture purified CNTs	Phenolic Compounds	Four types of solute-sorbents interactions i.e. hydrophobic effect, electrostatic interaction, hydrogen bonding and π-π electron-donor-acceptor interaction act simultaneously	Bai,Y.C.et al.[5]
CNTs activated by KOH etching	sulfamethoxazole , tetracycline, tylosin	More interconnected pore structure and less pore deformation of activated CNTs enhanced their absorption capacity.	Ji,L.L.,et al [6]
As-prepared and oxidized MWCNTs	naphthylamine, 1-naphthol, phenol	Oxidation of MWCNTs increased the surface area and added oxygen-containing functional groups to the surfaces of MWCNTs,	Sheng,G.D.et al.[7]
CNTs	Microcystins (MC)	Molecular size of MCs perfectly fit in the pores of CNTs. As a result of which adsorption affinity of CNTs towards MC is much higher as compared to activated carbon.	Yan,H.,et al [8]

Table-2 Selected CNTs for removal of removal of inorganic pollutants

Adsorbents	Pollutant	Function	Ref
CNTs supported with Al_2O_3	Fluoride	Surface modification of CNTs with nanosized clusters of Al_2O_3 increased adsorption affinity towards fluoride.	Li,Y.H.,et al[9]
CNTs purified by HNO_3	Lead	CNTs refluxed with acid showed higher adsorption capacity(11.2mg/g) as compare to activated carbon (5.5mg/g) due to oxygen containing functional group at the surface.	Li,Y.H.,et al[10]
Ceria nanoparticles supported on CNTs	Arsenate	The As (V)-loaded adsorbent can be efficiently regenerated.	Peng,X.J.,et al [11]

Adsorption study on CNT started several years later than its first report in 1991 [12] and boomed in the past decade. In table 1 and table 2 broad spectrum of organic compounds and metals has been examined as the pollutant on CNTs with different physical structures and surface chemistry. There are various interactions taking place between adsorbent and adsorbate which include hydrophobic impact, π-π interaction, π-π electron-donor-acceptor (EDA) interaction, electrostatic interaction, and hydrogen bonding. Gotovac et al. reported that CNTs sow higher affinity to organic compounds (nonpolar) such as naphthalene [13] because of hydrophobic nature of their outer surface. Availability of abundant π electrons on CNT surfaces empower a strong π-π coupling of aromatic pollutants with the CNT surface. Chen et al. [14] examined the adsorption of a few polar and nonpolar contaminations onto CNTs and asserted that hydrophobic impact was not the dominant mechanism.

Nanoscale curvature and chirality of graphene layers of CNTs impact the adsorption of organic contaminations, particularly for those with π-π stacking as the interactive force. Gotovac and collaborators watched striking distinction between the adsorption limits of tetracene and phenanthrene on the tube surface of CNTs due to the nanoscale curvature effect [15]. Because of morphology distinction of CNTs may indicate contrast in their collection inclination, which may assist affect their adsorption capacity. The aggregation tendency decreases with increased number of walls or reduced Nano curvature. The aggregation tendency of CNTs follows an order: single-walled CNTs (SWCNTs) > double-walled CNTs (DWCNTs) > multi-walled CNTs (MWCNTs). Zhang et al. [16] created conditions to compute the adjustments in pore volume and particular surface region which is result of aggregation. They found that aggregation of CNTs was unfavorable for the adsorption of several synthetic organic compounds (SOCs) on CNTs.

Adsorption behavior of CNTs is greatly influenced by its Surface Chemistry. Acid oxidation or air oxidation of CNTs introduce various functional groups such as -OH, -C=O and -COOH on the surface of CNTs. This surface functionalization of CNTs make them more hydrophilic for adsorption of polar and low molecular weight pollutants for example phenol [5] and 1,2-dichlorobenzene [4]. Rao et al. reported that adsorption of overwhelming metals on CNTs depends mostly on the particular complexation between metal particles and the hydrophilic functional groups of CNTs [17]. Therefore the surface functionalization of CNTs is positive for the for the uptake of metal ions.

CNT adsorption mechanisms could be explained from two aspects: Thermodynamics and kinetics. Information regarding energy changes during CNTs adsorption is provided by various thermodynamic parameters like change in free energy of adsorption (ΔG), enthalpy change (ΔH), entropy change (ΔS) and activation energy (Ea) . Adsorption of Pb^{2+} [18], trihalomethanes [19], 1-naphthol and phenol [7], methyl orange [20] were demonstrated to be spontaneous processes based on the negative ΔG and the positive ΔS. Study of adsorption kinetics showed that CNTs have faster rate of diffusion of pollutants to adsorption sites and it is attributed to more ordered pore structure. Lu et al. [21] studied the rate of adsorption of trihalomethanes to CNTs and powdered activated carbon (PAC). He claimed that adsorption equilibrium is achieved faster by CNTs as compared to PACs. Zhang et al. [22] examined the adsorption kinetics of phenanthrene and biphenyl on granular activated carbon (GAC) and CNTs. He observed that CNTs are superior to ACs in terms of sorption kinetics.

Adsorption selectivity or resistance to harsh environment is another important evaluation criterion for an adsorbent. Zhang et al. [16] observed that solution pH and ionic strength show insignificant impacts on the adsorption of phenanthrene, biphenyl, and 2-phenylphenol in spite of their variant planarity, polarity, and hydrogen/electron-donor/acceptor ability. In light of more grounded substance nanotube collaborations, customized surface science, fast equilibrium rates, and high sorption limit, CNTs were considered as predominant sorbents for an extensive variety of organic chemicals and inorganic contaminants than the traditional ACs.

In any case, for viable application in water treatment, the small particular size of CNTs will cause excessive pressure drops and the recuperation of spent CNTs is a genuine test. The plainly visible control of CNT monolithic blocks by means of appropriate techniques give answer for this issue. Gui et al. [23] made a solid CNT sponge by substance vapor deposition utilizing ferrocene as antecedent. Notwithstanding immediate adsorbents, CNTs can likewise be used as incredible platform for macromolecules or metal oxides with natural adsorption capacity.

The tunable surface science and controllable pore measure make CNTs great support for composite adsorbents. Chen et al. observed CNT decoration with iron oxide for europium adsorption [24]. Li et al. asserted that interesting electrical properties of CNTs could be used for improved adsorption with electrochemical help [25].

Overview of toxicity studies of Carbon Nanotubes used as sorbents.

Toxicity studies have revealed that unmodified/pristine CNTs tend to be water insoluble and toxic. Jia et al., 2005 reported that cytotoxicity of single-walled carbon nanotubes (SWCNTs) was higher than to multi-walled carbon nanotubes (MWCNTs) [26]. Shape and size of MWCNTs affect the cytotoxicity due to change in agglomeration and dispersion behavior. Wang et al, (2009) reported that MWCNTs with smaller diameters showed less cytotoxicity [27]. These results suggest that the cytotoxicity of MWCNTs was strongly affected by their size, purity, and surface conditions. Carbon nanotubes after functionalization with various functional groups (e.g. hydroxyl, carboxyl, amines, etc.) become more biocompatible. Cytotoxic response of human dermal fibroblast cells was also found to be dependent on the degree of functionalization of single walled carbon nanotubes. Modification of Carbon nanotubes with biomimetic polymers made them more biocompatible while the uncoated carbon nanotubes lead to cell death [28]. The results of rodent studies showed that CNTs produce inflammation, epithelioid granulomas, fibrosis and biochemical/toxicological changes in the lung [29]. Single-walled carbon nanotubes (SWCNTs) were found to be more toxic than quartz and carbon black. Toxicity of CNTs depends on many factors [28] such as size, type of modification, wall structure, and method of synthesis, disagglomeration, and dispersion [30]. Data related to toxicity of carbon nanotubes is not being evaluated on the basis of all the factors that control toxicity. The review of toxicity studies for the reported sorbents reflects only few relevant studies.

Conclusion

Development of nanotechnology has shown remarkable potential in waste water treatment. Nano structure adsorbents have shown higher efficiency and faster rates of adsorption as compared to traditional materials. Carbon nanotubes have pulled in boundless consideration as sorbents for evacuation of contaminants because of their exceptional structures and huge length/measurement proportion. CNTs in flawless and in addition altered structures are great adsorbents for multi-segment sorption from water. Alteration at first glance assumes an imperative part in expanding the sorption limit of Carbon nanotubes, yet the expanding utilization of the nanosorbents needs more consideration as far as their toxity. It is vital to investigate the potential health and ecological effects of these nanosorbents before their far reaching use. Emphasis should be given for choosing safer options. It is noticeable that functionalization of CNTs reduces the toxity in most of the cases except acid functionalization. The information holes like absence of toxicity studies of carbon based nanosorbents with promising execution for expulsion of contaminations from water ought to be filled before commercialization these sorbents to avoid any hazards to environment and human health.

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