

Advantages and risk related with carbon nanomaterials (CNMs) application for water remediation. Mini review.*

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Water is one of the most valuable substances in the world and its availability in the form of potable and drinking water is of great importance for any society. Conventional water treatment methods have been reported to be ineffective in removing some kinds of organic pollutants including endocrine disrupting chemicals (EDCs), personal care products (PCP), pharmaceuticals, etc. Nanotechnology - especially application of the carbon based nanomaterials (CNMs) to water decontamination – is promising technology. The physico-chemical properties of CNMs (e.g. high surface area to volume ratio, high equilibrium rate) make them an excellent adsorbent which can be effectively used to remove pollutants from water. The present mini-review provides an overview of the research progress about organic chemical adsorption on CNMs in relation to water decontamination. The paper also discussed the possible risk related with desorption pharmaceuticals from CNMs.

1. INTRODUCTION

Nanotechnology is one of the world's most promising new technologies of the 21st century and is set to have dramatic impact across the fields of physics, chemistry, biology, material science, engineering, and environmental sciences.

*This article is dedicated to Professor Roman Leboda on the occasion of his 65th birthday

Nanoscience involves the study of materials on the nanoscale level between approximately 1 and 100 nm and involves study of how to control the formation of two- and three-dimensional assemblies of molecular scale building block into well-defined nanostructures or nanomaterials [1]. There are many definitions of nanotechnology. Usually, the definition includes a range of size (<100 nm) as well as nanotechnology is usually defined as research, development, manipulation, control or use of materials at that level [2]. There are some definitions related with nanotechnology [3]:

- Nanoscale – having one or more dimensions of the order of 100 nm or less;
- Nanoscience – the study of phenomena and manipulation of materials on atomic molecular and macromolecular scales, where properties differ significantly from those on a larger scale;
- Nanomaterial – material with one or more external dimensions, or an internal structure, which could exhibit novel characteristics compared to the same material without nanoscale features;
- Nanoparticle – particle with one or more dimensions on the nanoscale;
- Nanocomposite – composite in which at least one of the phases has at least one dimension on the nanoscale;
- Nanostructured – having a structure on the nanoscale.

The use of nanomaterials, manufactured products having one or more dimensions of 100 nm or less, has increased dramatically in the last decade and promises to continue to increase in the future. Forecasts predict nanotechnology, the science of using nanomaterials and nanodevices, to be a \$10 billion industry by 2010, growing to \$1 trillion by 2015 [4]. The quantities currently used amount to 1,000–2,000 tones per annum worldwide, that will expand to around 10,000-100,000 tones per annum in 2011–2020. Due to the wide use and large quantity of production in the very near future, manufactured nanoparticles will inevitably end up into the environment such as water and soil through waste disposal and unintentional release. Therefore, there are serious environmental and health concerns over these invisible, tiny particles because they are more toxic per unit of mass than larger particles of the same materials.

Nanomaterials can be considered under the following three categories: natural, anthropogenic and engineered. Nanoparticles are not a human invention and have existed naturally in the environment. The examples include volcanic ash, some colloids and viruses. In soils, natural NPs include clays, organic matter, iron oxides, and other minerals that play an important role in biogeochemical processes. Human activities can generate nanoscale materials as incidental byproducts (e.g. diesel exhaust particles, byproducts of welding). The third group, i.e. engineered nanomaterials (ENs) are synthesized for a specific purpose. ENs can be composed of many different base materials and have

different structures. They can be made of element carbon, carbon-based compounds, metals or metal oxides or ceramics (Table 1). Typical nanomaterials include carbon-based fullerenes (buckyballs) and nanotubes, quantum dots, which are nanoscale semiconductor crystals, metal oxides, such as titanium oxide and zinc oxide as well as silver nanoparticles. This paper focuses on manufactured carbon based nanomaterials (fullerenes and carbon nanotubes).

Tab. 1. Examples of nanoproducts.

| Structure | Base material | Examples |
|--------------------|--|--|
| Tubes | Carbon | Single-walled carbon nanotubes Multiwalled carbon nanotubes |
| Wires | Metals, semiconductors, tellurium nanowires | Silicon nanowires, cadmium oxides, sulfides |
| Crystals, clusters | Semiconductors, metals, metal oxides | Quantum dots, titanium dioxide, silicon dioxide |
| Spheres | Carbon | Fullerenes |

2. TYPES OF CARBON BASED MANUFACTURED NANOMATERIALS (CNMs)

There can be distinguished two main groups of carbon based manufactured nanomaterials, e.g. fullerenes and carbon nanotubes. A fullerene is a spherical particle most commonly comprising 60 carbon atoms arranged as 20 hexagons or 12 pentagons (Figure 1A). The diameter of a C₆₀ fullerene is approximately 10 Å or 1 nm. There are also higher mass fullerenes with different geometric structures, such as, C₇₀, C₇₆, C₇₈ and C₈₀. C₆₀ is soluble in a small range of organic solvents but almost insoluble in water limiting its utilization in biological applications. These materials possess unique chemical, mechanical, electrical, optical, magnetic and biological properties that make them candidates for a variety of novel commercial and medical applications. One aspect of fullerenes that makes them particularly attractive for applications ranging from drug delivery to cosmetics is that they may be derivatized in an infinite number of variations to tailor the fullerene's properties to a given application.

The manufactured carbon nanotubes (CNTs) exist in two forms, single-wall (SWCNTs) and multiwall (MWCNTs). Structurally a SWCNT is a rolled-up, single-layer graphene sheet (Figure 1B) with a diameter of 1 nm and a length of several micrometers or longer, whereas a MWCNT contains two or more concentric layers with various diameters and lengths (Figure 1C). The physical, chemical and electronic properties of carbon-based nanomaterials are strongly

coupled to carbon's structural conformation and, thus, its hybridization state [5]. Properties of carbon nanotubes have been widely investigated and CNTs possess important mechanical, thermal, photochemical and electrical properties. Carbon nanotubes and their derivatives are used in plastics, catalysts, battery and fuel cell electrodes, supercapacitors, water purification systems, orthopedic implants, conductive coatings, adhesives and composites, sensors, and components in the electronics, aircraft, aerospace, and automotive industries.

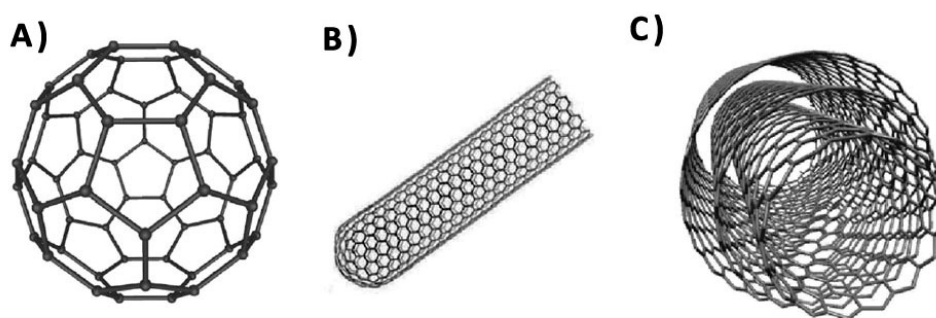


Fig. 1. Examples of carbon based nanomaterials (CNMs). A – Fullerene C60, B – single-walled carbon nanotubes, C – multiwalled carbon nanotubes.

3. CNMs IN THE ENVIRONMENT

Fullerenes and carbon nanotubes are produced in large quantities in factories of the capacities as high as 1500 tonnes/year. Increased production results in an increased potential for release to the environment, either deliberately in discharges or accidentally in spillages, and a greater possibility of adverse environmental effects [6]. Moreover, manufactured CNMs can enter the environment through unintentional releases such as atmospheric emissions and solid or liquid waste streams from production facilities. Fullerenes also occur in emissions from coal-burning power plants [7], in petrol, diesel and fuel-gas soot [8, 9]. They have also been found in quite high concentrations in Chinese ink sticks made from soot obtained by the slow burning of oils [10]. Nanoparticles reaching land have the potential to contaminate soil, migrate into surface and groundwater, and interact with biota. The model of nanoparticles fate and movement through the environment is presented in Figure 2.

Water solubility is a principal factor which affects the environmental fate of nanomaterials. Water solubility correlates with the potential for dispersion over vast areas and increases the potential for exposure. Nanomaterials with low

water solubility will bind with organic molecules in the aquatic environment to increase their affinity for the aqueous phase and potentially increase exposure to biota.

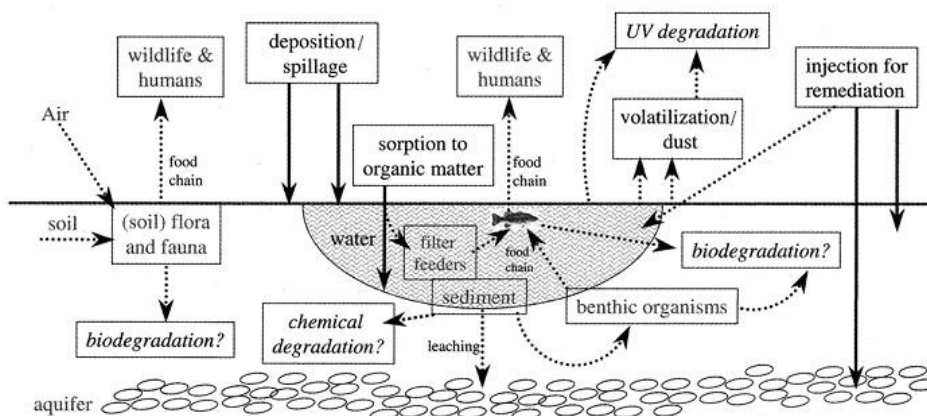


Fig. 2. Routes of exposure, uptake, distribution, and degradation of nanoparticles in the environment [39].

An additional factor that will affect nanomaterials is the ability to form large colloidal aggregates. The aggregation state of CNMs has strong influence on their fate and transport in the environment. Understanding the factors governing the aggregation behavior of CNMs is a key for evaluating their environmental transport, fate, and potential interaction with biological species. In the environment the formation of aggregates and therefore of larger particles that are trapped or eliminated through sedimentation affects the concentrations of free nanoparticles (Figure 3). There is still not enough information about environmental factors affecting CNMs aggregation. Carbon nanotubes form aggregates of much larger dimensions than the individual nanosized particles [11]. The large surface areas of smaller nanoparticles may allow for enhanced bioavailability and consequently greater potential for exposure and toxic effects. Saleh et al. [12] show that multiwalled carbon nanotubes (MWCNTs) can be relatively stable under solution chemistries typical of aquatic environments. An increase in solution pH from acidic (pH 3) to basic (pH 11) conditions resulted in a substantial decrease in MWCNTs aggregation kinetics. The presence of humic acid in solution markedly enhanced the colloidal stability of MWCNTs, reducing the aggregation rate.

Summing up, environmental fate depends on the chemistry of the specific nanomaterials and can be further influenced by environmental conditions such as physical binding or chemical reactivity with other compounds, water solubility, aggregation, and oxidation-reduction reactions.

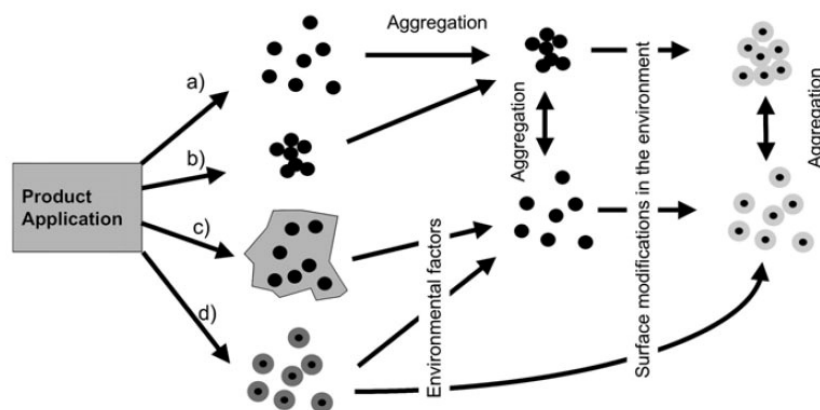


Fig. 3. Release of NP from products and (intended or unintended) applications: (a) release of free NP, (b) release of aggregates of NP, (c) release of NP embedded in a matrix and (d) release of functionalized NP. Environmental factors (e.g. light, microorganisms) result in formation of free NP that can undergo aggregation reactions. Moreover, surface modifications (e.g. coating with natural compounds) can affect the aggregation behavior of the NP [37].

4. ADSORPTION OF ORGANIC CONTAMINANTS BY CNMs

Research has shown that nanoparticles represent a new generation of environmental remediation technologies that could provide cost-effective solution to some of the most challenging environmental problems. One of these problems is decontamination of water from organic pollutants.

Properties of carbon nanotubes like large surface area and affinity for hydrophobic organic compounds make them an efficient adsorbent, creating applications both for wastewater treatment and water decontamination. Sorption studies using carbon-based nanomaterials report rapid equilibrium rates, high adsorption capacity and effectiveness over a broad pH range. Carbon nanomaterials have shown high adsorption capacity for polycyclic aromatic hydrocarbons [13, 14], pesticides [15, 16], endocrine disrupting chemicals [17], pharmaceuticals [18, 19] and other contaminants [20, 21]. Adsorption by CNMs is characterized by higher capacity than active carbon which is very often used in water decontamination. For example Lu et al. [21] reported a higher adsorption and shorter equilibrium time needed for trihalomethanes on carbon nanotubes than activated carbon. Pan et al. [17] also noted higher adsorption of two endocrine disrupting chemicals by carbon nanotubes than activated carbon.

Direct sorption of organic contaminants to the nanomaterials surface is driven by the same fundamental hydrophobic, dispersion, and weak dipolar

forces that determine sorption energies in conventional systems [22]. In binding of organic pollutants by carbon based nanomaterials besides hydrophobic interactions some authors propose other mechanisms including π - π interactions (between the bulk π systems on CNT surfaces and the organic molecules with C=C double bonds or benzene rings), hydrogen bonds (because of the functional groups on the CNT surfaces), and electrostatic interactions (because of the charged CNT surface) [23-25]. The available sorption sites of CNT bundles include the surface area, the interstitial and groove areas formed between the CNTs, and the inner pores of the tubes. External surface and groove areas are generally available for adsorption, but the interstitial and inner pores are not [25].

CNTs can contain functional groups such as -OH, -C=O, and -COOH. Functionalization of CNTs is aimed at easy processing, but at the same time, their adsorption properties with organic chemicals can be altered greatly. Functional groups can change the wettability of CNT surfaces, and consequently make CNT more hydrophilic and suitable for the adsorption of relatively low molecular weight and polar compounds. Functional groups may also increase diffusional resistance and reduce the accessibility and affinity of CNT surfaces for organic chemicals. Functionalized nanosorbents may provide an optimized approach for targeting specific micropollutants, removing low concentration contaminants, or improving subsurface mobility [26, 27]. For example carbon nanotubes functionalized with hydrophilic -OH and -COOH groups exhibited superior sorption of low molecular weight and polar compounds [21].

5. DESORPTION FROM NANOTUBES AS A POSSIBLE ENVIRONMENTAL RISK

There is a risk that structure: organic contaminants adsorbed onto nanotubes, can form during water treatment and subsequently enter the environment (water, sediments and soils). This process can occur both in surface and groundwater where these contaminants may already be present. If the pollutants would not be released from the adsorbent in significant concentrations, they would remain ostensibly non-toxic for living organisms. On the other hand, with significant desorption there exists the hazard that contaminants released from CNTs could adversely affect the environment and organisms. Even small concentrations of contaminants released from the environmental matrix into water can pose a danger to the water environment by causing chronic toxicity effects [28, 29]. This potential threat makes it vital to understand interactions between the CNMs and the organic pollutants, especially the pollutants' desorption range as a potential source of secondary water contamination. Recent studies have focused principally on either understanding the adsorption mechanisms of organic

contaminants on CNMs [23, 24, 30, 31] or applying this knowledge to water treatment [18, 20, 32]. Reversible adsorption has been observed in adsorption/desorption systems for a large group of contaminants such as naphthalene, cyclopentane vapor, PAHs and fullerene [14, 33, 34] as well as bisphenol A, 17 α -ethinyl estradiol, atrazine and carbon nanotubes [15-17]. The reversible adsorption of organic contaminants can pose a real threat for organisms when the desorbed contaminants enter the environment. It has been shown [19] that changes in environmental conditions e.g. pH (Figure 4A) can increase the desorption rate which may subsequently result in high health and environmental risks. This potential dangerous influence on organisms by CNTs and adsorbed pharmaceuticals can vary directly with the initial amount of adsorbed pharmaceuticals (Figure 4B).

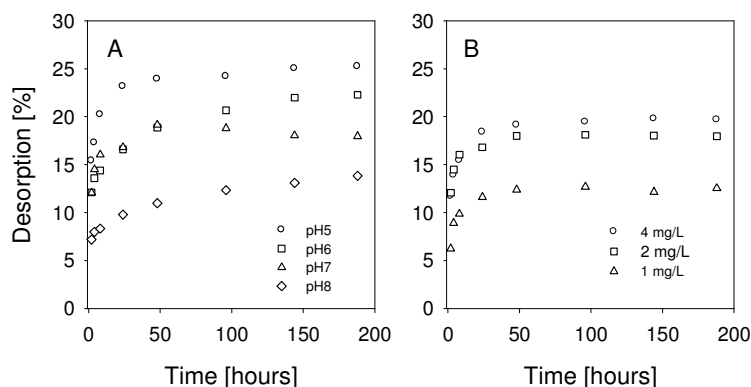


Fig. 4. Effect of pH changes (A) and initial adsorbed concentration (B) on desorption rate of oxytetracycline [19].

6. FUTURE RESEARCH

So far, it has not been established what influence nanoparticle - organic pollutant structures created exert on the organisms. Nanoparticles are toxic for living organisms [35]. They also influence significantly their other life functions, including toxic, mutagenic and carcinogenic effects [36]. However, the above mentioned studies refer to „free” nanoparticles. In the environment, individual pollutants rarely occur as free. Very often pollutants undergo interactions with other elements of the environment or other pollutants enhancing or weakening toxic effects of their influence. Hence, it is important to learn both mechanisms and scope of interactions among pollutants, as well as their influence on the living organisms and environment.

The pollutants adsorbed by nanoparticles can permeate to the environment and create problems which have not been identified so far. It can be assumed that in such conditions, nanoparticles can play the role of a carrier of organic pollutants transferring not only pollutants adsorbed in the environment (from site to site) but also making bioaccumulation of such pollutants by the organisms easier. In the environment, the pollutants adsorbed, can be resistant to biological decomposition. However, in the variable environmental conditions or in an organism, such pollutants can be gradually released which may lead to environmental pollution, illness or death of the organism concerned. Baun et al. [37] found that an increase in the pollutants bioaccumulation by algae is accompanied by the presence of fullerene. However, these studies are the only ones covering this issue.

7. CONCLUSIONS

Both nanoparticles and organic contaminants (e.g. pharmaceuticals, endocrine disrupting chemicals, etc.) can enter wastewater effluents and then make their way into surface or groundwater constituting public water supplies. It is important to understand the interaction between these two kinds of pollutants to recognize possible risks to the environment. Nanoparticles are a relatively new group of pollutants which are currently the focus of intense research. Evaluation of their desorption, as a potential source of secondary water contamination, is in its nascent stages. Sorption and desorption of these contaminants affect their chemical fate and toxicity to human and aquatic life. It is important to increase research efforts targeting the influence of CNTs on pharmaceuticals. Understanding the factors affecting their adsorption and desorption may allow researchers to counteract potential negative environmental effects.

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