

Nanotechnology in Water Treatment

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ABSTRACT

Drinking water is unfortunately becoming a rare luxury on our planet. On the other hand, with a trend of population growth, need for water which is essential to life, is becoming bigger every day. Practical application of nanotechnology in saving water worldwide is in using nanoparticles in detection of water pollution and water purification. This knowledge has importance in medicine and public health, so as in environment safety. Possible application areas of nanotechnology in field of purification and treatment of water are in filtration, catalytic and separation processes, ion exchanging, sensitive pollutant detection, etc. Nanotechnology could be the main solution in future fortreatment of surface water, groundwater, and waste water contaminated by toxic metal ions, organic and inorganic solutes, and microorganisms.

I. INTRODUCTION

According to WHO reports over a billion people around the world has no access to drinking water. [1] Water supply losing battle with population growth, global climate change, and water quality deterioration. This is becoming the biggest problem of mankind. Springs of drinkable water are increasingly polluted by men. In developed industrialized countries rivers carry a lot of substances which are proven to be hazardous for human health. The most of them are salts of heavy metals: mercury, lead, cadmium; than cellulose pulp, oils, detergents, etc... These substances are dangerous for human health and makes this water unusable for drink. There are plants, animals and microorganisms which can grow in these kind of environment (for example: *E. coli*, *Giardia lamblia*, *Salmonella*, and many others), but for others like fishes are lethal.

Conventional water-treatment technologies includes filtration, ultraviolet radiation, chemical treatment and desalination, whereas the nano-enabled technologies include a variety of different types of membranes and filters based on carbon nanotubes, nanoporous ceramics, magnetic nanoparticles and other nanomaterials.

Nano-enabled technologies for water treatment are already on the market — with nanofiltration currently seeming to be the most mature — and many more are on their way. Although the current generation of nanofilters may be relatively simple, many researchers believe

that future generations of water-treatment devices will capitalize on the new properties of nanoscale materials and may prove to be of interest in both developing and developed countries. [2]

The goal of writing this paper lies in bringing to the wider community as well as to the professionals, the new achievements that have been developed in order to improve the process of water purification. Nanotechnologies are seen as the future in the treatment of drinking water, waste water, as a cleaner, less expensive, and most effective methods.

II. NANOMATERIALS

Nanoparticles are the smallest parts of matter that could be manipulated with. Materials at the nanoscale usually have different optical or electrical properties from the same material at the micro or macroscale [3]. Nanotechnology is theoretically suitable for use in almost all sectors and technologies — including environmental technology. Nanostructured materials exhibit a considerably large proportion of surface atoms. Such atoms are particularly reactive due to their unsaturated bondings. Using nanoparticles for water treatment is less polluting than traditional methods and includes less people to work on the project, less capital, and energy [3].

Nanotechnology could potentially lead to more effective outcome of filtration that removes more contaminating materials than traditional methods, doing it faster, economically and have high

potential of selectivity. Nanotechnology is - generally used in areas where we need to treat contamination materials at the molecular level. As membrane technology nanotechnology has been in use as a technique for water treatment for a long time[4].

Nanoscale metals (silver, titanium, gold and iron) and their oxides are in use for processes of environmental safety. Silver nanoparticles are effective in disinfecting biological pollutants such as bacteria, viruses and fungi. Photocatalyst nano-TiO₂ can degrade phenolic recalcitrant compounds, microbial and odorous chemicals into harmless species. Gold and iron nanoparticles are especially suitable for removing inorganic heavy metals from surface and waste waters[5].

Nanomaterials are not only effective in disintegrating various pollutants, but also they are active in bimetallic coupling with other metals and metal oxides which synergistically improve pollution catalysis. Various nanomaterials can be used to make composite membranes. This enhances salt retention ability, curtails costs, land area and energy for desalination[6].

Zeolite nanoparticles are mixed with polymer matrix to form thin film RO membrane. It increases water transport and >99.7% salt retention ability and it is widely used for water desalination. Silica nanoparticles were doped with RO polymer matrices for water desalination [6]. It improved polymeric networks, pore diameters and transport properties. Carbon nanotubes (CNT) and graphene were used for adsorption based desalination because of their extraordinary adsorption capacities [7].

III. NANOTECHNOLOGY IN WATER TREATMENT

A. Nanofiltration membrane

Nanofiltration (NF) membrane technology is widely applied for removal of dissolved salts (i.e., desalination) from salty (i.e., brackish) water, removal of micro pollutants (e.g., arsenic and cadmium), water softening (i.e., removal of calcium and magnesium ions), and wastewater treatment. This technology is a dominant technology among methods for water purification. Membranes that are commonly used in water treatments are: microfiltration, reverse osmosis and nano-particle enabled membranes.

Contaminated or salty water is most often treated using two techniques. The more used method involves 7 stages:

- pre-treatment,
- coagulation,
- flocculation,
- sedimentation,
- disinfection,
- aeration, and
- filtration.

Using this method enables that all suspended solids, impurities and particles are removed; but it may not be effective for dissolved salts or for some soluble inorganic and organic substances. The second technology commonly used is pressure-driven membrane technology. This technology is based on a membrane which separates two homogenous phases[8].

Which one of methods are going to be used depends on purpose for water treatment. Nanofiltration using membranes does not affect water alkalinity, unlike reverse osmosis. Aim is to use nanoparticles that will improve the performance of membranes, for example, nanoparticles designed to limit the fouling of reverse osmosis (RO) membranes. Membranes for reverse osmosis are primarily for purification. Salty or contaminated water is pumped at extremely high pressure through the pores of the membrane, letting the water pass through but blocking the transit of salt ions and other impurities[9].

Traditional RO membranes become polluted when bacteria and other particles build up on the surface. As a result additional energy is needed to pump the water, and this raises costs of cleaning and replacement of the membranes. In membranes currently being developed, nanoparticles are designed to attract water, soaking it up like a sponge, while repelling nearly all the contaminants that might ordinarily stick to the surface. This creates a water purification process that is as effective as current methods but may have lower energy requirements [10].

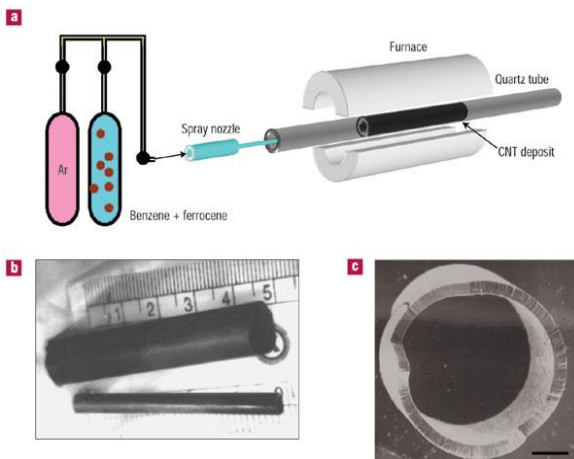
Carbon nanotubes

Carbon nanotubes (CNTs) are very thin, hollow cylinders made of carbon atoms and have exceptional thermal, electrical, and mechanical properties, which makes them suitable for potential wide applications in various industries[11]. These

nanotubes can be as small as 1 nm in diameter, with the length reaching several microns. They are made by using various thermal processes to form a hexagonal network of carbon atoms that is rolled up into a cylinder, or tube. CNTs can be single-walled (SWCNT) when composed of a single plane of graphene or multi-walled carbon nanotubes (MWCNT), which have multiple concentric layers. Synthesized nanotubes can be used as smart nanophase extraction agents. Both SWCNT and MWCNT have been used for direct water desalination.

Free energy extracted from molecular dynamics simulations of water confined in CNTs (0.8-2.7 nm \varnothing) was studied [7]. Water inside CNTs was found to be more stable than in the bulk, but thermo-dynamic properties change dramatically with CNT diameter.

The cylindrical membranes were proved that are capable remove bacterial pathogens (*Escherichia coli* and *Staphylococcus aureus*) and Poliovirus sabin from contaminated water. These carbon nanotube filters were also re-usable and could be cleaned by ultrasonication or autoclaving. It is anticipated that the properties of carbon nanotube filters, which combine the exceptional thermal and mechanical stability of nanotubes with the high surface area and cost-effective fabrication of the nanotube membranes, may in future allow them to compete with ceramic and polymer-based separation membranes used commercially.



Picture 1: Nature Materials 3, 610-614(2004), Carbon nanotube filters A. Srivastava et al., Nature Materials AOP[19]

- a. Schematic of the process
- b. Photograph of the bulk tube.

c. SEM image of the aligned tubes with radial symmetry resulting in hollow cylindrical structure (scale 1 mm).

Advantages of carbon nanotubes:

- Much less pressure required to move water across filter
- Much more efficient
- Filter easily cleaned by back flushing
- Selective adsorption properties of nanotube surfaces
- Incredibly large surface area
- Manmade nanotube membranes allow fluid flow 10,000 to 100,000 times faster than conventional fluid flow theory would predict.

Problems to Overcome

- Processes need to be designed to mass produce them
- By using a continuous spray pyrolysis method it has been possible to synthesise hollow carbon cylinders various centimetres in diameter and several centimetres long. Larger cylinders needed if this is to become practical.

Dendrimers:

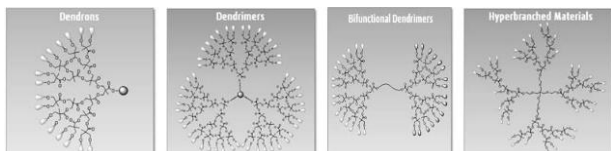
Dendrimers are enhancing filtration membranes, core-shell structures that can be precisely synthesized for a wide range of applications while specialized chemistry techniques enable precise control over their physical and chemical properties. They are constructed generation by generation in a series of controlled steps that increase the number of small branching molecules around a central core molecule. Up to ten generations can be incorporated into a single dendrimer molecule. The final generation of molecules added to the growing structure makes up the polyvalent surface of the dendrimer.[12]

Dendrimers are spheroid or globular nanostructures that are precisely engineered to hold molecules encapsulated in their interior voids or attached to the surface. Size, shape, and reactivity are determined by the generation and chemical composition of the core, interior branching and surface functionalities [13].

Dendrimers show some potential to selectively attract contaminants and retain them in their branched structures and, due to their large size, to prevent them passing through membranes. The presence of numerous chain-ends is responsible for the high solubility and miscibility and for the high

reactivity of these structures. There are more than a hundred families of dendrimers – they vary in the functions of surface, interior and core – meaning this technology presents a large spectrum of possible applications. Currently, dendrimers are principally used in the biomedical context as in-vitro diagnostics, for targeted drug delivery or as vectors in gene therapy. However, dendrimers can also be used for environmental purposes such as in environment friendly industrial processes or for water treatment[12,13].

In the case of water treatment, dendrimers could be used to enhance water filtration techniques. Examples of dendrimers that may be used in this type of process include cation-binding dendrimers, anion-binding dendrimers, organic compound-binding dendrimers, biological compound-binding dendrimers, viral-binding dendrimers and combinations of these. Ultra-filtration membranes requires less energy than nano-filtration or reverse osmosis, but the membranes are not effective in removing certain dissolved organic and inorganic solutes due to their small size. Coupling dendrimers with ultrafiltration membranes could enable the efficient removal from water of toxic metal ions, radionuclide, organic and inorganic solutes, bacteria and viruses[13].



Picture 2:Source:adapted from: Polymer Factory (2009), “Dendritic Materials”, www.polymerfactory.com/web/page.aspx?pageid=28902

IV. HEAVY METAL REMOVAL USING CNTs

Groundwater is often contaminated by spills, products of treatments in agriculture, past waste disposal practices and leaking underground storage tanks [14]. The presence of different organic and heavy metal contaminants in water sources has a large environmental, public health and economic impact. The large specific surface area and the high thermal and chemical stabilities of CNTs associated to their easy large-scale synthesis make them good candidates for adsorption of pollutants. The adsorption capacity of CNTs was much higher than that of the activated carbon (AC). This is due to the high surface area that helps strong interaction

between CNTs and dioxins. The CNTs have a great potential application of removing heavy metals such as zinc (Zn), cadmium (Cd), lead (Pb), nickel (Ni), and copper (Cu), as well as fluoride and radioactive nuclides[15]. Because of significant level of toxic metallic cations such as arsenic (As), lead (Pb), chromium (Cr), cadmium (Cd), and mercury (Hg), inorganic anions such as nitrate (NO_3^-) and perchlorate (ClO_4^-) are becoming common pollutants it is necessary to take serious measures in advancing the techniques for water treatment.

These ions are non-degradable, highly toxic and carcinogenic and can result in accumulative poisoning, cancer and nervous system damage[15]. Some of these elements, and ions are highly dangerous for human health. High levels of nitrates in drinking water may be harmful to newborn babies and contribute to cancer, perchlorate, which has emerged as a high profile contaminant and has consequently received considerable regulatory attention, has been reported to lead to hypothyroidism in adults [16]. The unique properties of nanomaterials and their convergence with current treatment technologies present new ideas and chances for water and wastewater treatment.

A. Zn

Zinc is one of the most common heavy metals occurring in wastewater. Zn ion is highly toxic to aquatic organisms and has a high potential to bio-accumulate. Therefore, it is important to remove Zn from wastewater during the treatment. The time taken for the adsorption to reach the equilibrium for the SWCNTs and MWCNTs are 1 hour, while for the powdered activated carbon (PAC) it took twice that long or 2 hours. In case study, Lu et al. [17] reported that the amount of Zn^{2+} sorbed on to the CNTs increased with a rise in temperature. Using the same conditions, the Zn^{2+} sorption capacity of the CNTs was much greater than that of the commercially available PAC, reflecting that the SWCNTs and MWCNTs are effective sorbents. The thermodynamic analysis revealed that the sorption of Zn^{2+} onto the CNTs is endothermic and spontaneous. The Zn^{2+} ions could be easily removed from the surface site of the SWCNTs and MWCNTs by a 0.1 mol/L nitric acid solution and the sorption capacity was maintained after 10 cycles of the sorption/desorption process. This suggests that both CNTs can be reused through many cycles of water treatment and regeneration [8].

B. Ni

Yang et al.[18], in their study on adsorption of Ni²⁺ on oxidized MWCNTs, found that the CNT adsorption capacity increases with the increase of pH in the pH range of 2–9 from zero to~99%. They found that oxidized MWCNTs were the most suitable material for the solidification and pre concentration of Ni²⁺ from aqueous solutions. CNTs were found to be the most effective nickel ion absorbent based on the high adsorption capacity as well as the short adsorption time [8].

C. Cr

Chromium at low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damages as well as damaging the circulatory and nerve tissues. It is important to eliminate such traces in our wastewater by the aid of the CNTs. Using carbon nanotubes supported by activated carbon (AC) can efficiently remove Cr⁶⁺ ions from polluted water. The highest adsorption capacity by using AC-CNT coated adsorbent obtained from batch adsorption experiments was 9.0 mg/g. Therefore, it seems that AC coated with CNTs is most effective for the removal of chromium ions[8].

D. Pb

Pb compounds are soluble in soft and slightly acidic water. The Pb from pipes may partially dissolve in the water flowing through. It occurs in almost all water resources as well as wastewater. The role of functional groups in the adsorption of Pb²⁺ to create a chemical complex was critical for efficient adsorption. 75.3% of Pb²⁺ adsorption capacity was achieved. Pb²⁺ is in the form of PbO, Pb(OH)₂, and PbCO₃ is adsorbed on the surface of the acidified MWCNTs, which is only 3.4% of the total Pb²⁺ adsorption capacity.

Mn oxide-coated carbon nanotubes (MnO₂/CNTs) were used to remove Pb²⁺ from aqueous solution. The Pb²⁺ removal capacity of MnO₂/CNTs decreased with the decrease of pH. From the Langmuir isotherms, maximum adsorption capacity was 78.74 mg/g, comparing with CNTs, significant improvement of Pb²⁺ adsorption shows MnO₂/CNTs can be good Pb²⁺ absorbers. The adsorption of Pb²⁺ by MnO₂/CNTs occurred during the first 15 minutes of contact time, and full equilibrium was reached in 2 hours [8].

E. RISKS OF USING NANOTECHNOLOGY IN WATER PURIFICATION

Each of new technologies, with all the useful contributions to the development of mankind, brings a number of risks and uncertainties about the possible misuse or negative and adverse effects of its use. Contact with the unfamiliar and uncharted nanotreated materials, especially so small in size that easily penetrate into any part of the human body, certainly evokes caution and the need for prior checking. Therefore, it is necessary to better connect research sector, industry and relevant government institutions to jointly assess the advantages and disadvantages of the possible use of nanotechnology in the process of water purification.

Although in recent years nanotechnology becoming an issue increasingly present in public, its possible applications that is still unknown to a large part of the people. Many areas are using nanotechnology, but just in the field of efficient water treatment she could really help a large part of humanity. The high performance of CNTs in separation process technology was noticed inducing major developments. We are convinced that wastewater treatment in large scale to remove heavy metals and separation in conjunction with carbon nanotubes is expected to create a major breakthrough in the coming future [20].

The unique characteristics of nanoparticles and nanomaterials are responsible for their toxicity and interaction with biological macromolecules within the human body. This may lead to the development of diseases and clinical disorders. A loss in cell viability and structure can also occur in exposed tissues as well as inflammation and granuloma formation. It is often overlooked that there are natural NPs in our environments: water and air. NPs <50 nm that enter the body are excreted. Larger NPs are trapped in biological membranes, e.g., blood-brain barrier. NPs <20 nm may enter the cells. Many concerns about safety of NPs are unfounded; several studies are ongoing to determine safety of NPs[20].

CONCLUSION

Problems with environmental pollution are especially serious when it is a drinking water involved. There is less drinking water globally, but the number of people around the world are arising. It puts the problem of, water safety in the first place



for emergency in finding sustainable solutions. The economic, social, and environmental challenges resulting from the lack of access to clean water and basic sanitation are topic of many scientific, researches, and project in order to effectively solve the problem.

Nanotechnology-based water treatment devices are already available and many more are in their final stages of testing. Nanotechnology is increasingly using in treatment of water systems. It is especially useful for treatment and remediation, sensing and detection, and pollution prevention. Nanotechnology-based water schemes propose more operative, cost-effective, durable, and reasonable methodologies to water purification by removing specific types of pollutants from water [21]. Processes of nanofiltration, ultrafiltration, reverse osmosis, and nanoreactive membranes are considered as key components of advanced water purification and desalination technologies that remove, reduce, or neutralize water contaminants that threaten human health and/or ecosystem productivity and integrity. But the problem is that scientific achievements of these technology is still mostly at demonstrating the proposed solutions, and there is still a lot of work in terms of measuring the performance and economic potential in real application.

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