

A Historical Perspective of the Usage of Nanotechnology for Water Purification

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Abstract: - The needs for water consumption for its different uses are enormous, while many related challenges are faced by both developing and developed countries, to different degrees. Since current technologies for water disinfection and reuse are reaching their limits, there is an urgent need to develop basic and affordable water treatment methods. In this respect, nanotechnology possesses all these characteristics that may provide high efficiency, multiple functions and flexibility in water and wastewater treatment systems. This paper summarizes the research on the development of nanotechnologies for the purification and reuse of water and wastewater, as they were captured in the early 21st century. Nanotechnologies show most promising signs for full-scale application in the near future, based on their stages in research and development, the commercial availability and cost of the nanomaterials used, and the compatibility with existing infrastructure.

Key-Words: - Nanotechnology, Nanomaterials, Nanoparticles, Water purification, Adsorption, Nanoadsorbents, Dendrimer Polymeric Nanoadsorbents, Molecularly Imprinted Polymers

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1 Introduction

The availability and security of water are inextricably linked to economic development, global health and energy production. The needs for water consumption for its different uses are enormous, while climate change is expected to lead to a reduction in the available quantities. Many related challenges are faced by both developing and developed countries, to different degrees. As there is therefore an urgent need to develop basic and affordable water treatment methods [1],[2],[3] current technologies for water disinfection and reuse are reaching their limits.

Consequently, new technologies are needed that provide high efficiency, multiple functions and flexibility in system size and configuration. Nanotechnology possesses all these characteristics and, therefore, can offer opportunities for technological leaps in terms of water and wastewater treatment systems. From the research that has been done, nanotechnology shows improved performance in treatment processes, compared to conventional technologies. However, its potential and limitations

as an integral and independent element of a water supply system have not yet been sufficiently explored.

In this paper, we summarize the research on the development of nanotechnologies for the purification and reuse of water and wastewater, as they were captured in the early 21st century. We try to answer two important questions: “when” and “where” it makes sense to use nanotechnology to enable sustainable water management. The “when” includes the timeframe when nanotechnology is expected to be applied to water supply and sanitation systems, as well as the scale and objectives for which it should be preferred, and the “where” deals with the geographical location of the water supply system, the size, density and socio-economic status of the population it serves. Also, the location within a treatment system with various techniques, which could be integrated into nanotechnology. Based on these analyses, we offer a vision for the future of integrated water and wastewater treatment systems and their reuse [4].

2 Nanotechnology

Nanotechnology is a term used to describe the creation and use of functional structures between 1 and 100 nanometers in size, that is, on the order of 10^{-9} meters. The dimensions are more easily understood by stating that a nanometer is approximately 1/80000th of a human hair or the length of 10 hydrogen atoms in a row. The term Nanoscience is defined in a similar way, referring to sciences that study phenomena at this scale. Although the field of Nanotechnology has only recently begun to develop substantially, its potential had already begun to become apparent since the time when physicist Richard Feynman gave a speech in December 1959 at the California Institute of Technology (Caltech), entitled "There's Plenty of Room at the Bottom", talking about the large margins that the laws of nature leave for the control of matter at the atomic level. In its development so far, the significant improvement of the electron microscope has played an important role, while milestones can be considered the discoveries of carbon structures in the form of a sphere, known as fullerenes, as well as in the form of a tube, known as carbon nanotubes, each with special properties [5].

One challenge of Nanoscience is the effort to understand how materials behave, when their size is close to atomic dimensions. Nanofibers are 10 to 100 times smaller in diameter than conventional textile fibers. Compared to a human hair that has a diameter of 80,000 nm, nanofibers are 1,000 times smaller in diameter. When the characteristic size of a structure is from 1 to 100 nm (nanoscale), then it is included in a scale of special physical phenomena, where size and shape significantly affect behavior. This fact leads to unique properties and the possibility of using such nanostructured materials in innovative applications and devices. The phenomena of this scale are at the center of interest of physicists, chemists, biologists, electrical and mechanical engineers and computer scientists, generating research in the field of nanotechnology. At the nanoscale, the properties of materials (physical, chemical and biological) differ considerably, depending on the behavior of matter in the macrocosm. The purpose of nanotechnology is to understand these properties and to create new, improved materials, devices and systems based on these. One of the main reasons why nanotechnology has become the subject of much research and discussion is that it helps us fill a large gap in our understanding of matter. So far, with the contribution of Physics and Chemistry, we know quite a lot about subatomic particles and the behavior of individual

atoms and molecules. We have also learned a lot about the behavior of matter in the macrocosm. Nanotechnology has given us the ability to study matter extensively in these dimensions and this has created great expectations for multiple and innovative applications [6].

Major milestones in the development of nanotechnology were the discovery of the Scanning Electron Microscope (SEM) in 1981, as well as the first publication that spoke of molecular mechanics with atomic precision by Eric Drexler. In 1985, the discovery of fullerenes and in 1986 the discovery of the Atomic Force Microscope (AFM) gave great momentum, which is confirmed by the publication of many research papers on nanomaterials and the publication of many new scientific journals that concern exclusively nanodimensions.

When monitoring the development of nanotechnology, it does not matter what the profits of this particular market will be in the near future or in the long term, since nanosciences will hardly become an industry with self-sufficient dynamics, but will constitute a science with a multitude of applications, with the potential to redefine even the direction of many different industries. This fact allows one to recognize that nanotechnology is not just another technology, but a set of technologies, producing a series of technical achievements that will be adopted in many different markets. Within such a framework, the world of nanotechnology could be divided into three broad categories: nanostructured materials, nanotechnologies, and nanodevices.

2.1 Nanostructured Materials

Nanostructured materials are materials with a characteristic microstructure on the nanoscale (typically 1-100 nanometers). Microstructure refers to the chemical composition, arrangement of atoms (atomic structure), and size of a solid in one, two, or three dimensions. Potential factors affecting the properties of nanostructured materials include size effects (where the critical size scale of physical phenomena is comparable to the characteristic size of the building blocks of the microstructure), changes in the dimensions of the system, changes in atomic structure, and changes in chemical composition. Nanomaterials can be grouped into: nanoparticles (the building blocks), nanointermediates, and nanocomposites.

They can be at or very far from thermodynamic equilibrium. For example, nanostructured materials consisting of nanometer-sized silver (Ag) or sodium chloride (NaCl) crystallites with different crystallographic orientations or different chemical compositions differ greatly from their

thermodynamic equilibrium. Nanomaterials whose synthesis results from supramolecular chemistry can yield nanosystems that are in thermodynamic equilibrium [5].

Nanomaterials are of great interest in terms of their properties and applications, which is why they are often referred to as "materials of the future" and nanotechnology as "technology of the future". Some properties of nanomaterials remain unknown to this day, while others are not easy to predict. Materials on a microscopic scale exhibit the same properties as on a macroscopic scale (e.g., glass or steel fibers). In contrast to nanomaterials, which have different properties on a macroscopic scale. Some of these properties of nanomaterials are due to the following factors [7]: The large percentage of atoms on the surface of the material, the high surface energy, the low probability of defects, and the dispersion. These properties can vary within a range of values by varying the size, shape or degree of aggregation. Some of these unique properties of nanomaterials are presented below:

- a) Nanomaterials have a significantly lower melting point or transition temperature, due to the very high percentage of surface atoms in their total number of atoms.
- b) In terms of mechanical properties, they can reach theoretical strength values that are one or two orders of magnitude higher than the corresponding values for single crystals on a macroscopic scale.
- c) Optical properties can also vary significantly; it is characteristic that the color of metal nanoparticles differs, depending on their dimensions.
- d) The electrical conductivity of materials decreases with the reduction of their dimensions due to the dispersion of the electric charge from the surfaces; of course, the electrical conductivity of nanomaterials can be significantly increased due to the order in their microstructure, as is the case in polymer fibrils.
- e) The magnetic properties of nanomaterials are also very different from those of a larger-scale crystal; the ferromagnetism of a material on a macroscopic scale is converted into supermagnetism on the nanometer scale, due to the enormous surface energy [5].

In nanotechnology, the diameter of nanoparticles is less than 100nm. Mainly, materials manufactured with the help of nanotechnology are applied in the field of engineering. These materials consist of very small molecules, which exhibit special characteristics, resulting in changes in their physical, chemical, and biological behavior. These nanoparticles can take various forms in terms of their shape and arrangement in space such as: tubular, spherical or irregular. Nanoparticles (NPs) are not new to science, they are by-products of fires, volcanic

eruptions, and other natural processes. Nanoparticles are natural components of living elements: proteins, enzymes, and RNA/DNA meet the criteria to belong to nanoparticles. Nanoparticles are present in various products that are widely consumed such as: titanium oxide and zinc oxide, which are ingredients of cosmetics. Like titanium dioxide, zinc dioxide is completely hypoallergenic and safe to use. The molecules of the component are not absorbed by the skin and therefore do not affect the human body. The future application of nanoparticles is very promising in advancing the field of medical care and environmental technology [5].

2.2 Categories of Nanoparticles

The main categories of nanoparticles are as follows.

2.2.1 Fullerenes

Discovered in the 1980s, they consist entirely of carbon and have the form of hollow spheres or tubes. Common graphite consists of sheets of carbon atoms, which are joined together to create a hexagonal lattice (graphene). The structures of carbon when they have a spherical shape are known as fullerenes. The simplest structure of a fullerene is achieved if it consists of 60 carbon atoms, and is known as C₆₀. There are a multitude of fullerenes of different shapes and sizes, such as C₇₀, C₈₂, etc. Nanotubes and fullerenes are naturally found in carbon black, which is characterized as carbon powder and includes a mixture of amorphous carbon, fullerenes and nanotubes. Usually the ends of a nanotube consist of a hemisphere, just like half a fullerene [5].

2.2.2 Nanowires

They are microscopic interconnecting wires of crystalline structure that are manufactured with a similar arrangement as standard semiconductors. Titanium carbide nanowires are non-oxidizing ceramic materials that have a high melting point, hardness and corrosion resistance, resulting in many applications such as microelectronics and hydrogen storage. Methods for the synthesis of nanowires include the usage of other nanotubes as model reagents, catalyzed by nanoparticles. However, these do not provide good control over the purity, shape, size, aspect ratio, crystal orientation and crystal structure of the nanowires produced [5].

2.2.3 Quantum Dots

Quantum dots are inorganic semiconductor nanocrystals made of inorganic materials, where their length ranges from 2 nm to 10 nm. Their size is smaller than the length of the Bohr exciton radius, which is the distance between the electron and hole

pair in a semiconductor. Their most common shape is spherical, in which the Schrödinger equation is more easily calculated, because they resemble real atoms. Quantum dots can produce electrons or electron-hole pairs which, due to the small size of the dots, are limited to zero dimensions [8]. Quantum dots can be prepared by either physical or chemical methods:

a) Physical methods: (1) Etching, (2) Shaped electric field, (3) Diffusion between the barrier and the quantum well, (4) Selective growth, and (5) Self-organized growth.

b) Chemical methods: (1) Precipitation of colloidal particles from a homogeneous solution, and (2) Sol-gel technique [9].

2.2.4 Nanotubes

This category consists of fullerenes and carbon molecules that have been elongated to form tubular structures and have a diameter of 1 nm to 100 nm. Carbon nanotubes exhibit high tensile strength, which is equal to or even 100 times greater than the tensile strength of steel. Nanotubes also maintain a very low weight compared to steel and other structural materials. Additional properties that nanotubes exhibit are: high conductivity, increased hardness, unique electrical properties, and optical properties.

The electrochemical self-organization for the construction of ordered titanium oxide nanotubes has aroused great interest in science and technology in recent years. The method for the construction and complete orientation of nanotubes on the surface of the metal, such as titanium, is the optimized and controlled anodic oxidation of titanium, by fluoride ions contained in the electrolyte [10].

By achieving the best combination of electrochemical parameters, we have the complete formation and appropriate orientation of well-ordered nanotubes within a TiO_2 layer. The diameters of these nanotubes range from 20 nm to 200 nm, with the characteristic thicknesses of their walls ranging from 10 nm to 20 nm. Titanium oxide is a highly functional material that has, for example, semiconducting or catalytic surface properties and therefore high potential for technological exploitation.

Carbon nanotubes have attracted the interest of researchers and investors worldwide, due to their numerous applications. The following are indicative of their main potential applications in the next 20 years [5]: transistors, replacement of silicon, diodes, nanocapacitors; quantum computers; flat organic displays; signal amplification in devices with antennas (mobile phones and not only); replacement

of optical fibers and electrical cables; nanosensors of exceptional sensitivity; reinforcement of materials (stronger alloys and polymers in vehicles, e.g., spaceships, airplanes, cars, in bulletproof vests, tools, etc.); super-concentrated hydrogen storage cells; artificial muscles. These applications are very important. The main obstacles to their advancement are the limited ability to produce nanotubes in a short period of time, as well as the difficulty of combining them into macrostructures (threads) that will maintain their properties. Recent research and experiments show that these obstacles can be overcome [11].

3 Water Purification and Nanotechnology

Nanomaterials are usually described as materials that are smaller than 100nm in at least one dimension. At this scale, materials often have different properties than those at larger sizes, many of which have been investigated for applications in water and wastewater treatment. Some of these applications can use the special properties of nanomaterials related to their large specific surface area, such as fast dissolution, high reactivity and strong adsorption, and improve their performance. They can also take advantage of their discontinuous properties, such as supermagnetism, clean surface that helps in detection and quantum confinement forces. The applications listed below are based on nanomaterial functions that are still at the stage of laboratory research [5].

3.1 Adsorption

Adsorption is mainly used as a polishing step for the removal of organic and inorganic pollutants from water and wastewater treatment. The performance of conventional adsorbents is usually limited by their surface area, their placement, their lack of selectivity and their mobility. Nanoadsorbents offer significant improvement due to their extremely high specific surface area and relative adsorption spaces, small interparticle diffusion distance and pore size.

3.1.1 Nanoadsorbents

Nanoadsorbents have a very high and specialized adsorption capacity for this and have wide application in water purification. Nanoadsorbents are not yet widely available commercially and their applications are very few, mainly in the USA and Asia, but research is underway to be as effective as possible and to cover the large number of various specific pollutants in water. Some of the properties

and characteristics related to the use of nanoadsorbents are the following:

- a) Carbon-based nanoadsorbents: Water containing nickel ions (Ni^{2+}) have a high specific surface area, excellent chemical resistance, mechanical strength and good adsorption capacity [12].
- b) Regenerable polymer nanoadsorbents: Many organic and inorganic impurities in wastewater [13].
- c) Nanoadsorbents with clay: Hydrocarbon and phosphorus dyes.
- d) Nanoadsorbent carbon with iron oxide: Activated carbon serves for adsorption, while elemental iron acts as a reactive substance and can remove various impurities [14].
- e) Nanoadsorbent networks: Complex three-dimensional networks induced by the ion beam, providing better performance [15].

Magnetic nanoadsorbents also help in wastewater treatment and prove to be very interesting materials, especially for the removal of organic impurities. Since most of the impurities are not magnetic in nature, filtration assistance is required for the absorption to work, which is usually followed by magnetic separation. Nanoadsorbents used for magnetic separation are prepared by coating magnetic nanoparticles. Different methods, such as magnetic forces, cleaning agents, ion exchangers and many more, are used to remove the nanoadsorbents from the processing site to avoid unnecessary toxicity. Regenerated nanoadsorbents are always more economical and are more commercially promoted [16].

3.1.2 Carbon Nanoadsorbents

Regarding biological removal, carbon nanoadsorbents have shown higher efficiency than activated carbon in the adsorption of various organic chemicals. Their high adsorption capacity mainly stems from their large specific surface area and the various interactions of carbon adsorbents. The surface available for adsorption is their external surface. In the aqueous phase, carbon nanoadsorbents form loose bundles (aggregates), due to the hydrophobicity of the graphite on their surface, thus reducing the effective surface area. On the other hand, nanoadsorbent aggregates contain interstitial spaces and grooves, which are high-energy adsorption regions for organic molecules. Although activated carbon of similar measured specific surface area, such as in carbon nanoadsorbent bundles, contains a significant number of micropores, it does not achieve sufficient adsorption on bulky organic molecules, such as many antibiotics and drugs. Thus, carbon nanoadsorbents have a much higher adsorption capacity for some bulky organic

molecules, due to their larger pores (in bundle form) and more accessible adsorption sites [17]. A significant disadvantage of activated carbon is its low adsorption towards low molecular weight polar organic compounds. Carbon nanoadsorbents strongly adsorb many of these polar organic compounds due to the different interactions of carbon impurities, hydrogen bonds, covalent interactions and electrostatic forces. Electrostatic attraction facilitates the adsorption of positively charged organic chemicals, such as some antibiotics at appropriate pH [18].

Regarding the removal of heavy metals, oxidized carbon nanoadsorbents have high adsorption capacity for metal ions with fast kinetics. The functional group surface (e.g., carboxyl, hydroxyl, and phenol) of carbon nanoadsorbents is the most important adsorption site for metal ions, mainly through electrostatic attraction and chemical bonds. As a result, surface oxidation can significantly enhance the adsorption capacity of nanoadsorbents. Various studies show that carbon nanoadsorbents are better adsorbents than activated carbon for heavy metals (e.g., Cu^{2+} , Pb^{2+} , Cd^{2+} , and Zn^{2+}), and also the adsorption kinetics are extremely fast due to the highly accessible adsorption sites and short diffusion distance [19]. Overall, carbon nanoadsorbents may not be a good alternative to replace activated carbon as a broad-spectrum adsorbent. Instead, their surface chemistry can be tuned to target specific contaminants, they can have unique polishing applications, they can be used to remove resistant compounds, or they can detect trace concentrations of organic pollutants. These applications require a small amount of materials and are therefore much more economical. Graphene oxide is an excellent low-cost adsorbent, produced by chemical reduction of graphite oxide, mechanical exfoliation, crystal growth on silicon carbide, crystal growth on a metal substrate, or cutting of nanotubes. It was found that sand grains coated with graphene oxide were effective in removing Hg^{2+} and a bulky dye molecule (Rhodamine B). Its performance was comparable to that of activated carbon [20].

3.1.3 Metal Nanoadsorbents

Metal oxides such as iron oxide, titanium dioxide, and alumina are effective, low-cost adsorbents for heavy metals and radionuclides. Sorption is mainly controlled by complexation between dissolved metals and oxygen on the metal oxides. It is a two-step process: rapid adsorption of metal ions on the outer surface, followed by slow intraparticle diffusion along the microporous wall. Adsorbents of this nanoscale have higher adsorption capacity and

faster kinetics due to higher specific surface area, shorter interparticle diffusion distance, and a greater number of surface reaction sites (i.e., corners, edges, vacancies). For example, when the particle size of nanomagnetite was reduced from 300 to 11 nm, the adsorption capacity of arsenic increased more than 100-fold [5].

Much of the observed increase in adsorption was attributed to the increase in specific surface area, where 300 nm and 20 nm magnetite particles have similar adsorption surface area capacity. However, when the particle size was reduced below 20 nm, magnetite nanoparticles adsorbed three times more. This nanoscale effect is attributed to the change in the surface structure of magnetite that creates new adsorption sites [21].

In addition to their high adsorption capacity, some iron oxide nanoparticles, for example, nanomagemite and nano-magnetite, can be superparamagnetic. The magnetism is highly volume-dependent, as it results from the collective interaction of the atomic magnetic dipoles. If the size of a ferromagnet is reduced to a critical value (40 nm), the magnet acquires a higher magnetic susceptibility. As the size is further reduced, magnetic particles become superparamagnetic, by losing permanent magnetic fluxes while responding to an external magnetic field, which allows for easy separation and recovery with a low magnetic field gradient. These magnetic nanoparticles can either be used directly, as adsorbents, or as the core material in a shell structure of nanoparticles, where the shell provides the desired function, while the magnetic core performs magnetic separation.

Metallic iron oxide nanocrystals can be compressed into porous spheres, without significantly damaging their outer surface when moderate pressure is applied. The volume and size of the pores can be controlled by adjusting the stabilization pressure. Thus, they can be applied in forms of both fine powders and porous spheres that can be used in industry [22].

Metal-based nanomaterials have been used to remove various heavy metals, such as arsenic, lead, mercury, copper, cadmium, chromium, nickel, and have shown great potential to successfully compete with activated carbon. Among them, the demand for arsenic removal has attracted much attention. Although activated carbon is a good adsorbent for many organic and inorganic contaminants, it has limited capacity for arsenic, especially for As(V). Several metal oxide nanomaterials, including nanosized magnetite and TiO₂, have shown greater

adsorption of arsenic than activated carbon. Also, metallic iron oxide nanoparticles can be impregnated onto the backbone of activated carbon or other porous materials to achieve simultaneous removal of arsenic and organic contaminants, which favors the point-of-use application of portable water purification devices [5].

Portable water purification devices, better described as POU (point-of-use), are water treatment systems and belong to the field of water disinfection techniques. They are self-contained units that can be used by recreational enthusiasts, military personnel, survivors of natural disasters, and others who need drinking water from various sources (e.g., rivers, lakes, etc.). These personal devices make unchlorinated drinking water safe and palatable to drink. Many commercial portable water purification systems and chemical additives are available for hiking, camping, and other travel excursions to remote areas. However, these devices are not only used for remote or rural areas, but also for treating municipal water for taste, chlorine, odor, and heavy metals, such as lead and mercury.

Metal oxide nanoadsorbents can be easily regenerated by changing the pH of the solution. In many cases, the adsorption capacity of metal oxide nanoadsorbents remains after several cycles of regeneration and reuse. However, decreased adsorption capacity after regeneration has also been reported. Furthermore, metal nanoadsorbents can be produced at relatively low cost; their high adsorption capacity, easy separation and regeneration, are the factors that make them a technologically and economically advantageous solution [23].

3.1.4 Dendrimer Polymeric Nanoadsorbents

Dendrimers are tailored adsorbents that are capable of removing both organic and heavy metals. Their inner shell can be hydrophobic for the adsorption of organic compounds, while their outer branches can be tailored (e.g., hydroxyl or amine) for the adsorption of heavy metals. Adsorption can be based on complexation, electrostatic interactions, hydrophobic effect and hydrogen bonds. A dendrimer ultrafiltration system was designed for the recovery of metal ions from aqueous solutions. The system achieves almost complete removal of Cu²⁺ ions with an initial concentration of 10 mg/L, and Cu²⁺ polyamide amines NH₂ with a ratio of 0.2. After adsorption, the dendrimer-loaded metal ion was recovered by ultrafiltration and regeneration by reducing its pH to 4 [24].

3.1.5 Regeneration and Reuse of Adsorbents

Regeneration is an important factor determining the cost-effectiveness of adsorbents. The adsorption of metal ions on carbon nanotubes can be easily reversed by reducing the pH of the solution. The metal recovery rate is usually over 90% and often close to 100% at pH<2. Furthermore, the adsorption capacity remains relatively stable after regeneration. Experiments have shown that in the purification of the heavy metal zinc Zn^{2+} the adsorption capacity of carbon nanotubes decreased by less than 25% after 10 cycles of regeneration and reuse, while that of activated carbon decreased by more than 50% after one regeneration cycle. A statistical analysis based on the Zn^{2+} removal study showed that carbon nanotube adsorbents can be successfully regenerated and reused up to a hundred times for Zn^{2+} removal, while maintaining satisfactory adsorption capacity [5].

3.2 Molecularly Imprinted Polymers (MIPs)

Molecularly imprinted polymers (MIPs) are technologically advanced polymeric materials that have found application in selective separations of small molecules and substances of biological interest. They are produced by the copolymerization of a functional monomer and a cross-linked star monomer in the presence of a specific molecule, the template molecule, which functions as a molecular “template”. The functional monomers have the ability to form bonds (covalent or non-covalent) with the template molecule in the initial polymerization solution, and thus after polymerization and removal of the template molecule, a three-dimensional cavity is formed in the solid, highly branched, polymeric carrier. This cavity is both geometrically and chemically complementary to the imprinting molecule, and thus the polymer now possesses a kind of molecular memory. They can thus re-bind the imprinting molecule with high affinity and selectivity, just as antibodies recognize antigens. Molecularly imprinted polymers exhibit greater thermal and chemical stability compared to natural antibodies, and can be used repeatedly without losing their ability to recognize the imprinting molecule [25].

The development of molecularly imprinted polymers in recent decades has been rapid, both for basic research and for their use in practical applications, and is reflected in the number of relevant publications that show an almost exponential increase. The initial idea for the development of molecularly imprinted polymers could be considered the theory of antibody production by Linus Pauling in 1967, although the idea of molecular interactions was much older. The production of molecularly imprinted polymers was first formally reported by

Wulff in 1973, where both covalent and non-covalent interactions are described, although the latter are used in synergy with the covalent ones. The most frequently followed methodology for the production of molecularly imprinted polymers today, imprinting using non-covalent bonds, was developed by the research group of Professor Mosbach in 1994. This technique is the most widespread and this is due to several factors, such as the fact that it is more direct with fewer synthetic steps and there is a wide variety of monomers with different types of intermolecular interactions available to someone. This approach is also similar to the interactions observed in physical and biochemical processes, making it the most promising technique for mimicking the selectivity observed in nature [5].

The star monomer is used to permanently stabilize the functional monomers at specific positions within the recognition cavity and is therefore used in high amounts. This results in its strong influence on both the morphology and the chemical environment of the molecularly imprinted polymers. The most widely used star monomer is ethylene glycol dimethylacrylate (EGDMA), because it provides materials with chemical and thermal stability, good wetting ability in most rebinding media, fast mass transfer and good recognition properties. Recently, trimethylpropanecrylene (TRIM) has been used successfully in several cases and provides polymers with similar recognition properties for a variety of imprinting molecules. Subsequent polymerization gives an insoluble star-shaped polymer network around the imprinting molecule (step 3), which after removal of the imprinting molecule can selectively recognize it for subsequent use. The imprint that remains after removal of the template from the polymer helps in the identification of the properties of the molecularly imprinted polymers and are generally called binding sites. It has been used for the detection and treatment of water pollutants, even at very low concentrations. Molecularly imprinted materials can also be used in combination with catalysts, forming a new composite adsorbent system or catalyst [5].

Molecularly imprinted polymer nanoparticles contained in nanofibers, using the electrostatic method, can be used for various pollution control applications including water treatment. Molecularly imprinted nanospheres (nano MIPs) are also being developed for the specific adsorption of very small pollutants from hospital wastewater using mini-emulsion, a polymerization technique that is very complex, but can be operated in a single reaction

chamber, resulting in particles with a size of 50nm-500nm. A magnetic core can also be introduced into the process to allow the final separation of the molecularly imprinted polymer nanoparticles and more importantly to help in the easy identification of pollutants in wastewater [26].

3.3 Potential Applications in Water Treatment

Nano-adsorbents can be easily integrated into existing treatment processes, sludge reactors or adsorbents. Nano-adsorbents applied in powder form in sludge reactors can be particularly effective, since all surfaces of the adsorbents can be used, and mixing greatly facilitates mass transfer. However, an additional separation unit is required to recover the nanoparticles. Nano-adsorbents can also be used in fixed or fluidized bed adsorbents in the form of pellets or porous granules. Fixed bed reactors are usually associated with mass transfer limitations but do not require a subsequent separation process. Applications of nano-adsorbents for arsenic removal have been commercialized and their performance and cost have been compared with other commercial adsorbents in pilot studies [27].

ArsenXnp is a hybrid ion exchange medium, composed of iron oxide nanoparticles and polymers. ADSORBSIATM is a nanocrystalline titanium dioxide medium in the form of beads from 0.25 to 1.2 mm in diameter. Both nano-adsorbents were highly effective in arsenic removal, and ArsenXnp in particular requires minimal water flow. The estimated treatment cost for ArsenXnp is \$0.25 - \$0.35 per 1000 gallons, if the media is regenerated, similar to the \$0.37 per 1000 gallons of Bayoxide E33, a high-performance granular iron oxide adsorbent. ArsenXnp and ADSORBSIATM have been used in small to medium-sized drinking water treatment systems and have been shown to be cost-effective [28].

4 Conclusion

Nanotechnology for water and wastewater treatment is becoming increasingly well-known and ongoing trials are accelerating globally. The unique properties of nanomaterials and their convergence with current purification technologies present great opportunities to revolutionize the science of water and wastewater treatment. Although many nanotechnologies, highlighted in this paper, are still in the laboratory research stage, some are already being used in pilot tests or are even commercially available.

Nanotechnologies show most promising signs for full-scale application in the near future, based on their stages in research and development, the commercial availability and cost of the nanomaterials used, and the compatibility with existing infrastructure. These technologies already have products on the market, although they have not been applied on a large scale in water purification and wastewater treatment. Also, clay-based nanomaterials show good results in the purification and binding of organic pollutants from liquid waste.

Of course, all these techniques must be judged with more detailed results and indications, after some time of their application. Also, more research must be done on where these nanoparticles end up after their use for water and wastewater purification, and to what extent their toxicity burdens humans and the environment.

The challenges faced by water and wastewater treatment using nanotechnologies are significant, but many of these challenges are perhaps only temporary, including technical obstacles, high costs, and possible environmental impacts on humans. To overcome these obstacles, collaboration between research institutions, industry, government and other stakeholders is deemed necessary and essential.

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