A Survey on the History of Wastewater Treatment Systems Through Membranes and Photocatalysis With Additional Use of Nanomaterials

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Abstract: - The reuse of wastewater has become a common need even as a source of drinking water, but unfortunately collection and treatment systems and water supply have not been designed to meet this imperative need. Moreover, in developed countries there is a need to produce higher quality water with lower energy consumption and cost. In the past few years wastewater has been considered as source of water rather than as a pollution problem. This is from the one side due to the increased need for water of inferior quality in urban and industrial centres, and from the other side due to the need of achieving more efficient wastewater treatment prior to disposal and reuse. During planning and application of wastewater treatment systems, the types of re-use determine the required degree of treatment as well as the degree of reliability of treatment methods. The present study is focused on the usage of the technologies of membranes and photocatalysis with the additional use of nanomaterials for water treatment, as they were developed in the early 21st century. These technologies are effective, but more study is needed on the effects of nanomaterial release in water supplies.

Key-Words: - Water pollution, Wastewater, Purification, Membrane, Photocatalysis, Nanomaterials, Environment, Pollutants

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1 Introduction

Water is one of the most essential resources for sustaining life, the security and availability of which is inextricably linked to global health, energy production, and economic development. Although water and wastewater treatment in the 20th century had multiple applications, such as improving public health and developing agriculture, it also faced many problems. Worldwide, 884 million people do not have access to adequate drinking water and 1.8 million children die each year from diarrhea, mainly due to water contamination. There is an urgent need to develop basic and affordable water treatment methods in developing countries, where drinking water is often non-existent. Water systems in developed countries also face multiple challenges. Current technologies are reaching their limits in addressing increasingly stringent water quality standards and emerging contaminants such as pharmaceuticals, personal care products, and various viruses [1].

The aging infrastructure and water transportation systems are responsible for high energy consumption, water loss, and secondary pollution, while utilities are not adequately addressing much-needed repairs or upgrades to water supply systems (e.g., waterworks). Meanwhile, rapid population growth places 700 million people below the water consumption threshold of 1700 m^3/person per year, and the population is expected to increase to 10 billion. The reuse of municipal wastewater is becoming a necessity in many areas, sometimes as a source of drinking water, but wastewater collection systems and water supply are not designed to serve this need. Clearly, separate central water and wastewater systems are not the solution for a sustainable urban water supply system [2]. Although the existing infrastructure does not contribute to a substantial change and improvement of the system, these enormous challenges require a change to the integrated management of water and wastewater with a decentralized, differentiated treatment and reuse, based on quality standards depending on their origin, use and destination [3].

In this paper, we summarize recent research on the purification and reuse of water and wastewater, utilizing membrane and photocatalysis technologies with the additional use of nanomaterials. Based on these analyses, we offer a vision for the future of integrated water and wastewater treatment systems and their reuse [4].

2 Water Purification

The dilemma between effective disinfection and the formation of toxic disinfection by-products (DBPs) is a major challenge for the water industry. It is now known that conventional disinfectants, such as chlorine and ozone-based disinfectants, can form toxic DBPs (e.g., halogenated disinfection by-products, carcinogenic nitrosamine, etc.). UV disinfection has emerged as an alternative to oxidative disinfection, since it produces minimal toxic DBPs, while requiring high dosage for some viruses (e.g., adenoviruses). These limitations encourage the development of alternative methods that can enhance disinfection efficiency while avoiding the formation of toxic by-products. Many nanomaterials, including nano-Ag, nano-ZnO, nano-TiO_2, nano-Ce_2O_4, CNTs and fullerenes, exhibit antimicrobial properties without strong oxidation and therefore have a lower tendency to form toxic DBPs [5].

2.1 Antimicrobial Mechanisms

Nanosilver is currently the most widely used antimicrobial nanomaterial. Its potent antimicrobial activity, broad antimicrobial spectrum, low toxicity to humans, and ease of use makes it a promising option for water disinfection and microbial control. It is now widely accepted that the antimicrobial activity of nano-Ag largely results from the release of silver ions. Silver ions can bind to thiol groups in vital proteins, resulting in enzyme damage. It has also been reported that silver ions can prevent DNA replication and cause structural changes in the cell envelope. Thus, the release rate and bioavailability of silver ions are crucial for the toxicity of nano-Ag. Studies have shown that the physicochemical properties of nano-Ag play an important role in its antimicrobial activity. However, the influence of size, shape, coating and crystallographic forms appears to be mainly related to different release kinetics of silver ions. The presence of common ligands reduces the bioavailability of silver ions and mitigates their toxicity [6].

A study found that low concentration (sublethal) silver ions or nano-silver enhances the growth of E.coli, which could be counterproductive for antimicrobial applications. CNTs kill bacteria by causing physical disruption of the cell membrane and oxidative stress through a vital cellular component upon direct contact with bacterial cells. Graphene and graphite materials exhibit antimicrobial properties by similar mechanisms. The cytotoxicity of CNTs strongly depends on their physicochemical properties. Dispersed and metallic CNTs with small diameter are more toxic [7].

2.2 Potential Applications of Nano-Antimicrobials in Water Treatment

Antimicrobial nanomaterials are predicted to find applications in the future in important challenges for water and wastewater, such as disinfection, and membrane fouling. Nano-silver has good application prospects in point-of-use (POU) water treatment. It can improve water quality for high-quality use or create another barrier against pathogens for vulnerable population groups. Commercial devices using nano-Ag are already commercially available. Ceramic microfilters have also been incorporated into nano-Ag as an extra barrier to pathogens, which can be used in remote areas in developing countries [8].

The antimicrobial properties such as the fibrous form and high conductivity of CNTs allow the creation of new filters for both bacteria and virus removal. The thin layer of CNTs effectively removes bacteria by size exclusion and viruses from the filtration depth. The retained bacteria are largely inactivated within hours. With a small switching voltage (2-3 V) multi-walled carbon nanotubes can directly oxidize bacteria and viruses and lead to their inactivation within seconds. The applied electrical potential also enhances viral transport to the CNT anodes. Such CNT filters can be used as high-efficiency point-of-use (POU) water treatment devices for water disinfection with minimal to no power requirements (Rahaman et al. in [3]).

A common drawback of many disinfection nanomaterials is the lack of disinfection residue, which is crucial for controlling microbial growth during water storage and distribution. However, the ability to disinfect with chlorine or other chemical disinfectants can reduce DBP formation. Another important uncertainty for all of the above technologies is long-term efficacy. Antimicrobial nanomaterials that rely on the release of biocidal ions will be depleted or regenerated. Because nanomaterials rely on direct contact, contamination can largely suppress or even eliminate their antimicrobial activity.

2.3 Subsection

Pathogen detection is of critical importance, as it is directly related to public health. Conventional indicator systems, such as coliforms, are slow and fail to monitor the presence of some important or emerging pathogens, including viruses (hepatitis A and E, coxsackieviruses, ecoviruses, adenoviruses), bacteria (Legionella and Helicobacter), and protozoa (Cryptosporidium and Giardia). Many of these pathogens are causative agents in drinking water-related outbreaks. In addition, pathogen detection is a key component of diagnostics based on the water disinfection approach, in which disinfection is triggered by the detection of target microorganisms.

Active research is underway to develop nanomaterials with pathogen sensing potential. These sensors typically consist of three main components: the recognition means, the nanomaterials, and a signal transduction mechanism. Recognition agents that specifically interact with antigens or other epitopes of pathogens on the surface provide selectivity, sensitivity, and rapid response, and are achieved by the signal transduction of the nanomaterials (Vikesland & Wigginton in [3]). Agents that have been used include antibodies, aptamers, carbohydrates, and antimicrobial peptides. Nanomaterials improve sensitivity, detection speed, and target recognition with multiplexing due to their unique physicochemical properties, particularly electrochemical, optical, and magnetic. These sensors can be used to detect whole cells as well as biomolecules [9].

The most commonly used nanomaterials for pathogen detection are magnetic nanoparticles, alias Quantum Dots (QDs): quantum dots are fluorescent nanocrystals made of semiconductor materials that are small enough to exhibit quantum mechanical properties, noble metals, dye-enhanced nanoparticles and CNTs. Magnetic nanoparticles and CNTs have been extensively studied for contaminant concentration and purification. Quantum dots have broad absorption spectra, but narrow and stable fluorescence spectra. Thus, they are particularly suitable for multiplex detection using a light excitation source. The emission spectrum of QDs is 10-20 times brighter than an organic fluorochrome and up to thousands of times more stable than conventional dyes (Yan et al. in [3]).

2.4 Preservation and Reuse of Nanomaterials

Preservation and reuse of nanomaterials is a key aspect of nanotechnology that has enabled the design of devices, due to both cost and public health concerns. This can usually be achieved by using a device to separate or immobilize the nanomaterials in the treatment system. A promising separation method is membrane filtration, which allows continuous operation with small traces and minimal use of chemicals. Ceramic membranes are more advantageous than polymeric membranes in photocatalytic or catalytic ozonation applications as they are more resistant to UV radiation and chemical oxidants (Chin & Gentry in [3]).

Suspended particles in water are detrimental to the membrane of the hybrid system reactor, as they can be retained by the membrane and significantly reduce the reaction efficiency. For this reason, raw water requires pretreatment to reduce turbidity. Nanomaterials can also be immobilized on various platforms, such as resins and membranes, to avoid further separation. However, current immobilization techniques usually result in significant loss of process efficiency. Research in this area is needed to develop simple, low-cost methods for immobilizing nanomaterials without significantly affecting their performance. Magnetic nanoparticles/ nanocomposites, with low magnetic separation field, are a potential energy-efficient option.

2.5 Multifunctional Devices

The technological progress and development of nanomaterials in functional systems and their convergence with conventional purification technologies create conditions for the design of a new category of nanotechnology, multifunctional water treatment devices that are able to perform multiple tasks in a single device. Such multifunctional systems can improve overall efficiency and avoid excessive discharges, minimizing the carbon footprint. Therefore, multifunctionality as a concept is particularly beneficial in decentralized and small-scale applications.

Different functional nanomaterials can be integrated into a common platform, based on the needs of the specific treatment method. In addition to magnetic nanoparticles, membranes are a good platform that deserves to be studied extensively for the construction of multifunctional devices. It is worth noting that electrospun nanofibers have attracted particular attention as an excellent carrier for nanomaterials. Due to their high efficiency, small footprint, and unique design of nanotechnology devices, which allows for multiple functions, they can be assembled in spherical shell-like planes or in layers arranged in rows, allowing for the optimization of each function individually. Also, the capacity and functionality of these nanotechnology multi-devices allow the system to be easily modified by inserting or pulling out external layers [4].

3 Membrane Processes

The main objective of water treatment is the removal of unwanted components. Membranes provide a physical barrier to these components based on their size, allowing the use of unconventional water sources. They provide a high level of automation, require less land and chemical use, and due to their modular configuration, allow for flexible design.

A major challenge of membrane technology is the inherent trade-off between membrane selectivity and permeability. High energy consumption due to the need for high pressure is a major obstacle to the widespread application of membrane processes. Membrane fouling increases energy consumption and complexity of design and operation. In addition, it reduces the lifetime of membranes and measurement units. The performance of membrane systems largely depends on the membrane material. The incorporation of functional nanomaterials into membranes offers a great opportunity to improve membrane permeability, fouling resistance, mechanical and thermal stability, as well as enable new functions for doping and self-cleaning [4].

3.1 Nanostructured Catalytic Membranes (NCMs)

Nanostructured catalytic membranes are widely used for water purification. They offer many advantages, such as high uniformity of catalytic sites, optimization potential, limitation of catalyst contact time, thus allowing sequential reactions, and ease on an industrial scale. Many functions including decomposition of organic pollutants, inactivation of microorganisms, antifouling action, and physical separation of water impurities are performed by nanostructured titanium dioxide (TiO_2) films and membranes under ultraviolet and visible light irradiation [10]. N-doped, zinc oxide (ZnO) nanostructured materials forming multifunctional membranes are very effective in removing water impurities by enhancing the activity in the presence of visible light radiation. They have also shown high antibacterial activity and helped in producing clean water with a constant high flux [11].

Various studies have been conducted on the immobilization of metal nanoparticles on membranes (such as cellulose acetate, polyvinylidene fluoride - PVDF, polysulfone, chitosan, etc.) for the effective degradation and dechlorination of toxic substances, which offers many advantages, such as high reactivity, organic sealing, prevention of nanoparticles, lack of aggregation and reduction of surface contamination [12]. Nanocomposite films have been prepared from polyetherimide (a transparent plastic) and palladium acetate, and in particular, interactions between hydrogen and Pd nanoparticles have been shown to increase water treatment efficiency. Metal nanoparticles are produced within the matrix by annealing the film under different conditions using both in situ and ex situ methods. This provides opportunities for designing materials with multiple properties. With the advancement in the field of nanotechnology, several new nanostructured catalytic membranes have been synthesized with increased permeability, selectivity and resistance to anchoring. The techniques include bottom-up approaches and hybrid processes to activate its multiple functions [13].

3.2 Biomimetic Membranes for Water Treatment

The biomimetic membranes developed by Sandia National Laboratories in Albuquerque, New Mexico (USA) and the University of New Mexico, represent a new and advanced way to purify water based on specific design and construction. The invention uses self-assembly and atomic deposition of a layer of coordinated nanopores that generally gives a high desalination flux. The membranes remove impurities such as salt and others from water with applied pressure powered by electricity. The non-porous biomimetic design allows for high salt rejection and very fast water flow at quite low pressures of about 5.5 bars. The process basically uses reverse osmosis with a doubling of the efficiency due to the low-pressure requirement.

With this method, a huge improvement in water purification was observed. The technology uses pressurized water to filter through protein channels in biological membranes, using nanotechnologies that create strong synthetic porous membranes. Some of the advantages of this technique are reduced cost, better water flow, and improved performance with high salt rejection [14].

A biomimetic membrane can be prepared by fusing the vesicle into a dense water-permeable layer, such as an NF membrane. The process uses the electrostatic principle by maximizing the attraction and minimizing the repulsion between the head groups. The biomimetic membrane should have high permeability and selectivity with chemical stability. Chemical stability can be provided by the use of various synthetics, such as aquaporins, carbon nanotubes, etc. Many more developments are expected from this technology in the coming years [15].

3.3 Nanofiber Membranes

Electrospinning is a simple, effective and inexpensive way to create thin fibers using various materials (e.g., polymers, ceramics or even metals). The resulting nanofibers have high specific surface area and porosity and are mat-like in shape with complex pore structures. The diameter, morphology, composition, secondary structure and spatial alignment of the electrospun nanofibers can be easily tailored for specific applications. Although nanofiber membranes have been used commercially for air filtration applications, their potential in water and wastewater treatment is still largely untapped.

Nanofiber membranes can remove microparticles from the aqueous phase at a high rejection rate without significant pollution. Thus, they have been proposed to be used as a pretreatment before ultrafiltration or reverse osmosis (RO). The excellent characteristics and multiple properties make electrospun nanofibers an ideal platform for the construction of multi-membrane filters, either directly by using inherently multifunctional materials, such as TiO_2, or by introducing functional materials. For example, by incorporating ceramic nanomaterials, a nanofiber scaffold can be designed to remove heavy metals and organic pollutants during filtration [16].

Researchers from South Africa have built a filter the size (and shape) of a tea bag, which, at a cost of less than a penny, is intended for water purification. One bag can purify up to one liter of contaminated water. The sachet contains a combination of nanofibers with activated carbon granules.

3.4 Nanocomposite Membranes

A significant number of studies on membrane nanotechnology have focused on creating multiple functionalities by adding nanomaterials to polymeric or inorganic membranes. Nanomaterials used for such applications include hydrophilic metal oxide nanoparticles (e.g., Al_2O_3, TiO_2, and zeolite), antimicrobial nanoparticles (e.g., nano-Ag and CNTs), and photocatalytic nanomaterials (e.g., bi-metallic nanoparticles, TiO_2).

The main goal of adding hydrophilic metal oxide nanoparticles is to reduce fouling by increasing the hydrophilicity of the membrane. The addition of metal oxide nanoparticles including alumina, silica, zeolite and titanium dioxide (TiO_2) to polymeric ultrafiltration membranes has been shown to increase the membrane surface hydrophilicity, water permeability and impact resistance. These inorganic nanoparticles also contribute to improving the mechanical and thermal stability of polymeric membranes, reducing the negative effects of compression and heat on membrane permeability (Pendergast et al. in [3]).

Antimicrobial nanomaterials, such as nano-Ag and CNTs, can reduce membrane biofouling. Ag nanoparticles are grafted onto polymeric membranes to inhibit bacterial attachment and biofilm formation on the membrane surface, as well as inactivating viruses. However, the long-term efficacy of the membrane has not been confirmed. For the practical application of this technology, proper replenishment of the Ag nanoparticles must be implemented. High bacterial inactivation (> 90%) has been achieved using polyvinyl-N-carbazole-SWNT nanocomposites at 3 wt% [17].

While carbon nanotubes are insoluble in water and are not consumed, there is no need for replenishment. However, direct contact is required for inactivation and long-term filtration. The experiments required to determine the effect of impurities on the antimicrobial activity of CNTs require the addition of oxidized carbon nanotube walls at a low weight percentage (up to 1.5 wt%) to increase the hydrophilicity and permeability of polysulfone membranes (De Gusseme et al. in [3]).

Photocatalytic nanoparticles incorporated into membranes (also known as reactive membranes) combine the physical separation function and the activity of a catalyst to degrade impurities. Much effort has been made to develop photocatalytic inorganic membranes consisting of nanophotocatalysts (usually nano-TiO_2 or nano-TiO_2 variants). Metallic nanoparticles, such as nano-zero-valent iron (nZVI) and noble metals incorporated into nZVI, are used for reductive degradation of pollutants, especially chlorinated compounds. Also, nZVI serves as an electron donor and noble metals catalyze the reaction [18].

3.5 TFN Membranes

The development of Thin Film Nanocomposite (TFN) membranes focuses mainly on the incorporation of nanomaterials into the active layer of thin film composites (TFC) by doping in injection solutions or surface modification. Nanomaterials that have been investigated for such applications include nano-zeolites, nanosilver, nanotitanium dioxide and carbon nanotubes. The effect of nanoparticles on the membrane permeability and selectivity depends on the type, size and amount of nanoparticles added.

Zeolites are crystalline aluminosilicate materials consisting of interconnected tetrahedra of the type TO_4, where T=Al^{3+} or Si^{4+}. Each oxygen is shared between two tetrahedra, creating a three-dimensional lattice structure that defines a regular system of “openings” and “channels” of molecular dimensions. For each Al^{3+} atom in the lattice, a negative charge is created, which is balanced by the positive charge of a cation (Na^+, K^+ and others). Zeolites are often called “molecular sieves” due to their ability to separate different molecules based on their size, shape and polarity.

Typically, zeolite membranes are prepared by in-situ hydrothermal synthesis on flat or cylindrical porous substrates such as stainless steel, α-alumina or γ-alumina. Supported zeolite membranes have a thin and continuous zeolite separator layer, with the porous substrate providing mechanical strength. Membranes of various zeolites, such as ZSM-5, Y-type, silicalite-1, A-type, P-type and modernite, have been synthesized on porous substrates.

Nano-zeolites are the most commonly used dopants in thin nanocomposite membranes and have shown potential to enhance membrane permeability. The addition of nano-zeolites leads to more permeable, negatively charged polyamides with a thicker active layer. One study showed that permeability increased by up to 80% for a TFC membrane, with salt rejection largely maintained (93.9%). TFN membranes reinforced with 250nm nano-zeolites at 0.2 wt% achieve moderately higher permeability and better salt rejection (> 99.4%) than commercial RO membranes [19].

With UV irradiation, TiO_2 can degrade organic pollutants and inactivate microorganisms. This helps to reduce organic and biological fouling, as well as to remove pollutants that are not retained by the membrane. However, the close proximity between the photocatalyst and the membrane can also cause detrimental effects on the polymer materials of the membrane, which is aimed at long-term effectiveness (Chin & Gentry in [3]).

Another type of inorganic materials is nanosheet materials (e.g., aluminophosphate flakes). These consist of two-dimensional networks and have no porosity within the individual layers of which they are composed. Through treatment with appropriate active substances for intercalation, with various techniques used for the exfoliation of the individual layers and by incorporating them into suitable polymers, it is possible to produce composite polymeric membranes with remarkable properties in terms of their mechanical strength and their separation capacity.

3.6 Biological Membranes

Many biological membranes are highly selective and permeable. Aquaporins are transmembrane proteins (TMPs) - channels, located in the cell membrane and tonoplast. Aquaporins are found in a wide variety of cells, animal and plant organisms. They facilitate the transport of water across membranes. They are proteins that regulate water flow channels across cell membranes. Their high selectivity and permeability to water makes the use of polymeric membranes an attractive approach to improve the performance of the aquaporin-Z membrane in the treatment of E. coli [15].

Aligned CNTs have been shown both experimentally and theoretically to provide water flux much faster than predicted by the Hagene-Poiseuille equation, due to the atomic regularity of the nano-sized channel, and the dimensions of the water molecules arranged, passing through the nanotubes. Hoek in 2011 predicted that a membrane with only 0.03% of the surface area of aligned CNTs would have fluxes that would exceed current commercial seawater RO membranes. However, the high rejection for salt and small molecules is a challenge for the creation of aligned CNT membranes, due to the lack of CNTs with uniform diameter. A fairly low ionic strength was achieved by carboxyl grafting, however the KCl rejection rate was only 50% at 0.3 mM, and decreased to almost zero at 10 mM [20].

To date, chemical vapor deposition (CVD) is the most common way to align nanotubes. A continuous high-throughput CVD protocol has been developed to produce vertically aligned CNTs, paving the way for large-scale production. A post-fabrication alignment method using magnetic fields has also been developed.

Nanocomposite and TFN membranes have good scalability, since they can be fabricated using current industrial manufacturing processes. High water permeability can reduce the applied pressure on the required membrane area and, consequently, the cost. This strategy can significantly improve energy efficiency for the decontamination of waters with low osmotic pressure, but may have limited advantage in seawater, for which energy consumption is close to the thermodynamic limit [21].

NCSR Demokritos of Greece has developed a set of efficient and sustainable water detoxification technologies, exploiting solar energy and recent developments in nanostructured titanium photocatalytic membranes for the destruction of highly hazardous compounds in water, including new emerging pollutants. These technologies have been incorporated into water purification membranes that allow the purification of water from hazardous toxins and other organic compounds (phenols, pesticides, hormones, etc.) with greater efficiency than conventional means. The activity is part of the European Clean Water project, the implementation of which has also led to new developments in photocatalytic air purification, hydrogen production, and solar energy conversion (solar cells), thus opening new horizons in nanotechnology applications in the environment and energy.

3.7 Bioactive Nanoparticles

Water pollution has caused many infectious diseases due to various pathogens. Many of the microorganisms act as pathogens, which are highly resistant to antibiotics and for this reason are very difficult to remove from water. Recently, the concept of bioactive nanoparticles has provided the alternative solution to create new, chlorine-free biocides. Also, silver nanoparticles (AgNPs) can be synthesized extracellularly by the bacterium Bacillus cereus, which has very high antibacterial activity.

The silver-resistant strain was exposed to different concentrations of silver nitrate ($AgNO_3$) and observed by high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). The results showed that MgO nanoparticles with incorporated Ag nanoparticles are very effective biocides against gram-positive and gram-negative bacteria and bacterial spores. Current nanotechnology approaches for the detection of pathogenic microbial organisms are at a good stage, and future studies focus not only on pathogen detection but also on diagnosis (Nora et al. in [3]).

3.8 Forward Osmosis

Forward Osmosis (FO) uses the osmotic gradient to draw water from a solution of low osmotic pressure to a solution of high osmotic pressure. The diluted solution is then treated by reverse osmosis or thermal treatment to produce pure water. FO has two major advantages over reverse osmosis pressure ratio:

- it does not require high pressure, and
- the membrane is less susceptible to fouling.

The key to FO is to have a balanced solution of a substance with high osmotic pressure and easily separable from water. Chemical solutions for a balanced solution of a substance require sodium chloride and ammonium bicarbonate. However, recovering the water from the solution requires a large amount of energy for thermal treatment. Magnetic nanoparticles have recently been investigated as a new type of solute for easy separation and reuse (Liu et al. in [3]).

4 Photocatalysis

Photocatalytic oxidation is an advanced oxidation process for the removal of pollutants, trace elements and pathogenic microbial organisms. It is a useful pretreatment tool for hazardous and non-biodegradable contaminants and for enhancing their biodegradability. Photocatalysis can also be used as a polishing step for the removal of persistent organic compounds. The biggest obstacle to its widespread application is its slow kinetics, due to the limited light flux and photocatalytic activity.

4.1 Nanocatalysts

Nanocatalysts are also widely used in water treatment, as they increase the catalytic activity on the surface due to their special characteristics, such as larger surface area and shape. They also enhance the reactivity and degradation of pollutants. The most common nanoparticle catalysts are semiconducting materials, zero-valent metal and bimetallic nanoparticles that are used for the degradation of environmental pollutants such as PCBs (polychlorinated biphenyls), azo dyes, halogenated aliphatics, organochlorine pesticides, and halogenated herbicides [22].

Catalytic activity has been demonstrated in laboratory for various pollutants. Since hydrogen is used to manufacture active catalysts on a large scale from redox reactions, there is a need to reduce its consumption and save money by directly preparing catalysts in metallic form. Silver Ag-based nanocatalysts (AgCCA, supported by TiO_2 and ZrO_2) have been produced, which are particularly effective for the degradation of microbial pollutants from water and can be reused, as well as for waste treatment due to the modification made to TiO_2 nanoparticles, leading to a shift in the absorption band by ultraviolet light [23].

Wastes with specific impurities, such as traces of halogenated organic compounds (HOCs), can be selectively biodegraded using advanced nanocatalysts. The contaminants (HOCs) are first converted to organic compounds, using nano-sized lead (Pd) catalysts, followed by biodegradation in the treatment plant. The nanocatalysts can be easily recycled and reused due to their ferromagnetism, which aids in separation. The reducing agents for the reaction can be hydrogen or formic acid, depending on the level of contamination (Hildebrand et al. in [3]).

It has also been found that silver and amidoxime fiber nanocatalysts, created by coordination interactions, can be activated multiple times for the treatment of simple tetrahydrofurans and, therefore, can be effectively used for the degradation of organic dyes [18].

It has been discovered that when palladium (Pd) is incorporated with zinc oxide (ZnO), the nanoparticles have very high photocatalytic activity for the removal of E.coli bacteria from water. According to several analytical studies, the use of different concentrations of Pd on ZnO nanoparticles in water showed increased removal of E.coli, when used in combination with a 355 nm laser pulse. Another approach to improve the process is the combination of nanoadsorbents with a catalyst for the combined adsorption and degradation of pollutants. Finally, nanocatalysis has proven to be a very effective process in water treatment and reuse (Khalil & Nowack in [3]).

4.2 Optimization of Nanophotocatalysis

Titanium dioxide (TiO_2) is the most widely used semiconductor photocatalyst for water and wastewater treatment due to its low toxicity, chemical stability, low cost and abundance as a raw material. It produces an electron/hole pair by absorbing UV photons, which is later either transported to the surface in the form of reactive oxygen species (ROS) or undergoes unwanted recombination. The photoactivity of nano-TiO_2 can be improved by optimizing the particle size and shape, reducing the e-/h, recombining noble metals, maximizing reactive sites and surface treatment to improve pollutant adsorption.

The size of TiO_2 plays an important role in the solid phase transformation, adsorption and e-dynamics. Among the crystal structures of TiO_2, rutile is the most stable for particles larger than 35 nm, while anatase, which is more effective in ROS generation, is most stable for particles smaller than 11 nm. An important reason for the slow kinetics of the TiO_2 photocatalytic reaction is the rapid recombination of e- and h+. Reducing the size of TiO_2 particles reduces the volume of recombination of e- and h+, and enhances the interfacial charge transfer of the carrier. However, when the particle size is reduced to several nanometers, surface recombination dominates, reducing the photocatalytic activity. Therefore, the photocatalytic activity of TiO_2 has a maximum, due to the interaction of the aforementioned mechanism, which is in the nanometer range. TiO_2 nanotubes were found to be more effective than TiO_2 nanoparticles for the degradation of organic compounds. The higher photocatalytic activity was achieved by the shorter diffusion carrier paths in the tube walls and the faster mass transfer of the reactants to the surface of the nanotubes [24].

4.3 Potential Applications of Photocatalysis in Water Treatment

The overall performance of a photocatalytic water treatment process strongly depends on the configuration and operating parameters of the photoreactor. Two types of reactors are commonly used: sludge reactors and reactors using immobilized TiO_2. Various recovery/dispersion or catalytic immobilization techniques are used to maximize its efficiency. Extensive laboratory research on operating parameters has been carried out at pilot scale. A recent critical review describes the effects on water quality and a wide range of operating parameters, including TiO_2 loading, pH, temperature, dissolved oxygen, concentration, wavelength and light intensity [25].

Purifics company in Canada has developed a relatively small photocatalytic water purification plant, with a treatment capacity of more than 2 million gallons per day. Pilot tests have shown that this photocatalytic system is highly efficient in removing organic pollutants without producing waste, and operates with a relatively low specific energy consumption of about 4 kWh/m^3. Nano-TiO_2 has been extensively tested and appears to be a feasible option for producing drinking water, using solar disinfection (SODIS) in remote areas of developing countries. The SODIS system can be as small as a single person or as large as a medium-sized system with complex solar parabolic trough collectors [26].

Photocatalysis has great potential as a low-cost, environmentally friendly and sustainable technology for water treatment. However, there are several technical challenges for its large-scale application, such as:

a) Optimization of the catalyst to improve quantum yield or utilization of visible light;

b) Efficient design of the photocatalytic reactor and catalyst recovery/immobilization techniques;
c) Better selectivity of the reaction.

Metallic nitrogen oxide nanomaterials (e.g., TiO_2 or CeO_2), as well as carbon nanotubes, have been studied as catalysts in heterogeneous catalytic ozonation processes, and provide fast and comparatively complete degradation of organic pollutants. The adsorption of ozone and pollutants on the catalyst surface plays a critical role in both mechanisms. Nanomaterials have a large specific surface area and easily accessible surface area, leading to high catalytic activity. Some nanomaterials have also been reported to promote the decomposition of ozone into hydroxyl radicals, facilitating the degradation process via pathways. For future industrial applications, a better understanding of the mechanism of catalytic ozonation of nanomaterials is essential [27].

5 Conclusion

Membrane and photocatalysis technologies with the additional use of nanomaterials for water purification and disinfection are promising and effective. However, little is known about the release of nanomaterials from activated nanotechnology devices. The eventual release is expected to depend largely on the immobilization technique and separation process used. If no in situ separation is applied, nanomaterials coating the surfaces of the purification system are more likely to circulate in a relatively rapid and complete manner, while nanomaterials embedded in a solid matrix will have minimal circulation until their final disposal. For nanomaterials releasing metal ions, their solubilization should be carefully controlled (e.g., by coating or by size and shape optimization).

The detection of nanomaterial release is a major technical obstacle to risk assessment and remains a huge challenge. Some techniques can detect nanomaterials in complex aqueous substrates, although they are usually complex, expensive and have many limitations. The early detection of toxic and pollutant substances in water is an issue of major concern, due to the intrusion of these substances in the food chain and eventually in humans [28],[29]. Therefore, towards an early detection of water pollutants, robotic devices are recently being developed, which are programmed for autonomous movement in aquatic environments, collection of water samples and in-situ analysis of pollutants with various technologies such as spectroscopy [30].

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