INTERNATIONAL JOURNAL OF ENHANCED RESEARCH IN SCIENCE TECHNOLOGY & ENGINEERING
VOL. 1 ISSUE 2, NOV-2012 ISSN No: 2319-7463

Nanotechnology : An Emerging Future Trend in Wastewater Treatment with its Innovative Products and Processes

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Abstract- Rapid population growth has evolved the big problem of limited fresh water supply in the world and the wastewater treatment is the only recycling process which can overcome this problem. Technology advancement has led us to the nanotechnology which is having tremendous scope for wastewater treatment. Nanoadsorbents, magnetic nanoparticles, nanofiltration, nano zero valent iron, nanocatalysts, nanobiocides, nanofibers and mixed technology including catalytic wet air oxidation along with nanoparticles are the products and techniques which are evolved as a result of development in nanotechnology and are being used in wastewater treatment. Other than wastewater treatment, desalination is also a significant process to convert sea water into fresh water and this process is further improved by using nanoscale to make it more efficient at large scale. In this article, several experiences with nanotechnology in combination with biological methods in the wastewater treatment are described. Along with the benefits, the potential risks of nanotechnology for the environment are also addressed in this article.

Keywords- Catalyst, Desalination, Nanoadsorbents, Nanotechnology, Nano Zero Valent Iron, Wastewater Treatment.

I. INTRODUCTION

With the present rate of population growth, world's population will rise up to 9 billion by 2050, which will cause the severe shortage of fresh water in near future. Unfortunately, 97% of the world's water is salt water; of the remaining 3%, two thirds are frozen while the remaining 1% of the world's water supply is not evenly distributed, and this shortage is really a serious problem for developing countries. [1] Every day, 2 million tons of sewage and industrial and agricultural waste are discharged into the world's water (UN WWAP 2003), the equivalent of the weight of the entire human population of 6.8 billion people. The UN estimates that the amount of wastewater produced annually is about 1,500 km^3, six times more water than exists in all the rivers of the world. (UN WWAP 2003) The World Health Organization (WHO) has estimated that 80% of illnesses in the developing world are water related, resulting from poor water quality and a lack of sanitation. . Lack of adequate sanitation contaminates water courses worldwide and is one of the most significant forms of water pollution. There are 3.3 million deaths each year from diarrheal diseases caused by *E. coli*, Salmonella and Cholera bacterial infections, and parasites and viral pathogens. In the 1990s, the number of children who died of diarrhoea was greater than the sum of people killed in conflicts since World War II. [1] To overcome these problems, wastewater treatment is required to recycle the wastewater from different sources into the useful form. Here are numerous processes that are being used to clean up wastewaters depending on the type and extent of contamination. Most wastewater is treated in industrial-scale wastewater treatment plants which may include physical, chemical and biological treatment processes. New approaches are continuously being examined to supplement traditional water treatment methods. These need to be lower in cost and more effective than current techniques for the removal of contaminants from water. In this context also nanotechnological approaches are considered. For the purpose of improving the traditional treatment methods, the use of nanomaterials is being researched to fabricate the separation and reactive media which is of high quality in terms of reactivity and performance.[2] Nanomaterials and nanoparticles are the advanced and significant approaches for the bioremediation and disinfection of wastewater.[3][4] For instance, metal oxide nanomaterials such as TiO_2 are among promising nano-catalysts that are tested successfully for their antimicrobial activity. Major potential environmental benefits of nanotechnology were reported in the draft nanomaterials research strategy, which includes early environmental treatment and remediation, stronger and lighter nanomaterials and more accurate sensitive sensing devices.[5] Other benefits include the cost-effective use of renewable energy, low energy requirement and low waste generation devices, pollution control and the prevention and remediation using improved systems. Desalination process is also improved by using nanomembrane making it cost efficient process which is helpful in resolving the problem of limited fresh water supply. Nanotechnology is effecting the environment, fauna and flora with positive effects along with some potential risks.

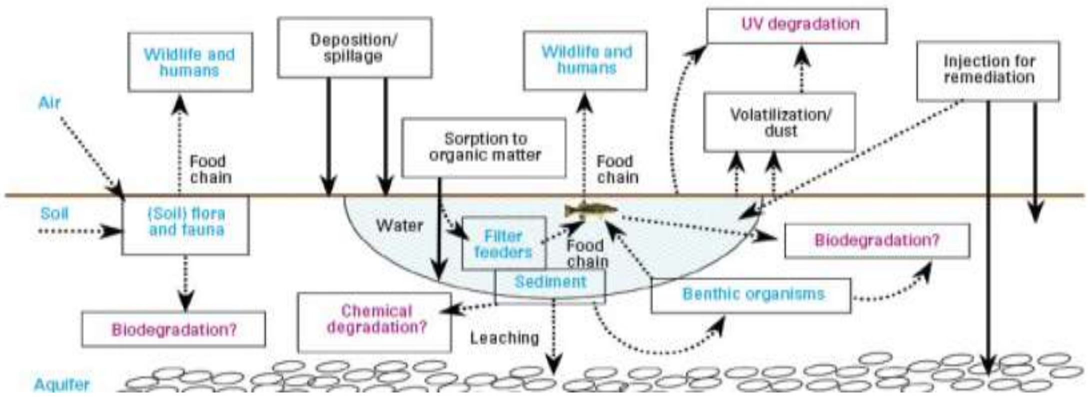

Figure 1. Suggested routes of exposure, uptake, distribution, and degradation of nanoparticles in the environment. Reprinted from Laurie Gneiding's (AMEC) 2008 STEAC Presentation.

II. NANOTECHNOLOGY BASED PROCESSES & PRODUCTS IN WASTEWATER TREATMENT AND WATER PURIFICATION

A. Nanoadsorbents

Adsorption had been reported as the most technically and economically viable option.[6] Furthermore, research in wastewater treatment by adsorption has resulted in development of different materials for removal of metals from solutions, these materials include: natural product , Activated Carbon, Zeolites, Aluminosilicate, Peat Kaolin and Clay and polysaccharides .[6][7][8][9][10][11] Recently, Carbon nanomaterials (CNMs) mainly in the form of Carbon nanotubes (CNTs) and Carbon nanofibers (CNFs) are being used as new adsorbents with superior performance due to their high specific surface area and high aspect ratio. Work on the effect of morphology, surface functional groups on adsorption capacity of heavy metals by CNMs had been carried out. [12][13][14] Multiwall carbon nanotubes (MWCNTs) are having metal-ion sorption capacity of 3–4 times larger than the widely used powder and Granular activated carbon (GAC) .[15] Adsorption is being carried out as per equation V(A) and V(B).

B. Magnetic Nanoparticles

Polyrhodanine-encapsulated Magnetic Nanoparticles (PR-MNPs) are a new efficient way of effectively removing heavy metal ions from solution. Particles are manufactured from an aqueous solution of Rhodanine (7.5mM), Iron Chloride (6.2mM), and Sodium Borohydride (26mM), and synthesized by a one-step chemical oxidation polymerization. Drag force on magnetic particle is determined by equation V(D). Adsorbing will commence due to the metal-binding functional groups provided by the Rhodanine monomeric unit. Harvesting of the final product is as simple as subjecting the solution to a magnetic field. The particles magnetic properties and large surface area also give it an edge when attracting unwanted metals. [16]. Treatment of chemically contaminated wastewater has strongly profited from the development of scale-up correlations for sewage treatment plants. Prior to exposure to oxide nanoparticle dispersions, the sludge is stabilized following the OECD guidelines. With the broad range of now available nanoparticles, detailed characterization of materials in their form of application is a prerequisite to both toxicological and environmental studies. All studies have shown a dominating effect of surface charge on the kinetics of agglomeration and, as a consequence, on the physical behavior of the nanomaterials.

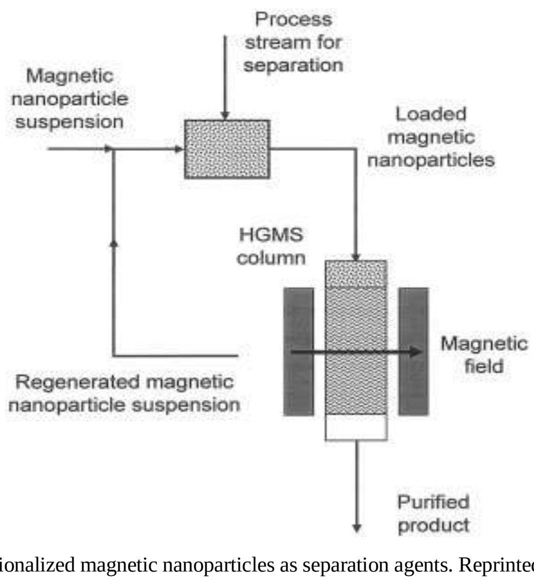

Figure 2. A generalized process using functionalized magnetic nanoparticles as separation agents. Reprinted from AIChE Journal, 2004, 50 (11): 2835-2848

C. Nanofiltration

Nanofiltration (NF) is a rapidly advancing membrane separation technique for water and wastewater treatment due to its unique charge-based repulsion property and high rate of permeation. NF can be defined as a pressure driven process wherein the pore size of the membrane (0.5-1 nm) as well as the trans-membrane pressure (5-21 atm) lies between reverse osmosis and ultrafiltration. Due to the lower operating pressure and higher flow rates, nanofiltration is inexpensive when compared to reverse osmosis. NF membranes allow partial permeation of monovalent salts such as sodium chloride while rejecting bivalent salts and hardness to a greater extent from aqueous solutions. NF can lower Total dissolved solids (TDS) and hardness, reduce color and odor, and remove heavy metal ions from ground water. [17][18] Flux rate is determined by equation V(C). NF systems are usually operated at medium pressures in the range of 10-50 bar, and have much higher water fluxes compared to RO membranes. NF can be applied for separation between ions with different valences and for separation of low- and high-molecular weight components. Polymeric NF membranes show diversity in separation behaviour but they are common in rejecting highly charged ions (such as Sulphate, Carbonate and Phosphate) in a higher degree, while in comparison, rejection of single charge ions (Cl^-, Na^+, K^+) is much less. The transportation of non-charged solutes through an NF membrane is usually characterized by the term of molecular weight cut-off (MWCO), which is a number expressed in Dalton indicating the molecular weight of a hypothetical non-charged solute that is in 90% rejected. The MWCO of NF membranes is usually given by the manufacturers and typically in the range of about 200-1500 Dalton. However, there are currently no standard methods for characterizing and reporting MWCO. The meaning of this information can vary between different membrane manufactures, thus limiting its value. The applied experimental technique has a significant impact on the measured MWCO. The experimental conditions, such as the hydrodynamic flow conditions, the temperature, the applied pressure or the range of the applied pressure-scan, the type of solute(s), are often not reported. Besides, the different techniques for MWCO make membranes from different manufacturers hardly comparable without further experimental investigations. Moreover, the concept of MWCO does not address the question of how great the permeation of solutes smaller and larger than the indicated MWCO can be. Membranes have been historically characterized by MWCO rather than by membrane pore size. It should be noted that this concept is based on practical aspects and has no true physical meaning. The molecular weight is not a straightforward measure of the size and it ignores the shape of the permeating molecule, and thus, it gives only a rough estimation of the membrane's ability to remove dissolved uncharged components. Several direct characterization methods are known for NF membranes such as permporometry, gas adsorption-desorption and microscopy techniques. However, the pore size determination of polymeric membranes seems to be still an unsolved problem. Permporometry analysis requires pores larger than 2 nm, and the nitrogen adsorption-desorption method only for inorganic membranes can be effectively applied.

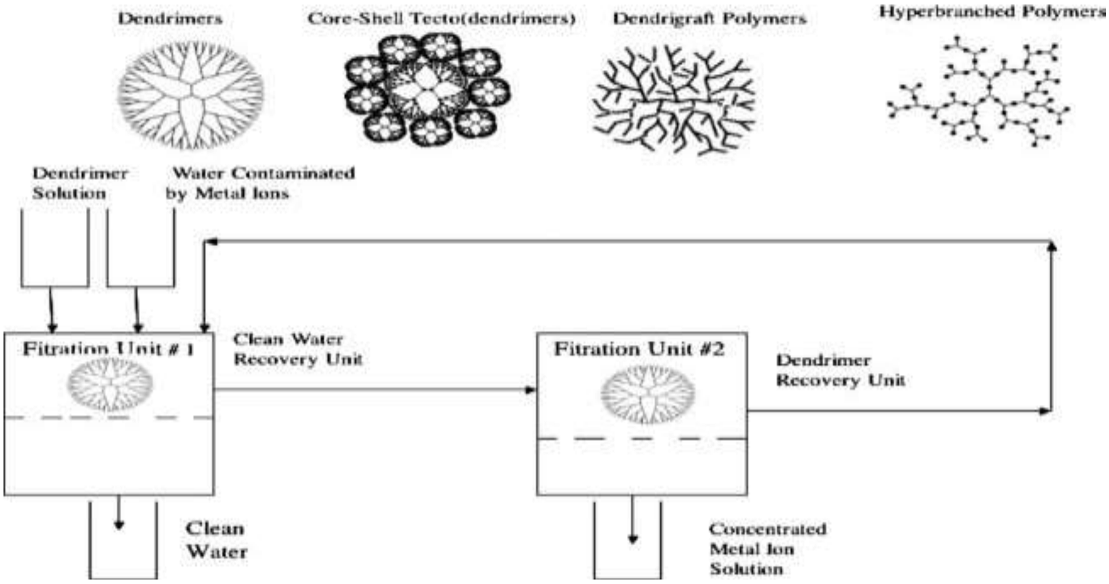

Figure 3. Recovery of metal ions from aqueous solutions by dendrimer enhanced filtration. Reprinted with permission from Environmental Science and Technology, 2005, 39: 1366–1377. Copyright 2005 American Chemical Society

D. Nano Zero Valent Iron

Nano Zero Valent Iron (nZVI) is emerging as new option for the treatment of contaminated soil and groundwater. Due to their small size, the particles are very reactive (more reactive than granular iron which is conventionally applied in reactive barriers) and can be used for in situ treatment. nZVI effectively reduces chlorinated organic contaminants and also inorganic anions (Perchlorate). It can even be used to recover/remove dissolved metals from solution (e.g. Cr (VI), U (VI)). The mobility and the lifetime of nZVI particles are limited. Therefore several modifications of nZVI are studied, tested and commercialized. The most important are surface-modified nZVI, emulsified nZVI (better miscibility with DNAPL), bimetallic nZVI (higher reactivity) and nZVI on carbon support (better distribution within the soil).

If nZVI reacts with ionic heavy metals such as Pb2+, the following reaction takes place:

$Pb^{2+} + Fe^0 \rightarrow Pb^0 + Fe^{2+}$

If chlorinated hydrocarbons are present, the following reaction takes place:

$R\text{-}Cl + Fe^0 + H^2O \rightarrow R\text{-}H + Fe^{2+} + Cl^- + OH^-$

nZVI is not particularly stable. In dry form, the powder ignites immediately when in contact with air. Storage in dry form is only possible in an inert atmosphere. For safety reasons, nZVI is thus in most cases provided as slurry. However, in suspension it also oxidizes fairly rapidly to iron oxides. Possible oxidants – besides the target contaminants - are oxygen, sulphate, nitrate or water. This fact has implications not only for the application in the soil, but also for its transport and storage. [19][20]

E. Nanocatalysts

Nanocatalysts have the advantage of very high reaction rates due to high specific surface areas and low mass-transfer restrictions. For special applications in wastewater treatment we were able to generate extremely active palladium catalysts on the basis of ferromagnetic carrier colloids. The magnetic nano-sized carriers (such as Zero Valent Iron or Magnetite) are spiked with traces of Pd. These nanocatalysts have been successfully tested in different reactor systems at the laboratory scale. Using Pd on nano-scale supports leads to enormous activity of the catalyst which is several orders of magnitude higher than reached in conventional fixed-bed reactors. The ferromagnetism of the carriers enables a separation of the catalysts from the treated water by means of magneto-separation.[21] This gives the chance to reuse the catalyst several times. N-doped TiO_2 are also the advanced nanocatalysts because of higher catalytic activity. [22]

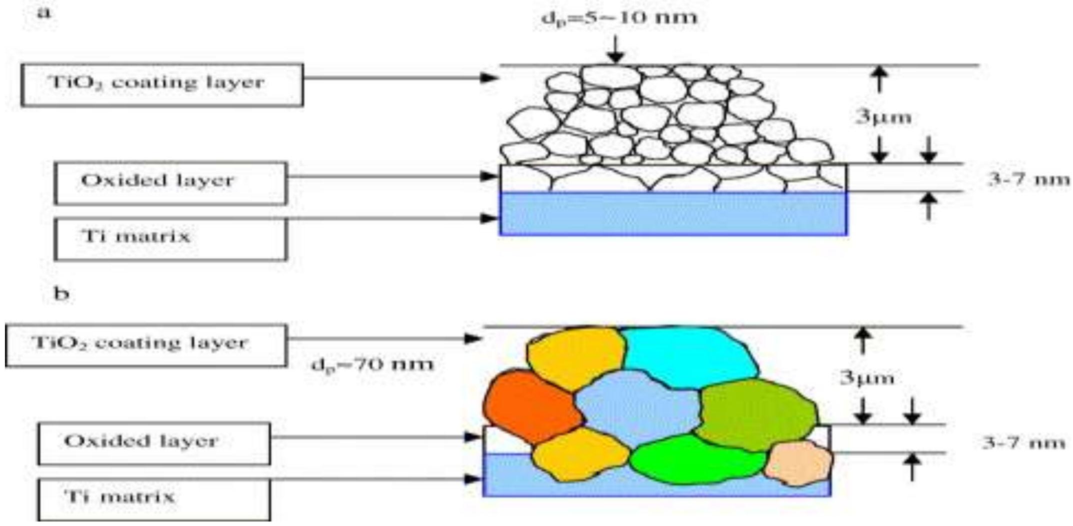

Figure 4. Sketch map of the changing process between nano-TiO_2 particles coating and oxided film at the sintering temperature. **(a)** nano-TiO2 particles coating on the oxided film of Ti matrix; **(b)** nano-TiO_2 particles conglomerate and grow up, and knit with the oxided layer on the surface of Ti matrix at the sintering temperature. Reprinted from Materials Letters, 59 (24-25): 3144-3148.

F. Nanofibers

Nanofiber technology in combination with biological removal of toxic xenobiotics is the advanced method in industrial wastewater treatment process. Microbial biofilm formation can be greatly supported using nanofiber structures, and the whole system provides stable and accelerated biodegradation. Nanofiber carriers are examined on various parameters like cleaning efficiency of toxic compounds, stability of carrier and nanofiber layer, rate of carrier ingrowths by relevant microorganisms, disintegration of nanofibers and sorption properties. Each biomass carrier must meet the basic parameters (microorganism colonization ability, chemical and physical stability, surface morphology, maximum specific surface). The exceptional properties of nanofiber carriers are primarily the large specific surface, high porosity and small pore size. Electrospun Polyacrylonitrile nanofiber mats are being used for heavy metal ion removal because of tremendous potential as a heterogeneous adsorbent for metal ions. [23] Depending on the type of polymer, nanofibers are durable, easily moldable and chemical resistant. The principal advantage of nanofiber materials is their comparability with the dimensions of micro-organisms, the surface morphology and biocompatibility, which allows for faster colonization of the nanofiber surface by the microorganisms. An important advantage of the technology is the possibility of a bacterial biofilm buildup not only on the surface of the carrier but also closer to its center (inside the carrier), where the bacteria are much more protected against the toxic effects of the surrounding environment and shear forces during hydraulic mixing. In addition, penetration of substrate and oxygen to the microorganisms is also possible. High specific surface of the nanofiber layer allows to the bacteria great adhesiveness and as a result it simplifies the immobilization of microorganisms, especially in the initial stages of colonization of the surface carriers and also even during difficult emergency conditions (reducing the required regeneration time). After a longer period of colonization the microbial biomass grows naturally on the places without the nanofibers thus making the process of wastewater treatment more efficient. Fe-Grown Carbon Nanofibers are being used for removal of Arsenic (V) in wastewater. [24]

Table 1. Polymers and solvents applied for electrospun nanofibrous material.

Polymer	**Solvent**	**Concentration (wt %)**	**Reference**
Polyurethane	Dimethyl formamide	10	Tsaia *et al.* (2002)
Polylactic acid	Dichloromethane	20	Bognitzki *et al.* (2001)
Polyethylene oxide	Isopropyl alcohol & water	5	Morozov *et al.* (1998)
Polyvinylcarbazole	Dichlormethane	10	Bognitzki *et al.* (2000)
Polystyrene	Tetrahydrofuran	7.5	Torres (2001)
Cellulose acetate (CA)	Acetone, acetic acid	17	Han *et al.* (2002)

G. Nanobiocides

Biofouling of membranes caused by the bacterial load in water reduces the quality of drinking water and has become a major problem. Several studies showed inhibition of these bacteria after exposure to nanofibers with functionalized surfaces. Nanobiocides such as metal nanoparticles and engineered nanomaterials are successfully incorporated into nanofibers showing high antimicrobial activity and stability in water. Nanofibers with embedded nanobiocides are currently being used in medical treatments and air filters. Nanobiocides are divided into three categories, namely, metal and metal oxides (nAg, ZnO, CuO, TiO_2), engineered/synthesized nanomaterials (Fullerenes e.g., nanomagnetite (nC60) and carbon nanotubes), and natural antibacterial substances (antimicrobial substances, chitosan). [25][26][27][28] Chitosan is also applied in a high flux ultrafiltration media by replacing flux-limiting asymmetric porous membrane with porous electrospun nanofibrous scaffolds. The demonstrated systems consisted of a three-tier composite structure:

- Nonporous hydrophilic coating that is water permeable i.e. Chitosan.
- Polyacrylonitrile (PAN), an electrospun nanofibrous support.
- Polyethylene terephthalate (PET), a non-woven microfibrous substrate.

PAN is resistant to most solvents and has therefore been widely used for ultrafiltration, nanofiltration and reverse osmosis. Carbon nanofibers were also fabricated with electrospun PAN as precursor. The PAN fibrous networking is used to support a top coating layer based on chitosan .Chitosan has been used for anti-fouling enhancement of filtration membranes duo to its insolubility in neutral pH conditions and thus water resistance.

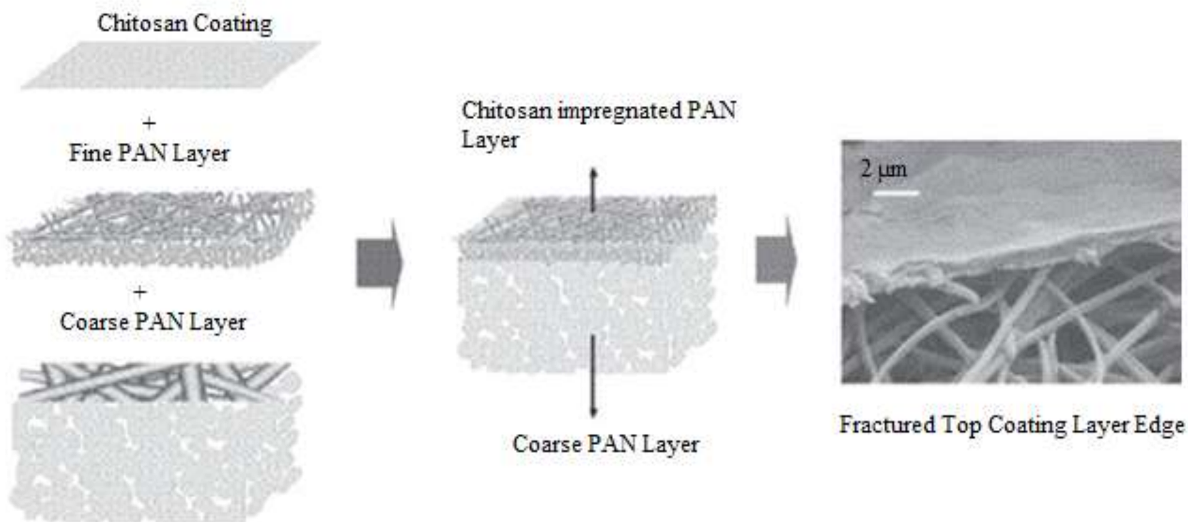

Figure 5. Fabrication schematics of the electrospun scaffold with a coating layer. SEM image represents the fractured composite membrane containing PAN nanofibrous scaffold (with 4 + 12 wt% sequential electrospinning) and chitosan coating (Yoon *et al*., 2006).

H. Catalytic Wet Air Oxidation using Nanoparticles

A great challenge in nanotechnology is to design highly selective catalysts comprising of an active site with the correct ensemble of metal atoms and other active components. The main advantage of nanocatalysts prepared in organic functional polymers is the easy tailoring via variation of the polymer nature. Such catalysts are characterized by high activity-selectivity-stability. Here we report the synthesis of Pt, Pd, Ru nanoparticles impregnated in hypercrosslinked polystyrene matrix as efficient catalysts for CWAO of phenol. CWAO treatment of phenol compounds realized on the base of hypercrosslinked polystyrene impregnated with platinum nanoparticles leads to high phenol conversion.[29] Catalytic wet air oxidation of Oxalic Acid using Platinum catalysts in Bubble Column Reactor provides an efficient method of combustion at very low temperature as compared to thermal incineration.[30]

I. Desalination by Nanomembrane

To overcome the problem of limited fresh water supply, an energy-efficient approach to converting sea water into fresh water could be of substantial benefit, but current desalination methods require high power consumption and operating costs, which make them difficult to implement and this problem can be resolved by using nanomembrane in desalination. In desalination process a continuous stream of sea water is divided into desalted and concentrated streams by ion concentration polarization. During operation, both salts and larger particles (cells, viruses and microorganisms) are pushed away from the nanomembrane, which significantly reduces the possibility of membrane fouling and salt accumulation, thus avoiding two problems that plague other membrane filtration methods. To implement this approach, a simple microfluidic device is fabricated and shown to be capable of continuous desalination of sea water (~99% salt rejection at 50% recovery rate) at a power consumption of less than 3.5 Wh l^{-1}, which is comparable to current state-of-the-art systems.[31][32]

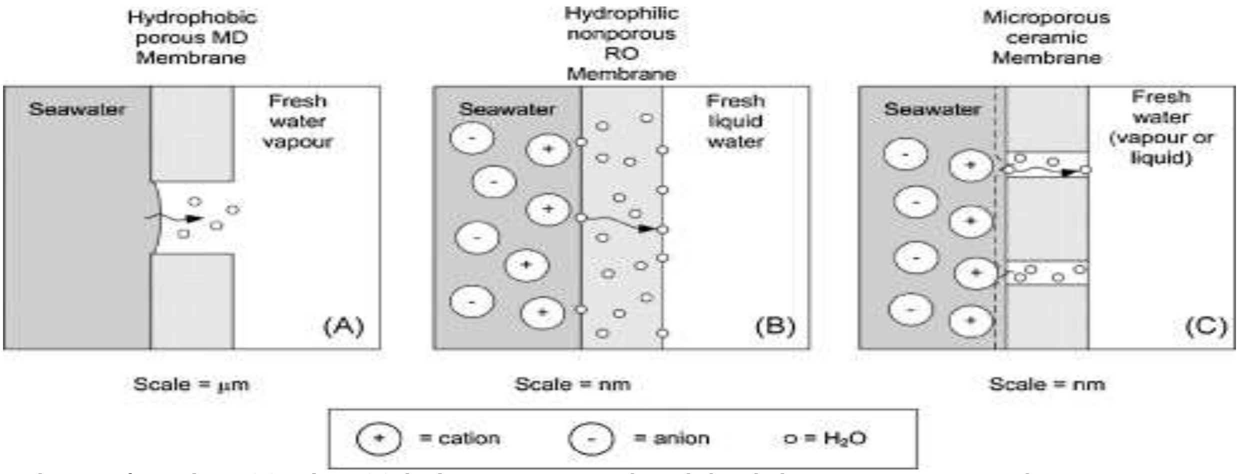

Figure 6. Schematic of typical MD (A) and RO (B) desalination processes at the scale by which governing separation mechanisms operate. Porous ceramic membrane process (C) describes the molecular level transport applicable to both MD and RO. Dotted line in (C) represents the negative surface charge applicable to silica based materials at neutral pH which creates a static double layer of ions in feed. Reprinted from Separation and Purification Technology, 2009, 68 (3): 343-350.

III. Benefits of Using Nanotechnology in Wastewater Treatment

A. *Increased Effectiveness*

Contaminants could be more effectively removed, even at low concentrations, due to the increased specificity of nanotechnology and the development of "smart" filters tailored for specific uses.

B. *Removal of New Contaminants*

Contaminants that were previously impossible to remove could now be removed. This will be achieved through novel reactions at the nanoscale due to the increased number of surface atoms.

C. *Simplification*

Nanotechnology could radically reduce the number of steps, materials and energy needed to purify water, making it easier to implement widely in rural communities.

D. *Reduced cost*

Substantial initial investment would be needed to incorporate or switch to nanotechnology–based water treatments. However, once adopted, these techniques could considerably lower water treatment costs over the long term

IV. Potential Issues

Nanotechnology risks can be best understood in conjunction with its benefits. The catalytic activity of a nanoparticle can be advantageous when used for the degradation of pollutants, but can induce a toxic response when taken up by a cell The complexity of the technology, the breadth of nanomaterials and applications, coupled with the possibility of its wide dissemination in the globalized world renders the technology unpredictable in many senses. The risks are heterogeneous as the field of nanotechnology itself and include environmental, health, occupational and socio economic risks. The unusual properties of nanomaterials that can enable rewarding applications for society might pose unknown or unforeseen environment, health and safety challenges. A consistent body of evidence shows that nanosized particles can be taken up by a wide variety of mammalian cell types, are able to cross the cell membrane and become internalized. [33][34] The pro-technology stance taken in several developed and developing countries at the cost of risk related research has led to an information gap around the impacts of nanomaterials. These aspects together with the commercialization and pervasiveness of nanoproducts serve to heighten the risk from this emergent technology. Another major challenge is the availability of suppliers of nanomaterials. As mentioned earlier, nanomaterials are known for their high surface area to mass ratio and can therefore perform their function at a more affordable price. However, if suppliers of these materials are not readily available, it could seriously undermine the potential advantages of using this technology. [35]

V. EQUATIONS

A. *Langmuir Equation*

$\theta = \alpha.P/ 1+ \alpha.P$

θ = Fractional coverage of the surface.
P = Gas pressure or concentration.

α = Constant.
The constant α is the Langmuir adsorption constant and increases with an increase in the binding energy of adsorption and with a decrease in temperature

B. *Freundlich Adsorption Isotherm*

$x/m = Kp^{1/n}$
x = Mass of adsorbate
m = Mass of adsorbent
p = Equilibrium pressure of adsorbate.
K and n are constants for a given adsorbate and adsorbent at a particular temperature.

C. *Nanofiltration Flux*

$J_w = \Delta p\text{--}\pi / \eta R_m$
J_w =Pure water ¯flux estimated from the resistance-in-series model.
ΔP = Transmembrane pressure.
η= Permeate viscosity.
R_m = Membrane resistance.
P = Osmotic pressure.

D. *Hydrodynamic Drag Force on Magnetic Particle*

$F_d = 6\pi \eta R_m \Delta v$
F_d = Drag Force
η = Viscosity of the medium surrounding the cell
R_m = Radius of the magnetic particle.
v = Difference in velocities of the cell and the water

VI. CONCLUSION

The world is facing formidable challenges in meeting rising demands of clean water as the available supplies of freshwater are decreasing continuously with increasing population. Nanomaterials are having various significant characteristics that make them particularly attractive as separation media for water purification. They are having much large surface areas than bulk particles. They also have high capacity/selectivity for toxic substances in aqueous solutions. Nanomaterials also provide unprecedented opportunities to develop more efficient water-purification catalysts like TiO_2 due to their large surface areas and their size and shape-dependent optical, electronic and catalytic properties. Nanomaterials are also being used to develop nanobiocides through functionalization with chemical groups and these nanobiocides are having good antimicrobial activity. Along with the benefits nanotechnology is having risks too in terms of side effects that are to be minimized. Nanomaterials will become essential component of industrial and public waste water treatment systems as more progress is made in nanotechnology in terms of economically efficient and ecofriendly technology development.

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