World Applied Sciences Journal 3 (3): 417-433, 2008
ISSN 1818-4952
© IDOSI Publications, 2008

Application of Nanoparticles in Waste Water Treatment

[1]Dhermendra K. Tiwari, [2]J. Behari and [3]Prasenjit Sen

[1,2]School of Environment Science, Jawaharlal Nehru University, 110067, New Delhi, India
[3]Schools of Physical Science, Jawaharlal Nehru University, 110067, New Delhi, India

Abstract: In the area of water purification, nanotechnology offers the possibility of an efficient removal of pollutants and germs. Today nanoparticles, nanomembrane and nanopowder used for detection and removal of chemical and biological substances include metals (e.g. Cadmium, copper, lead, mercury, nickel, zinc), nutrients (e.g. Phosphate, ammonia, nitrate and nitrite), cyanide, organics, algae (e.g. cyanobacterial toxins) viruses, bacteria, parasites and antibiotics. Basically four classes of nanoscale materials that are being evaluated as functional materials for water purification e.g. metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers. Carbon nanotubes and nanofibers also show some positive result. Nanomaterials reveal good result than other techniques used in water treatment because of its high surface area (surface/volume ratio). It is suggested that these may be used in future at large scale water purification. It is also found that the coliform bacteria treated with ultrasonic irradiation for short time period before Ag-nanoparticle treatment at low concentration, enhanced antibacterial effect. In future, combination of both may be the best option for treatment of waste water.

Key words: Nanoparticle . dendrites . zeolite . ceramics . nanosilver . nanorod . nanofiber synergic effect . minium inhibitory concentration

INTRODUCTION

Today most of the countries are facing drinking water problems and conditions are very severe especially in developing countries. The world is facing formidable challenges in meeting rising demands of clean water as the available supplies of freshwater are depleting due to (i) extended droughts, (ii) population growth, (iii) more stringent health based regulations and (iv) competing demands from a variety of users [1, 3, 4]. Clean water (i.e., water that is free of toxic chemicals and pathogens) is essential to human health. In countries such as India, 80% of the diseases are due to bacterial contamination of drinking water. The World Health Organization [2] recommended that any water intended for drinking should contain fecal and total coliform counts of 0, in any 100 mL sample. When either of these groups of bacteria is encountered in a sample, immediate investigative action should be taken. The removal or inactivation of pathogenic microorganisms is the last step in the treatment of wastewater [3]. The protection of water treatment systems against potential chemical and biological terrorist acts is also becoming a critical issue in water resources planning [4, 5].

Today a number of techniques are used for treatment of water i.e. chemical and physical agent such as chlorine and it's derivatives, Ultraviolet light [6], Boiling, Low frequency ultrasonic irradiation [7], Distillation, Reverse Osmosis, Water sediment filters (fiber and ceramic) Activated carbon, Solid block, Pitcher and faucet-mount filters, Bottled water, Ion exchange water Softener, Ozonisation, Activated alumina 'Altered' Water. Halogens such as chlorine (Cl) and bromine (Br) are well known and widely used as antibacterial agents, but the direct use of halogens as bactericides has many problems because of their high toxicity and vapour pressure in pure form. The most common cation in water affecting human and animal health is $NH4^{+.}$ In drinking water ammonia removal is very important to prevent oxygen depletion and algae bloom and due to its extreme toxicity to most fish species [8]. It can be replaced with biologically acceptable cations, like Na^{+}, K^{+} or Ca^{2+} in the zeolite. During the past few decades, several investigations have been carried out concerning the use of synthetic and natural zeolites, polymer films and metal ions (Ag^{+}, Cu^{++}, Zn^{++}, Hg^{++}, Ti^{+++}, Ni^{++}, Co^{++}) as bactericides for water disinfection [9-16].

Research is underway to use advance nanotechnology in water purification for safe drinking. Nanotechnology, the deliberate manipulation of matter at size scales of less than 100 nm, holds the promise of creating new materials and devices which take

Corresponding Author: Dr. J. Behari, School of Environment Science, Jawaharlal Nehru University, 110067, New Delhi, India

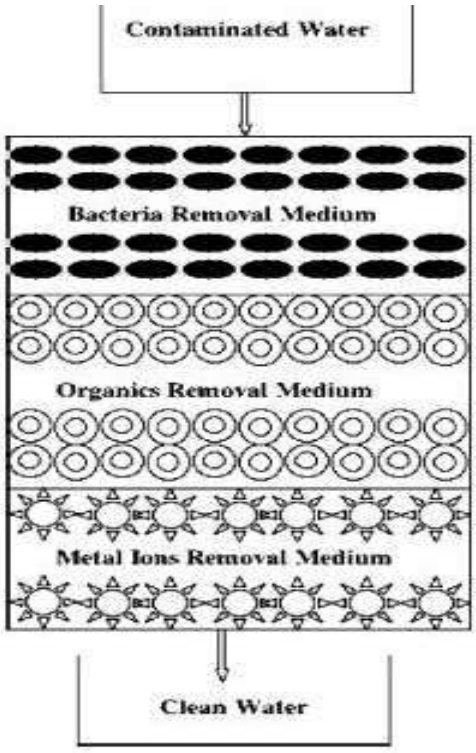


Fig. 1: Schematic of a composite nanomaterial packed bed reactor for purification of water Contaminated by mixtures of (i) metal ions, (ii) Organic solutes and (iii) bacteria [20]

advantage of unique phenomena realized at those length scales, because of their high reactivity due to the large surface to volume ratio [17]. Nanoparticles are expected to play a crucial role in water purification [18]. The environmental fate and toxicity of a material are critical issues in materials selection and design for water purification. No doubt that nanotechnology is better than other technique used in water treatment but today the knowledge about the environmental fate, transport and toxicity of nanomaterials [19] is still in infancy.

Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly diminished by using nonabsorbent, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, submicron, nanopowder, nanotubes, magnetic nanoparticles, granules, flake, high surface area metal particle supramolecular assemblies with characteristic length scales of 9-10 nm including clusters, micromolecules, nanoparticles and colloids have a significant impact on water quality in natural environment [20]. Nanotechnology used for detection of pesticides [21] chemical and biological substances including metals (e.g. Cadmium, copper, lead, mercury, nickel, zinc), Nutrients (e.g. Phosphate, ammonia, nitrate, nitrite), Cyanide Organics, Algae (e.g. Cyanobacterial toxins) Viruses, Bacteria, Parasites, antibiotics and Biological agents are used for terrorism. Innovations in the development of novel technologies to desalinate water are among the most exciting and seem to have promis [22]. Opportunities and challenges of using nanomaterials in the purification of surface water, groundwater and industrial wastewater streams is a matter of continuing concern. Misconceptions and One of the many impressions that people have about the future of nanotechnology is the expectation that nanoparticles can be used to kill harmful organisms, repair body tissue, in water quality improvment and to cure disease.

Recent applications of nanoparticulate silver have included open wound and burn treatment and preliminary studies have shown that a 20 ppm silver colloidal suspension (~30 nm diameter) in purified water has a 100% cure rate for malaria [23]. Titanium dioxide, especially as nanoparticulate anatase, is also an interesting antibacterial, with notable photocatalytic behavior. But ultrafine anatase has also been identified as cytotoxic and *in-vivo* studies have shown that it can be severely toxic in the respiratory system [24, 25]. Nanocapsules and nanodevices may present new possibilities for drug delivery, gene therapy, medical diagnostics, antimicrobial activity etc. The effect of particle size on the adsorption of dissolved heavy metals to iron oxide and titanium dioxide nanoparticles is a matter laboratory-scale experiments. Iron oxide and titanium dioxide are good sorbents for metal contaminants. Spherical aggregates of nanoparticles that have a similar size and shape to the resin beads already used in water purification. ligands, fulvic acids, humic acids and their aggregates have a significant impact on contaminant mobility, reactivity and bioavailability. Nanoparticles can also be designed and synthesized to act as either separation or reaction media for pollutants.

The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. Nanotechnology is a deliberate manipulation of matter at size scales of less than 100 nm holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions. Their extremely small feature size is of the same scale as the critical size for physical phenomena for example, the radius of the tip of a crack in a material may be in the range 1-100 nm. The way a

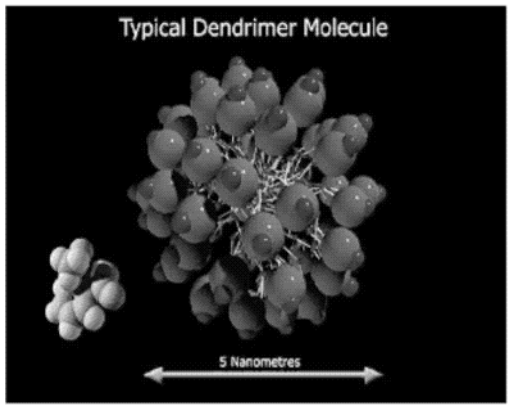
crack grows in a larger-scale, bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable. Fundamental electronic, magnetic, optical, chemical and biological processes are also different at this level.

NANOPARTICLE IN WASTE WATER TREATMENT

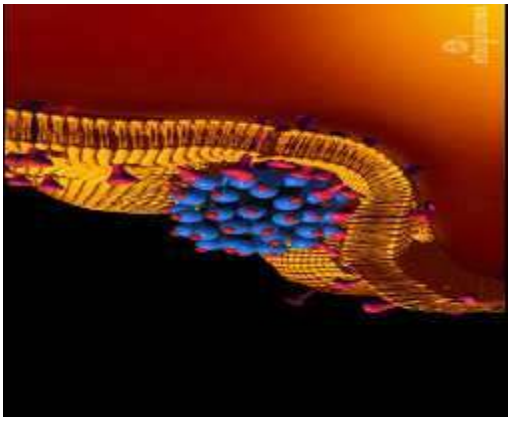
Four classes of nanoscale materials that are being evaluated as functional materials for water purification: (1) dendrimers (2) metal-containing nanoparticles, (3) zeolites and (4) carbonaceous nanomaterials. These have a broad range of physicochemical properties that make them particular attractive as separation and reactive media for water purification. Characterization of the interactions of the nanoparticles with the bacterial contaminant by Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and laser confocal microscopy show considerable changes in the integrity of the cell membranes, resulting in the death of the bacteria in most cases.

Dendrimer in water treatment: Reverse Osmosis (RO) membranes have pore sizes of 0.1-1.0 nm and thus are very effective at retaining dissolved inorganic and organic solutes with molar mass below 1000 Da [26]. Nanofilter (NF) membranes removing hardness (e.g., multivalent cations) and organic solutes with molar mass between 1000-3000 Da (e.g., natural organic material) [26]. However, high pressures are required to operate both RO and NF membranes. Conversely, Ultrafine (UF) membranes require lower pressure (200-700 kPa). Unfortunately, they are not very effective at removing dissolved organic and inorganic solute with molar mass below 3000 Da. Advances in macromolecular chemistry such as the invention of dendritic polymers are providing unprecedented opportunities to develop effective UF processes for purification of water contaminated by toxic metal ions, radionuclide, organic and inorganic solutes, bacteria and viruses.

Dendrite polymers, which include random hyperbranched polymers, dendrigraft polymers, dendrons and dendrimers, are relatively monodispersed and highly branched macromolecules with controlled composition and architecture consisting of three components: a core, interior branch cells and terminal branch cell [27] and tissue silver levels with 10% silver. Dendrimers are symmetrical and spherical macromolecules, comprising a relatively dense shell composed of a core, branching sites and terminal groups that usually form a well-defined surface. Their interior may be similar or very different from the



(A)



(B)

Fig. 2: The dendrimer attaches to multiple receptors on cell membranes or other biological structures such as a virus

surface of the molecule. Chemical and/or physical properties, such as reactivity, complex or salt formation, hydrophilicity and so forth can be varied and optimized. As a proof of concept study, Diallo *et al*. (2005) tested the feasibility of using dendron-enhanced ultrafiltration (DEUF) and poly (amidoamine) (PAMAM) Dendrimers with Ethylene Diamine (EDA) core and terminal NH2 groups to recover Cu (II) ions from aqueous solutions. On a mass basis, the Cu (II) binding capacities of the PAMAM dendrimers are much larger and more sensitive to solution pH than those of linear polymers with amine groups.

To obtain a dendrimer structure, several dendrons are reacted with a multifunctional core to yield a dendrimers. Using two key synthetic strategies, over one hundred compositionally different dendrimer families have been synthesized and over 1000 differentiated chemical surface modifications have been reported [28-37]. The first strategy, utilizes highly functionalized cores and branched monomers to create phosphorus dendrimers.Several variations of the

general synthetic scheme, which are interchangeable, have been developed, allowing multiplication of the number of terminal surface groups from 48 to 250 in one step. These dendrimers require just one step per generation performed in a minimum volume of solvent, allow facile purification (i.e., simple washings) and produce environmentally benign byproducts such as water and nitrogen [38, 39]. The second approach is based on dclickT chemistry, i.e., the nearperfect reliability of the Cu (I)-catalyzed synthesis of 1, 2, 3-triazoles from azides and alkynes to produce dendrimers with various surface groups in high purity and excellent yield. As early as 1984, PAMAM dendrimers were the first complete dendrimer family to be synthesized and characterized followed by commercialization in 1990 [40, 41]. They are synthesized by the divergent method, involving a two-step iterative reaction sequence that produces concentric shells of branch cells (generations) around a central initiator core. This PAMAM core-shell architecture grows linearly in diameter as a function of added generations, while the surface groups amplify exponentially at each generation. Poly (amidoamine) PAMAM dendrimers are obtained by the iterative branching of L-alanine repeat units. Due to their biofriendly nature [42-45] and unique carrier properties, they show promise to outperform other polymeric materials for medical applications. Diffusion of dendrimers through membranes is the function of generation (due to their spherical and monomodal character) and appropriately selected membranes may retain dendrimer hosts with 100% selectivity. PAMAMs are also stable and soluble in water. PAMAM dendrimers have a very low tendency to foul commercially available regenerated cellulose (RC) membranes [22]. They also have much smaller intrinsic viscosities than linear polymers with the same molar mass because of their globular shape [27]. Dendritic polymers exhibit many features that make them particularly attractive as functional materials for water purification. These 'soft' nanoparticles, with sizes in the range of 1-20 nm, can be used as high capacity and recyclable water soluble ligands for toxic metal ions, radionuclide and inorganic anions [46]. Dendritic polymers can also be used as (i) recyclable unimolecular micelles for recovering organic solutes from water [47] and (ii) scaffolds and templates for the preparation of redox and catalytically active nanoparticles.

Dendritic polymers have also been successfully used as delivery vehicles or scaffolds for antimicrobial agents such as Ag (I) and quaternary ammonium chlorides [14, 48]. Poly (amidoamine) dendrimer (PAMAM) based silver complexes and nanocomposites proved to be effective antimicrobial agents *in vitro*. Due to the atomic/molecular level dispersion of the guest in a dendrimer host, the activity is retained if the microorganism is able to contact with the organized silver domains of the nanocontainers. Macroscopically, the silver remained conjugated to the dendrimer in the form of ions, stable metallic silver clusters or silver compounds. Because the dendrimer host is soluble, it is able to deliver the immobilized silver in the agar medium by its own diffusion. The silver clusters remain active because of their extremely high surface area. Reaction with chloride and sulfate ions neither blocks the diffusion of the silver nor the activity against *S. aureus, Ps. aeruginosa and E. coli*. The protected silver and silver compounds displayed high antimicrobial activity in several cases without the loss of solubility. However, the diffusion of dendrimers can be totally prevented if common cellulose membranes are used.

Metal nanoparticle: Nanoparticles have two key properties that make them particularly attractive as sorbents. On a mass basis, they have much larger surface areas than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds. It has been found that the unique properties of nanoparticles to develop high capacity and selective sorbents for metal ions and anions. Characterization of the interactions of the nanoparticles with the bacteria by atomic force microscopy (AFM), Transmission Electron Microscopy (TEM) and laser confocal microscopy showed considerable changes in the integrity of the cell membranes, resulting in the death of the bacteria in most cases. Phototalytic nanomaterials allow ultraviolet light also used to destroy pesticides, industrial solvents and germs.

Stoimenov *et al*. showed that MgO nanoparticles and magnesium (Mg) nanoparticles are very effective biocides against Gram-positive and Gram-negative bacteria *(Escherichia coli and Bacillus megaterium)* and bacterial spores *(Bacillus subtillus)* [18]. Magnesium oxide nanoparticles or magnesia nanoparticles (MgO), nanodots or nanopowder are spinel, high surface area particles. Nanoscale magnesium oxide nanoparticles or magnesia particles are typically 5-100 nanometers (nm) with specific surface area (SSA) in the 25-50 m^2 g^{-1} range and magnesium (Mg) nanoparticles, nanodots or nanopowder are spherical black high surface area particles. Nanoscale magnesium particles are typically 20-60 nanometers (nm) with specific surface area (SSA) in the 30-70 m^2 g^{-1} range. Preparation of magnesium oxide (MgO) nanoparticles to absorb large amounts of halogen molecules up to 20 % by weight

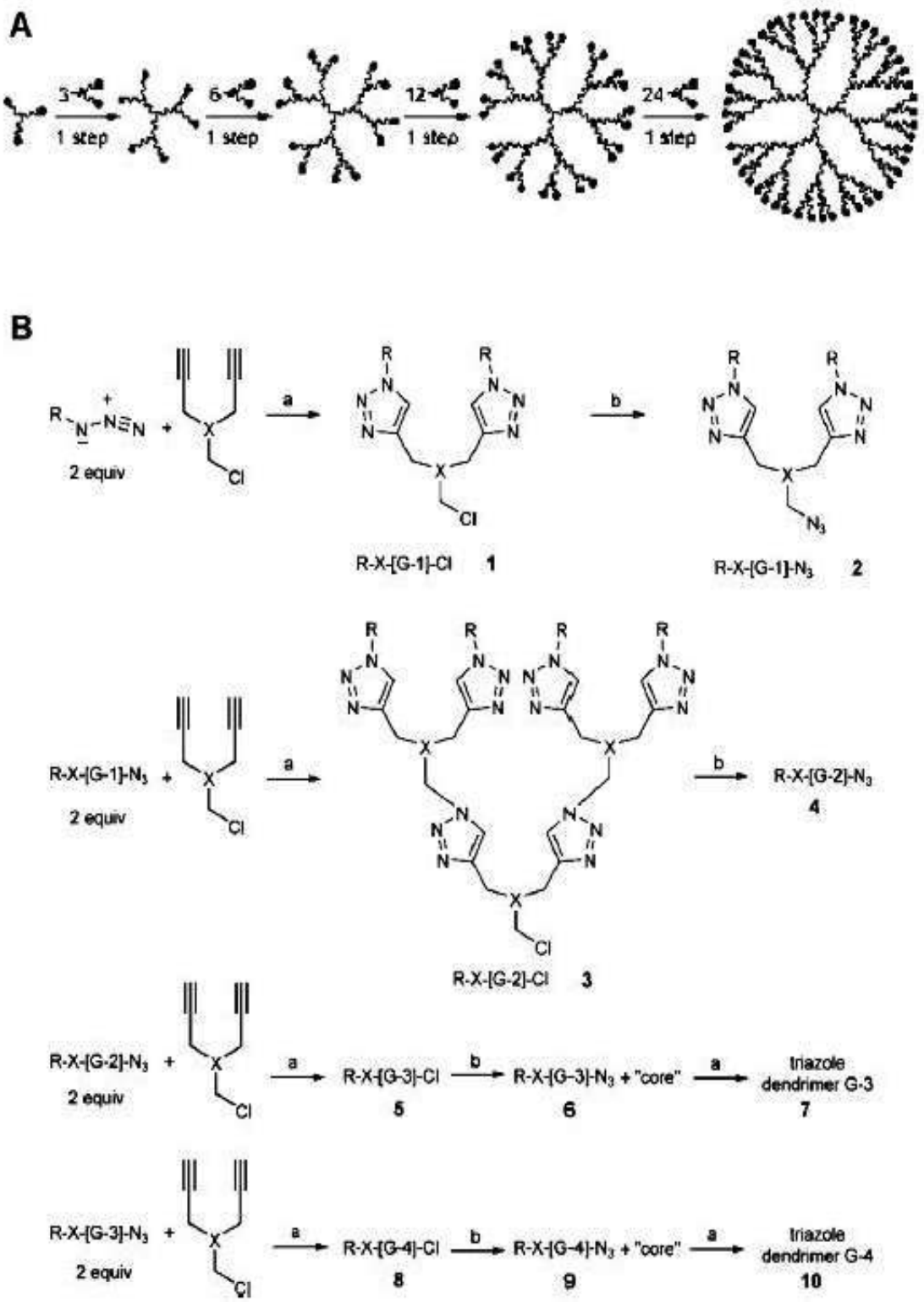


Fig. 3: (A) Divergent approach using dlegoT chemistry towards highly functionalized phosphorous dendrimers. (B) Convergent approach towards triazole dendrimers using dclickT chemistry [32, 33, 38, 39, 42, 43 American Chemical Society 2003]

making them safer to handle and measured their bactericidal activity on three representative strains of bacteria and bacterial spores [18]. These MgO nanoparticle particles are allowed to contact certain bacteria and spore cells. Bacteriological test data, Atomic force microscopy (AFM) images and Transmission electron microscopy (TEM) images are provided, which yield insight into the biocidal action of these nanoscale materials. The tests show that these materials are very effective against Gram-positive and Gram-negative bacteria.

Ag (I) and silver compounds have been used as antimicrobial compounds for coliform found in waste water [49]. Silver (Ag) nanoparticles, nanodots or nanopowder are spherical or flake high surface area metal particles having high antibacterial activity [50, 51] are used in wound. Nanoscale silver particles are typically 1-40 nanometers (nm) with an average particle size of 2-10 micron range with a specific surface area of approximately 1 m^2 g^{-1}. Applications for silver nanocrystals include as an anti-microbial, anti-biotic and anti-fungal agent when incorporated in coatings, nanofiber, first aid bandages, plastics, soap and textiles, in treatment of certain viruses, in self cleaning fabrics, as conductive filler and in nanowire and certain catalyst applications. It has been reported that Ag nanoparticles were active biocides against Gram-positive Gram-negative bacteria including Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae and Pseudomonas aeruginosa [49, 52]. Stable Ag nanoparticles of narrow size [53], various monometallic nanoparticles e.g. Au, Ag, Pt, Pd [54] and Sugar-assisted stable monometallic nanoparticles can be synthesized in the laboratory. Gold (Au) nanoparticles, nanodots and nanopowder are brown spherical high surface area metal particles. Nanoscale gold particles are typically 20-100 nanometers (nm) with specific surface area (SSA) in the 1-3 m^2 g^{-1} range. Nanoparticles of gold coated with palladium are very effective catalysts for removing tri-chloroethane (TCE) from groundwater 2,200 times better than palladium alone.

Zinc oxide nanoparticles have been used to remove arsenic from water, even though bulk zinc oxide can not absorb arsenic. Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron containing minerals, such as akaganeite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite. Adsorption of organics to the nanoparticle media was extremely rapid. More than 90% of the organics is adsorbed within 30 minutes. The isotherm studies indicated that, on a surface area basis, the adsorption capacities of the nanoparticle media were significantly (>2 folds) higher than the ferric oxide media typically used in water treatment [55]. The smaller size of magnetic nanoparticles, which are 2-3 orders of magnitude smaller than a bacterium, provides extra benefits compared to magnetic beads. When their surface is appropriately elaborated, magnetic nanoparticles can also provide efficient binding to the bacteria because their high surface/volume ratio simply offers more

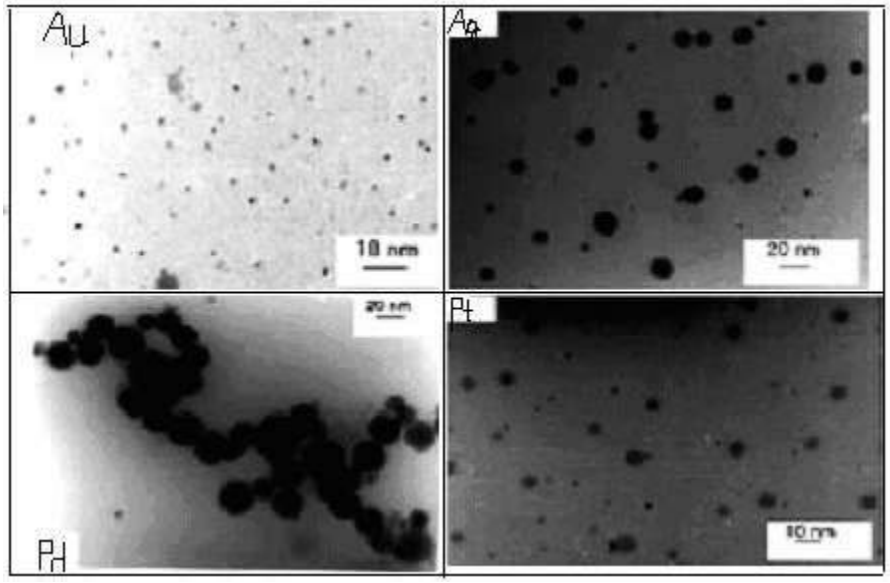


Fig. 4: The TEM images of the metal nanoparticles (Au, Ag, Pd and Pt) formed by fructose reduction [54]

contact area. Ferrite is a generic term for a class of magnetic iron oxide compounds. Ferrites posses the property of spontaneous magnetization and are crystalline materials soluble only in strong acid. Iron atoms in iron ferrite ($FeO.Fe_2O_3$) can be replaced by many other metal ions without seriously altering its spinel structure.Various ferrites and natural magnetite were used in batch modes for actinide and heavy metal removal from wastewater. Iron (Fe) nanoparticles, nanodots or nanopowder are spherical or faceted high surface area metal nanostructure particles. Nanoscale iron particles are typically 20-40 nanometers (nm) with specific surface area (SSA) in the 30-50 m^2 g^{-1} range. Other recent studies have demonstrated the magnetic enhanced removal of cobalt and iron from simulated groundwater. The magnetic field-enhanced filtration/sorption process differs significantly from magnetic separation processes used in the processing of minerals and more recently, for water treatment and environmental applications. Conventional processes use for example, fine stainless steel wool to form a magnetic matrix within a flow field of a solution containing mineral particles to be separated. For this reason, in order for such processes to remove metal ions and nanoparticles from solution, precipitating or flocculating agents must first be added to effect formation of large particles. In contrast, the magnetic filtration/sorption process is unique because metals are removed in most conventional wastewater treatment processes in the form of metal hydroxides since they have low solubility. As noted above, ferric hydroxide is often added to scavenge a wide variety of heavy metal contaminants. The use of iron ferrite and magnetite in wastewater treatment has a number of advantages over conventional flocculent precipitation techniques for metal ion removal. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions. The effect of particle size on the adsorption of dissolved heavy metals to iron oxide and titanium dioxide nanoparticles will be studied in laboratory-scale experiments. Iron oxide and titanium dioxide are good sorbents for metal contaminants.

Reduction of transition metal salts is the oldest, easiest and still a widely used method for the preparation of metal nanoparticles. As far as magnetic metals are concerned, the most common reducing agents are borohydride derivatives, extensively studied by Klabunde *et al*. This method provides an easy route to nanoparticles of Fe, Co and Ni as well as to alloys such as Fe/Pd. The drawback of the method is however the incorporation of boron into the particles which leads to a modification of the magnetic properties of the particles. Cobalt particles were for example prepared with the microemulsion method in the binary system of DDAB (di-dodecyldimethylammonium bromide)/ toluene by reduction of CoCl2 with NaBH4. The average particle size of the samples could be varied from 1.8 to 4.4 nm by controlling the concentration of $CoCl_2$ in the solution of DDAB in toluene.

Zeolite: Zeolites are effective sorbents and ion-exchange media for metal ions. NaP1 zeolites (Na6Al6 Si10O32, 12H2O) have a high density of Na^+ ion exchange sites. They can be inexpensively synthesized by hydrothermal activation of fly ash with low Si/Al

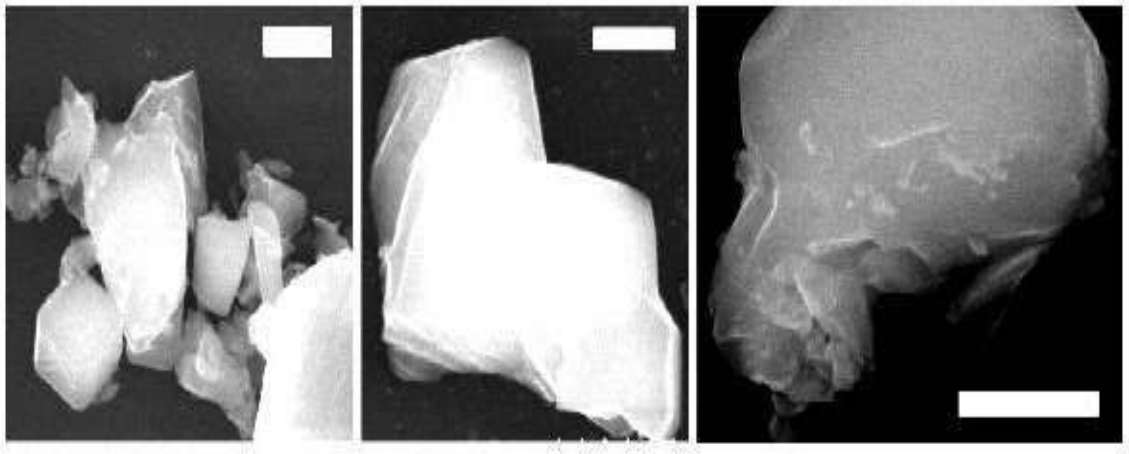


Fig. 5: Several examples of zeolite LTA microparticles that have been fragmented by laser-induced fracture [58]

ratio at 150°C in 1.0-2.0 M NaOH solutions [55]. NaP1 zeolites have been evaluated as ion exchange media for the removal of heavy metals from acid mine wastewaters. Alvarez-Ayuso *et al*. reported the successful use of synthetic NaP1 zeolites to remove Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from metal electroplating wastewater [57]. Nonporous ceramic oxides with very large surface areas (1000 $m^2 g^{-1}$) and high density of sorption sites that can be functionalized to increase their selectivity toward target pollutants. Zeolite nanoparticles are prepared by laser-induced fragmentation of zeolite LTA microparticles using a pulsed laser. Zeolite nanoparticle formation is attributed to absorption of the laser at impurities or defects within the zeolite microcrystal generating thermoelastic stress that mechanically fractures the microparticle into smaller nanoparticle fragments. Experimentally, it is found that nanoparticles have a wide size and morphology distribution. Large nanoparticles (>200 nm) are typically irregularly shaped crystals of zeolite LTA, whereas small nanoparticles (<50 nm) tend to be spherical, dense and amorphous, indicative of destruction of the original LTA crystal structure. Increasing the laser energy density irradiating the sample was found to be a trade-off between increasing the amount of fragmentation and increasing the amount of structural damage to the zeolite crystal. It is suggested that in the presence of strongly absorbing defects, plasma formation is induced resulting in dramatically higher temperatures. On the basis of these results it is concluded that the optimal laser processing conditions are 355 nm and 10 mJ/pulse laser energy for our LTA samples (Figure-5) [58].

Carbonaceous nanoparticle: Carbonaceous nanomaterials can serve as high capacity and selective sorbents for organic solutes in aqueous solutions. A number of polymers that exhibit antibacterial properties were developed for this purpose including soluble and insoluble pyridinium-type polymers which are involved in surface coating, [59] azidated poly (vinyl chloride) [60] which can be used to prevent bacterial adhesion of medical devices, PEG polymers that can be modified on polyurethane surfaces and also prevent initial adhesion bacteria to the biomaterial surfaces [61] and polyethylene mine (PEI) [62] that exhibit high antibacterial and antifungal activity. High activity of polycationic agents is related to absorption of positive charged nanostructures onto negative by charged cell surfaces of the bacteria. This process is thought to be responsible for the increase of cell permeability and may disrupt the cell membranes.

Cross linked polycations are prepared as nanoparticles. These are formed from PEI by crosslinking and alkylation followed by methylation in order to increase degree of amino group substitution [63]. Because of its positive charge and hydrophobicity, PEI nanoparticles have attracted attention as possible antimicrobial agents. Studies on PEI nanostructured compounds are made to evaluate its antibacterial properties as a function of hydrophobicity, molecular weight, particle size and charge that can play a significant role in antibacterial effect of the tested compound. The antibacterial activity is evaluated against *Streptoccocus mutants* cariogenic bacteria. Various PEI nanoparticles from 100nm to 1 micron in diameter are prepared having different degree of cross-linking, particle size and zeta potential that are achieved by alkylation with a bromoalkane followed by methylation. Their antibacterial effects are examined against *Streptoccocus* mutans in direct contact with bacteria. One important feature of the antibacterial agent is to maintain antibacterial activity over a long time. However, only the PEI nanoparticle samples including long chain alkyls demonstrated high antibacterial effect against *Streptoccocus mutants* for more than four weeks [62].

STRATIGES FOR NANOPARTICLE SYNTHESIS

Nanomaterials are, of course, abundant in nature as living organisms operate basically at a nanoscale level. Anotechnologists seek to produce and utilize both novel nanomaterials and some natural nanomaterials in larger quantties and within a more consistent size range. Numerous techniques are used to fabricate different nanomaterials. Nanoparticles can be produced from larger structures (top down) by use of ultrafine grinders, lasers and vaporization followed by cooling. For complex particles, nanotechnologists generally prefer to synthesize nanostructures by a bottom-up approach by arranging molecules to form complex structures with new and useful properties.

Self assembly: Manipulation of physical and chemical conditions such as pH, temperature and solute concentrations can induce selfassembly of molecules to form fibrous nanostructures [63]. Vesicles, called polymerosomes, that may be useful for encapsulation, can also be self assembled by slow evaporation of an organic solvent [64].

Layer by layer deposition: Platforms for bilayer membranes that can be used for protein analysis can be fabricated by layering of sodium silicate and poly (allylamine hydrochloride) on gold followed by calcinations in a furnace. Lipid bilayers can fuse to the silicate layer and be used to detect specific proteins [65].

Preparation of functional nanoparticles by thermal plasmas: Functional nanoparticles of silicide and boride were prepared by induction thermal plasmas. Silicide and rare-earth boride are attractive materials because of their high melting temperature, high electrical conductivity and low work function. Therefore these nanoparticles would be applied for electromagnetic shielding and solar control windows with interaction with IR and UV light.

For the preparation of silicide, Si powders premixed with metal powder (Mo, Ti, Co, Fe, Cr, or Mn) are injected into the plasma. For the preparation of rare-earth boride, premixed powders of rare-earth oxide, B and C were introduced into the thermal plasma. In the thermal plasma, the injected powders are evaporated and reacted with boron. After the evaporation and reaction, the vapor is rapidly cooled after the plasma flame. The nanoparticles are prepared on condition that the vapor is quickly quenched by the water-cooled copper coil. Another purpose is to investigate the condensation mechanism of mixture vapor of feed powders in thermal plasmas. The characteristics of the prepared nanoparticles are affected by the vapor pressure ratio of the constituent materials. Investigation of physical and chemical processes in thermal plasma processing is indispensable for nanoparticle synthesis.

Gas phase synthesis and sol-gel processing: Major efforts in nanoparticle synthesis can be grouped into two broad areas: gas phase synthesis and sol-gel processing. Nanoparticles with diameters ranging from 1 to 10 nm with consistent crystal structure, surface derivatization and a high degree of monodispersity have been processed by both gas-phase and sol-gel techniques. Initial development of new crystalline materials was based on nanoparticles generated by evaporation and condensation (nucleation and growth) in a subatmospheric inert-gas environment [66, 67]. Various aerosol processing techniques have been reported to improve the production yield of nanoparticles [68, 69].

Crystallization: Hydroxyapatite-aspartic acid (or-glutamic acid) crystals were synthesized in the presence of solutions containing different amounts of the amino acids. Material, bringing in the consideration of the temporal stability of the structured materials [70].

Biogenic strategy: The complexity of biological materials represents the achievement of structural order over many length scales, with the full structure developed from the "nested levels of structural hierarchy" [71], in which self-assembled organic materials can form templates or scaffolding for inorganic components. These notions of a multilevel material structure with strong interactions among levels and interplay of perfection and imperfection forming the final material.

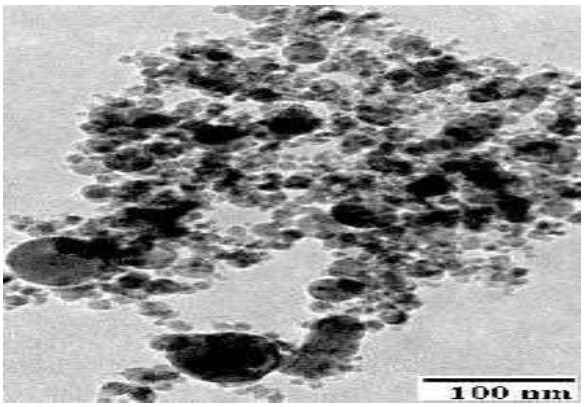


Fig. 6: LaB_6 nanoparticles prepared from the La_2O_3B powders injected into argon induction plasmas

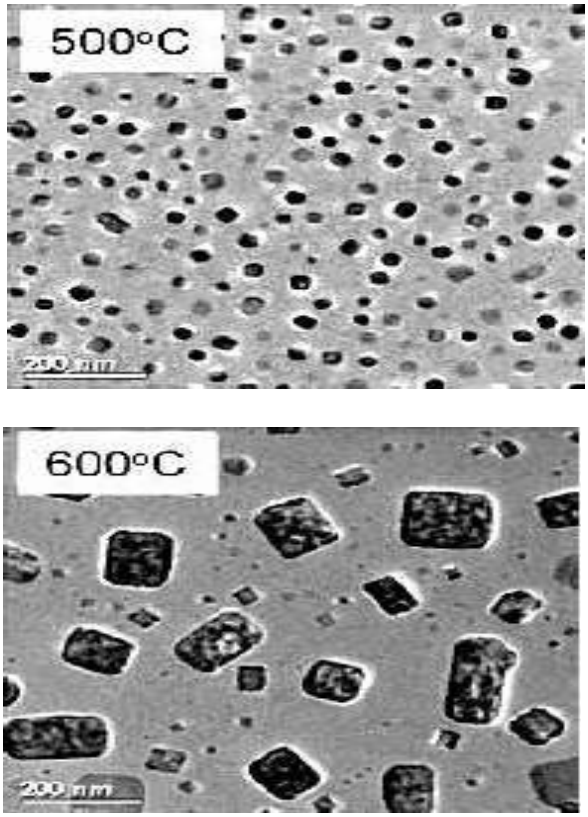


Fig. 7: TEM images for NaCl particles at furnace temperature of 500 and 600°C

Microbial synthesis: Living cells have been harnessed to produce nanoparticles, for example, silver

nanoparticles produced extracellularly by the fungus *Aspergillus fumigatus* [72]. Gold and silver nanoparticles can also be produced by other fungi and a number of bacterial species [73].

Biomass reactions: Gold nanorods and nanoparticles with other shapes were produced by incubation of dead oat stalks with an acidic aqueous solution of gold ions (Au III) (1). Some living plants are also known to take up and sequester heavy metals (to prevent being poisoned by these metals) and these plants may also be useful in producing nanoparticles of metals [73].

Alternative preparation method: Low temperature nanoparticle preparation methods have spanned a wide range of systems. One that has been in existence for decades but has not been put into use in other industries is the method of preparing silver halide particles. Eastman Kodak in France, England and the United States has utilized solution precipitation technology with well-controlled mixing and nucleation control to produce a wide range of grain sizes. "Lippmann"-type grains have a size of about 50 nm. There are other methods of creating nanoparticles of organic materials such as filter dye applications in photographic films and spectral sensitizing dyes for use in silver halide grains. Ultrafine grinding media are used to almost sandpaper organic crystals to nanoparticle ranges of 20-80 nm. Similar technology has been utilized in both pharmaceutical preparations and ink jet applications with good success [74]. One other exciting area is in polymer science, where dendrimer molecules, often 10 nanometers in diameter, are prepared synthetically and trying to use in water treatment.

Other strategies: Additional nanoparticle synthesis techniques include sonochemical processing, cavitation processing, microemulsion processing and high-energy ball milling. In sonochemistry, an acoustic cavitation process can generate a transient localized hot zone with extremely high temperature gradient and pressure [75]. Such sudden changes in temperature and pressure assist the destruction of the sonochemical precursor (e.g., organometallic solution) and the formation of nanoparticles. The technique can be used to produce a large volume of material for industrial applications. In hydrodynamic cavitation, nanoparticles are generated through creation and release of gas bubbles inside the sol-gel solution [76]. By rapidly pressurizing in a supercritical drying chamber and exposing to cavitational disturbance and high temperature heating, the sol-gel solution is mixed. The erupted hydrodynamic bubbles are responsible for nucleation, growth and quenching of the nanoparticles. Particle size can be controlled by adjusting the pressure and the solution retention time in the cavitation chamber.

ANTIBACTERIAL EFFECT ENHANCED BY ANTIBIOTIC-NANOPARTICLE INTERACTION

Ping Li *et al*. studied that the Ag nanoparticle shows enhanced antibacterial effect against *E. coli* used with amoxicillin, a ß-lactum antibiotics [77]. When amoxicillin and silver nanoparticles are combined, it results in greater bactericidal efficiency on Escherichia coli cells than when they were applied separately. Nanosilvers and amoxicillin can kill bacteria with a different mechanism. If bacteria have resistance to one of them, another antimicrobial agent would kill the bacteria in a quite different way. This plays an important role especially when the bacteria gain antimicrobial resistance.

Till now, scientists have established the antibacterial mechanism of ß-lactam antibiotics [78, 79]. The silver application on burning therapy has existed for more than a century [80, 81]. Some hypotheses indicated that catalytic oxidation of silver ions, with nascent oxygen, reacts with bacterial cell membranes, leading to cell death. More recently, it has been demonstrated that the bactericidal effect of silver was caused by silver (I) chelation preventing DNA from unwinding [82].

If the bacterium does not show any resistence, the synergistic effect may be caused by a bonding reaction between amoxicillin and nanosilver. Amoxicillin molecules contain many active groups such as hydroxyl and amido groups. These groups react easily with nanosilver by chelation. Amoxicillin molecules themselves can bind each other through Vander-waals interaction and other weak bonds. Ultimately, the antimicrobial groups come into being, which are made up of a nanosilver core and the surrounding amoxicillin molecules (Fig. 8). Whenever antimicrobial groups act on one point at the surface of the bacterial cells they cause more destruction. Thus, the process of antimicrobial group forming is actually that of increasing the antimicrobial agents' concentration.Vancomycin antibiotic bind with FePt-nanoparticles because of multivalent nature of the particle and helps to enhance the antibacterial nature of antibiotics (Fig. 9).

A more probable cause of the synergistic effect may be the action of nanosilver's drug carrier. Phospholipids and glycoprotein, present in cell membrane, which are all hydrophobic groups. Nanosilver, but not amoxicillin, is likely to approach the membrane of the target cells because amoxicillin molecules are hydrophilic and nanosilver is not.

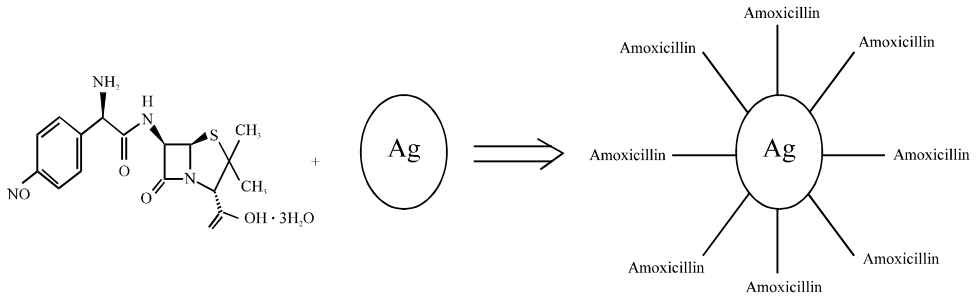


Fig. 8: The structure of amoxicillin and the bonding route for nanosilver chelated with amoxicillin [77]

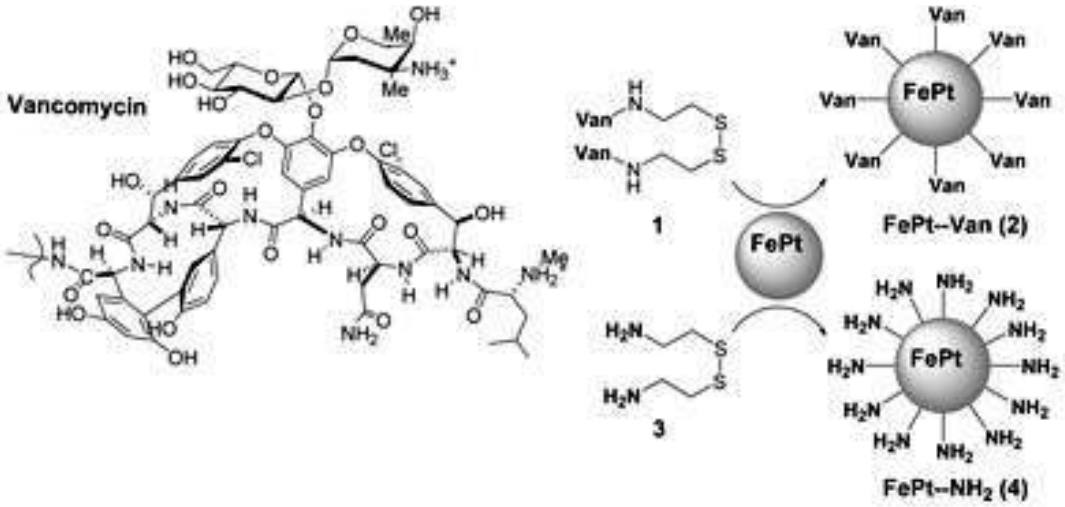


Fig. 9: The structure of vancomycin and synthesis of vancomycin conjugated FePt nanoparticles [83]

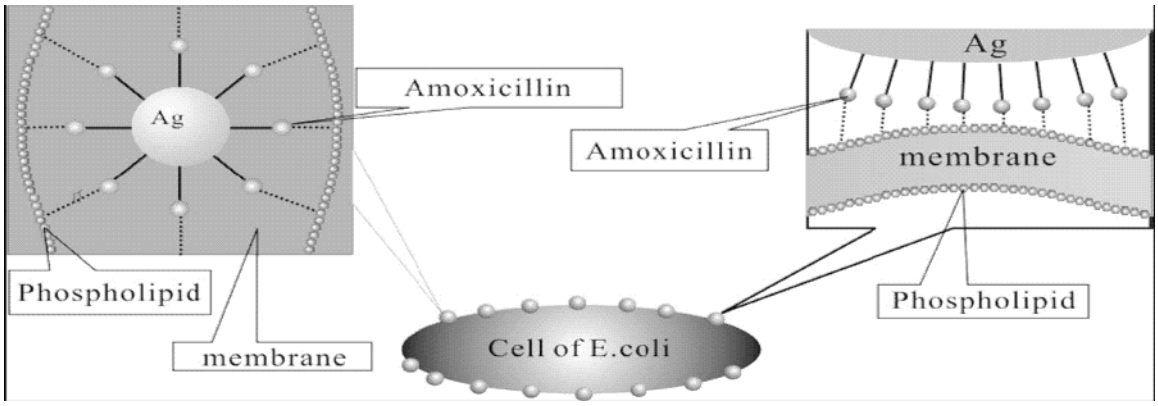


Fig. 10: A diagram of the combination of nanosilver and amoxicillin reacted with cells extracellularly and intercellularly [77]

Therefore, antimicrobial groups facilitate the transport of amoxicillin to the cell surface.

LB medium was used for growing Escherichia coli (DH5a) test strains at 37°C until approximately 10^5-10^6 CFU of bacteria were reached. The cultures were filtrated twice and the cells were washed and suspended in distilled water until the inocula reached approximately 5.0×10^6 CFU. 15 LB medium tubes were prepared and test culture inoculated in highly sterilized 0.000, 0.150, 0.300, 0.375, 0.450 and 0.525 mg ml^{-1}

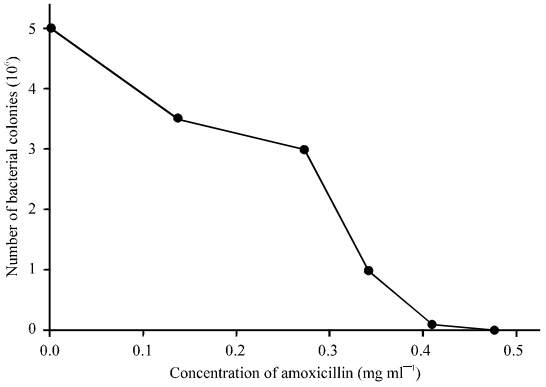


Fig. 11: Effect of different conc. of amoxicillin put into 5×106 CFU of Bacterial colonies

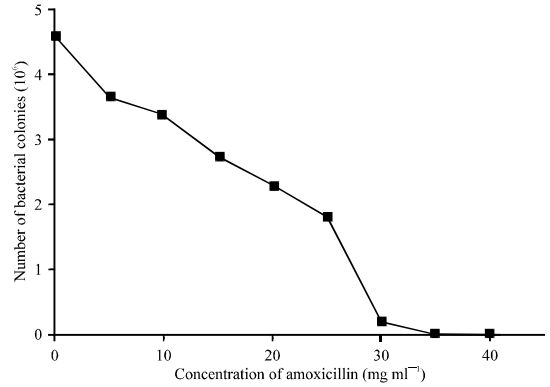


Fig. 12: Effect of different concentration of nanosilver put into 5×106 CFU of Bacterial colony

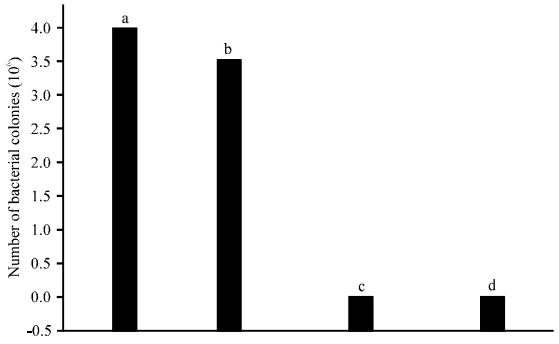


Fig. 13: Effect of amoxicillin and nanosilver, individually and jointly, on 5×10^6 bacterial colonies: (a) 5 μg ml-^{1} nanosilver; (b) 0.150 mg ml-^{1} amoxicillin; (c) 0.150 mg ml-^{1} amoxicillin plus 5 μg ml-^{1} nanosilver; (d) 0.150 mg ml-^{1} amoxicillin plus 10 μg ml-^{1} nanosilver

condition. Out of fifteen six tube were incubated with amoxicillin, shaken at 37°C for 24 h. The same procedure was performed with 0, 5, 10, 15, 20, 25, 30, 35 and 40 μg ml-^{1} of nanosilver. The minimal inhibition concentrations (MICs) of amoxicillin and nanosilver were calculated respectively. To get the MIC of the mixture of amoxicillin and nanoparticles, the cells of the bacteria were spotted into LB medium and incubated under different conditions as follows: 0.150 mg ml-^{1} amoxicillin +5 μg ml-^{1} nanosilver and 0.150 mg ml-^{1} amoxicillin +10 μg ml-^{1} nanosilver instead of amoxicillin or nanosilver alone. All assays were carried out in three duplicates in an effort to eliminate other random factors. Broth dilution experiments were conducted at 37°C and performed in 204 well rinsed plates. All stock solution was made in an LB agarose plate and diluted twofold with the duplicates. The MICs of amoxicillin and nanosilver, individually and jointly, were determined. The MIC of amoxicillin tested in the experiment shown in Fig. 11 is about 0.525 mg ml^{-1}. In Fig. 12, the MIC of nanosilver appeared to be 40 μg ml^{-1}. Comparing the individual antibacterial effect of amoxicillin or nanosilver with their combination, the augmentative antibacterial efficiency by the β-lactam antibiotic in combination with nanosilver is quite obvious. Either the 0.15 mg ml^{-1} amoxicillin or the 5 μg ml^{-1} nanosilver alone had hardly any effect on *E. coli* as demonstrated from this experiment.

COMBINED EFFECT OF AG-NANOPARTICLE/ULTRASONIC RRADIATION

Because ultrasound attacks the bacterial cell walls, the bacterial cells release iso-enzymes that biocatalyst hydrolytic reactions. This results in acceleration in the breakdown of organic material into smaller readily biodegradable fractions. Ultrasound treatment is one of several technologies that promote hydrolysis of the rate-limiting stage during sludge treatment. It can be generated at a broad range of frequencies (35 and 130 KHz) and acoustic intensities [84]. The basic principal of ultrasound is based on the destruction of both bacterial cells membranes and difficult-to-degrade organics. Because ultrasound attacks the bacterial cell walls, the bacterial cells release various enzymes, which catalyzed hydrolytic reactions and ultimately cell death. This results in acceleration in the breakdown of organic material into smaller readily biodegradable fractions.

Synthesis of nanoparticle: The synthesis of Ag @citrate was done according to the literature procedure [85]. Briefly, the synthesis involves the following materials and methods: 25 mL of 0.005 M stock solution of silver nitrate in water was diluted to 125 mL

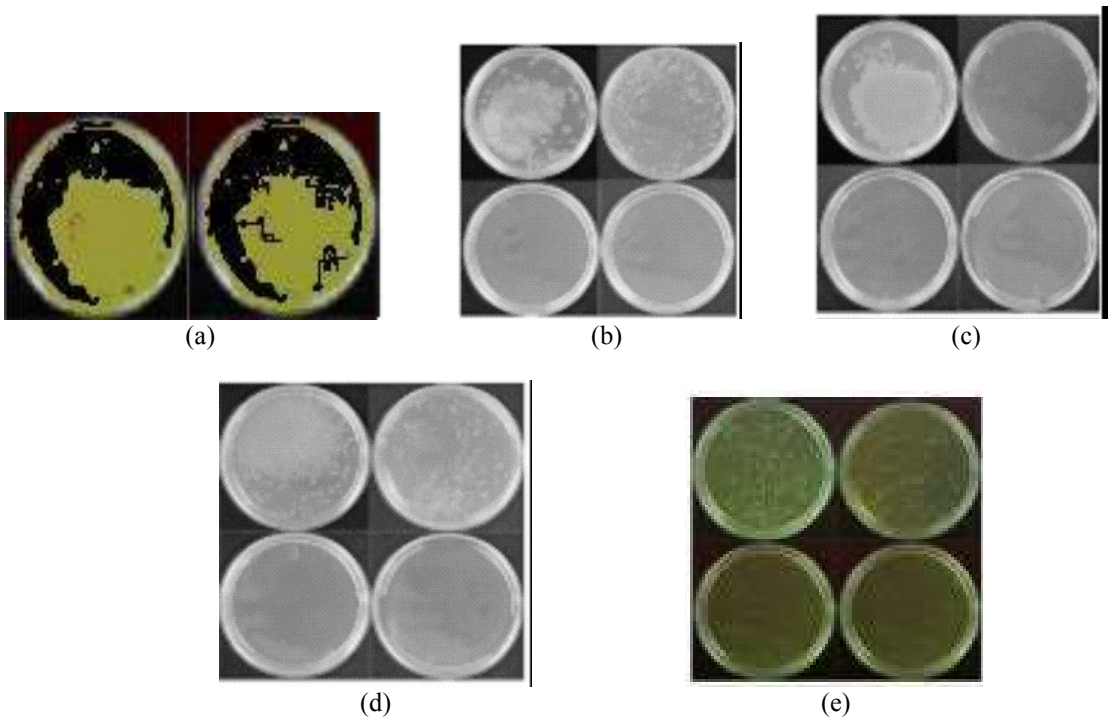


Fig. 14: (a) Culture growth on LB medium without any treatment (b) Bacterial growth after Ultrasonic treatment with varying time interval at 35 KHz (c) in presence of varying concentration of Ag nanoparticle (d) Treatment of both Ultrasonic waves (35 KHz) with time interval according to (a) and Ag nanoparticle (10^{17} molecules/cc) (e) Treated with both Ultrasonic waves (35 KHz) with time interval according to (a) and Ag nanoparticle (10^{21} molecules/cc)

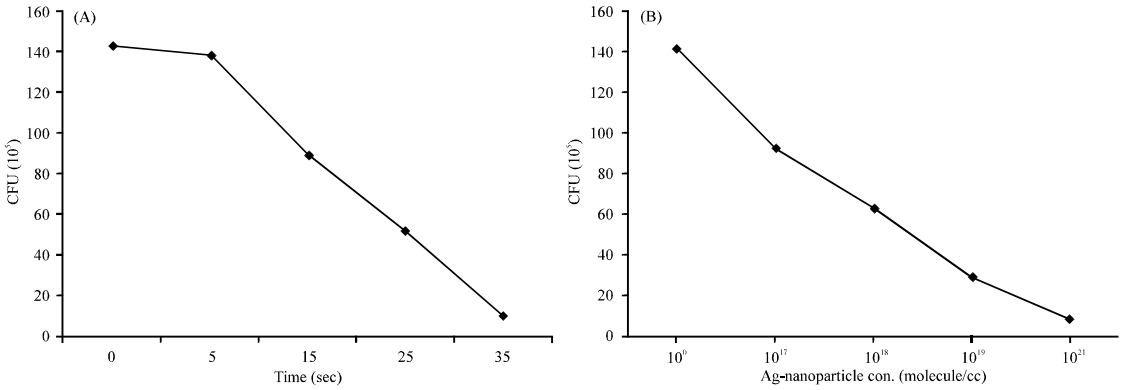


Fig. 15: CFU count of *E. coli* culture (isolated from waste water) after treatment with Ultrasonic waves at 35 KHz in varying time interval (B) treated with varying concentration of Ag-nanoparticle

and heated until it begins to boil. Then 5 mL of 1% sodium citrate solution was added; heating continued until the color was pale yellow. The solution was cooled to room temperature.

Microbiological test: Study is based on the combined antibacterial effect of Ag-nanoparticle and ultrasonic irradiation on *E. coli* cells isolated from waste water. The inocula of *E. coli* cell were prepared by growing test strain in LB medium at 37°C until approximately 10^4-10^5 CFU reached.Prepared 24 test tube containing 10 ml LB broth + 100 µl culture of 10^5 cells ml^{-1}, in each test tube. 20 culture tubes were treated for 5, 15, 25 and 35 min. at 35 KHz ultrasound frequency. Out of

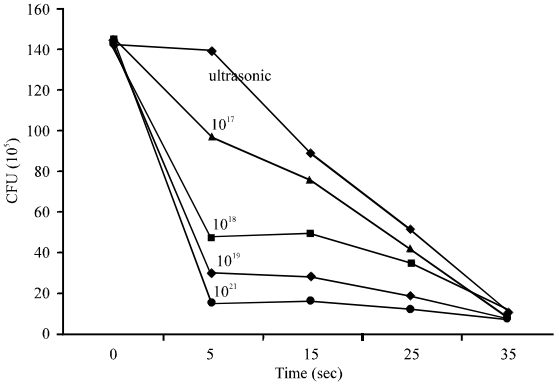


Fig. 16: CFU count of combined treatment of *E. coli* culture from ultrasonic irradiation and varying concentration (10^{17}-10^{21} molecules/cc) of Ag-nanoparticle solution

20 treated tubes, 16 tubes were treated with 1 ml of 10^{17}, 10^{18}, 10^{19} and 10^{21} molecules/cc of Ag nanoparticle solution according to the varying time interval treatment of ultrasonic irradiation. Four tubes were also treated with same Ag-nanoparticle concentration as above. Since after 15 minute all the 24 treated culture sample were poured in the Petriplates with 20 ml of LB-agar medium and incubated these Petriplates at 37°C for 24 hrs. CFU was calculated after 24 hrs of bacterial growth on LB agar Petriplates. All essays were carried out in duplicates in an effort to eliminate errors during procedure. Dilution experiment were conducted at 37°C and performed in 98 well brushed plate.

After 5, 15, 25 and 35 minute treatment with ultrasonic irradiation and varying concentration (10^{17}, 10^{18}, 10^{19} and 10^{21}) of Ag-nanoparticles was found continuous decrease in the number of colonies on agar plate (Fig. 13A and B). After 35 min treatment no growth was detected on agar plate (Fig. 13A) and very few colonies were appeared on agar plate when the culture treated with higher concentration of Ag-nanoparticle (10^{21} molecules/cc) (Fig. 13B). Low time exposure of ultrasonic irradiation (5 and 15 min.) was not as effective as low molecular concentration of Ag-nanoparticle (10^{17}, 10^{18} molecules/cc). It had been found that the least number of colonies appeared on the Petriplate treated with Ag nanoparticle after treatment of ultrasonic irradiation comparatively than the culture were treated either with ultrasonic irradiation for short time period (15 and 25 minute) or varying concentration of Ag-nanoparticle. It was shown that the antibacterial effect enhance when the culture treated combined with both Ag-nanoparticle and ultrasonic irradiations (Fig. 14).

REFERENCE

1. US Bureau of Reclamation and Sandia National Laboratories, 2003. Desalination and water purification technology roadmap a report of the executive committee Water Purification.
2. World Health Organization, 1996. Guidelines for drinking-water quality. Geneva: WHO, Vol: 2.
3. US Environmental Protection Agency, 1998b. Microbial and disinfection by-product rules. Federal Register, 63: 69389-69476.
4. US Environmental Protection Agency, 1999. Alternative disinfectants and oxidants guidance manual. EPA Office of Water Report 815-R-99-014.
5. US Environmental Protection Agency, 1998. Variance technology findings for contaminants regulated before 1996. EPA Opace of Water Report 815-R-98-003.
6. Droste, R.L., 1997. Theory and practice of water and wastewater treatment. New York: Wiley (Book).
7. Gupta, S., J. Behari and K. Kesari, 2006. Low frequency ultrasonic treatment of sludge. Asian J. Wat, Envi and Pollu., 3-2: 101-105.
8. Jung, J.Y., Y.C. Chung, H.S. Shin and D.H. Son, 2004. Enhanced ammonia nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. Water Res., 38: 347-354.
9. Feng, Q.L., J. Wu, G.Q. Chen, F.Z. Cui, T.N. Kim and J.O. Kim, 2000. A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*. J. Biomed. Mater Res., 52: 662-668.
10. Shearer, A.E.H., J.S. Paik, D.G. Hoover, S.L. Haynie and M.J. Kelley, 2000. Potential of an antibacterial ultraviolet-irradiated nylon film. Biotech and Bioeng., 67: 141-146.
11. Mclean, R.J.C., A.A. Hussain, M. Sayer, P.J. Vincent, D.J. Hughes and T.J.N. Smith, 1993. Antibacterial activity of multilayer silver copper surface-films on catheter material. Can. J. Microbiol., 39: 895-899.
12. Chohan, Z.H., C.T. Suparna and A. Scozzafava, 2004. Metalloantibiotics: Synthesis and antibacterial activity of cobalt (II), nickel (II) and zink (II) complex of kefzol. J. Enz. Inh. Med. Chem., 19: 79-84.
13. Ulkuseven, B., A. Tavman, G. Otuk and S. Birteksoz, 2002. Antimicrobial activity of Fe-III, Cu-II, Ag-I, Zn-II and Hg-II complexes of 2-(2-hydroxy-5-bromo/nitro-phenyl)-1H and 2-(2-hydroxyphenyl)-5-methyl/chloro/nitro-1H benzimidazoles. Folia Microbiol. 47: 481-487.

14. Chen,Y., L. Wang, S. Jiang and H.J. Yu, 2003. Study on novel antibacterial polymer materials preparation of zeolite antibacterial agents and antibacterial polymer composite and their antibacterial properties. J. Polymer. Mater., 20: 279-284.
15. Cik, G., H. Bujdakova, F. Sersen, 2001. Study of fungicidal and antibacterial effect of the Cu (II)-complexes of thiophene oligomers synthesized in ZSM-5 zeolite channels. Chemosphere, 44: 313-319.
16. Islam, M.S., H.M. Motahar, Banu, L. Arjuman, C. Sultana and M.A. Quadir, 2003. Antibacterial and antifungal activity of mixed ligand complexes of oxovanadium (IV), titanium (III) and cadmium (II) metal ions. Oriental J. Chem., 19: 547-554.
17. Ichinose, N., Y. Ozaki and S. Kashu, 1992. Superfine particle technology. Springer, London, (Book).
18. Stoimenov, P.K., R.L. Klinger, G.L. Marchin and K.J. Klabunde, 2002. Metal oxide nanoparticles as bactericidal agents. Langmuir, 18: 6679-6686.
19. Colvin, V.L., 2003. The potential environmental impact of engineered nanomaterials. Nature Biotech., 10: 1166-1170.
20. Mamadou, S.D. and N. Savage, 2005. Nanoparticles and water quality. J. Nano. Res., 7: 325-330.
21. Nair, A.S. and T. Pradeep, 2004. Reactivity of Au and Ag nanoparticles with halocarbons. Applied Nanoscience, pp: 59-63.
22. Diallo, M.S., S. Christie, P. Swaminathan, J.H. Johnson and W.A. Goddard, 2005. Dendrimer enhanced ultra-filtration recovery of Cu (II) from aqueous solutions using Gx-NH2-PAMAM dendrimers with ethylene diamine core. Environ. Sci. Technol., 39: 1366-1377.
23. A product manufactured by American Biotechnology Inc. (Baltimore, MD), under the name ASAP.
24. Oberdörste, G., 2001. Pulmonary effects of inhaled ultrafine particles. Intl. Arch. Occup. Environ. Health, 74: 1-8.
25. Ishibashi, K.I., 2000. Generation and deactivation processes of super oxide formed on TiO2 film illuminated by very weak UV light in air or water. J. Phys. Chem. B, 104: 4934-4938.
26. Zeman, L.J. and A.L. Zydney, 1996. Microfiltration and Ultra-filtration. New York: Marcel Dekker principles and applications, (Book).
27. Frechet, J.M.J. and D.A. Tomalia, 2001. Dendrimers and other dendritic polymers. New York: Wiley and Sons.
28. Bosman, A.W., H.M. Janssen and E.W. Meijer, 1999. About dendrimers: structure, physical properties and applications. Chem. Rev., 99: 1665-1688.
29. Tomalia, D.A. and I. Majoros, 2000. Dendrimeric supramolecular and supramacromolecular assemblies. In: Ciferri, A. (Ed.). Supramolecular Polymers, Marcel Dekker, New York, pp: 359-435.
30. Fischer, M. and F. Vo, 1999. gtle, Dendrimers: from design to application:a progress report, Angew. Chem., Intl. Ed. Engl., 38: 884-905.
31. Dendrimers, 1998. Topics Curr. Chem., Springer-Verlag, Heidelberg, Vol: 197.
32. Dendrimers II-Architecture, Nanostructure and Supramolecular Chemistry, Topics Curr. Chem., Springer-Verlag, Heidelberg, 2000, Vol: 210.
33. Dendrimers III-Design, Dimension, Function, Topics Curr.Chem., Springer-Verlag, Heidelberg, 2001, Vol: 212.
34. Dendrimers IV-Metal Coordination, Self Assembly,Catalysis, Topics Curr. Chem., Springer-Verlag, Heidelberg, 2001, Vol: 217.
35. Dendrimers, V., 2003. Topics Curr. Chem., Springer-Verlag, Heidelberg, Vol: 228.
36. Tomalia, D.A. and I. Majoros, 2003. Dendrimeric supramolecular and supramacromolecular assemblies. J. Macro Sci., 43: 411-477.
37. Fischer, M. and F. V gtle, 1999. Dendrimers: from design to application: A progress report, Angew. Chem., Intl. Ed. Engl., 38: 884-905.
38. Maraval, V., J. Pyzowski, A.M. Caminade, J.-P. Majoral, 2003.LegoQ chemistry for the straightforward synthesis of dendrimers, J. Org. Chem. 68: 6043-6046.
39. Maraval, V., A.M. Caminade, J.P. Majoral and J.C. Blais, 2003. Dendrimer design: how to circumvent the dilemma of a reduction of steps or an increase of function multiplicity. Angew. Chem., Intl. Ed. Engl., 42: 1822-1826.
40. Tomalia, D.A., 2004. Birth of a new macromolecular architecture: Dendrimers as quantized building blocks for nanoscale synthetic organic chemistry, Aldrichimica Acta, 37: 39-57.
41. Tomalia, D.A. and R. Esfand, 2001. Dendrons, dendrimers and dendrigrafts, Chem. Ind., 11(1997): 416-420.
42. Wu, P., A.K. Feldman, A.K. Nugent, C.J. Hawker, A. Scheel, B. Voit, J. Pyun, J.M.J. Frechet, K.B. Sharpless and V.V. Fokin, 2004. Efficiency and fidelity in a click-chemistry route to triazole dendrimers by the copper (I)-catalyzed ligation of azides and alkynes, Angew. Chem., Intl. Ed. Engl., 43: 3928-3932.

43. Sonke S. and D.A.Tomalia, 2005. Dendramer in Biomedical application-Reflection on the field. Adv. Drug Del. Rev 57:2106-2129
44. Tomalia, D.A. and R. Esfand, 1997. Dendrons, dendrimers and dendrigrafts. Chem. Ind., 11: 416-420.
45. Brothers, H.M., L.T. Piehler and D.A Tomalia, 1998. Slab-gel and capillary electrophoretic characterization of polyamidoamine dendrimers. J. Chromatogr., 814: 233-246.
46. Ottaviani, M.F., P. Favuzza, M. Bigazzi, N.J. Turro, S. Jockusch and D.A. Tomalia, 2000. A TEM and EPR investigation of the competitive binding of uranyl ions to starburst dendrimers and liposomes: Potential use of dendrimers as uranyl ion sponges. Langmuir, 19: 7368-7372.
47. Aorkas, M., D. Tsiourvas and C.M. Paleos, 2003. Functional dendrimeric ‘‘nanosponges’’ for the removal of polycyclic aromatic hydrocarbons from water. Chem. Mater, 14: 2844-2847.
48. Balogh, L., D.R. Swanson, D.A. Tomalia, G.L. Hagnauer and A.T. McManus, 2001. Dendrimer-silver complexes and nanocomposites as antimicrobial agents. Nano. Lett., 1: 18-21.
49. Jain, P. and T. Pradeep, 2005. Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. Biotech. Bioeng., 90: 59-63.
50. Furno, F., K.S. Morley, B. Bong, B.L. Sharp, P.L. Arnold, S.M. Howdle, R. Bayston, P.D. Brown, P.D. Winship and H.J. Reid, 2004. Silver nanoparticle and polymeric medical device: A new approach to prevention of infection. J. Anti. Chemo., 54: 1019-1024.
51. Moran, J.R., J.L. Elechiguerra, A. Camacho, K. Holt, J.B. Kouri, J.T. Ramirez and M.J. Yacaman, 2005. The bactericidal effect of silver nanoparticles. Nanotech, 16: 2346-2353.
52. Sons, W.K., J.H. Youk, T.S. Lee and W.H. Park, 2004. Preparation of antimicrobial ultrafine cellulose acetate fibers with silver nanoparticles, Macromol. Rapid Commun., 25: 1632-1637.
53. Sondi, I. and B.S. Sondi, 2004. Silver nanoparticles as antimicrobial agent: A case study on E-coli as a model for Gram-negative bacteria. J. Coll. Interf. Sci., 275: 177-182.
54. Panigrahi, S., S. Kundu, S.K. Ghosh, S. Nath and T. Pal, 2004. General method of synthesis for metal nanoparticles. J. Nano. Res., 6: 411-414.
55. Brittany, L., V. Carino, J. Kuo, L. Leong and R. Ganesh, 2006. Adsorption of organic Compounds to metal oxide nanoparticles (Conference presentation is part of: General Environmental).
56. Moreno, N., X. Querol and C. Ayora, 2001. Utilization of zeolites synthesized from coal ash for the purification of acid mines water. Environ. Sci. Techno., 35: 3526-3534.
57. Alvarez, A.E., A.G. Sanchez and X. Querol, 2003. Purification of metal electroplating waste waters using zeolites. Water Res., 37: 4855-4862.
58. Nichols, W.T., T. Kodaira, Y. Sasaki, Y. Shimizu, T. Sasaki and N. Koshizaki, 2006. Zeolite LTA Nanoparticles Prepared by Laser-Induced Fracture of Zeolite Microcrystals. J. Phys. Chem., 110: 83-89.
59. Li, G., 2000. A study of pyridinium-type functional polymers. Behavioral features of the antibacterial activity of insoluble pyridinium-type polymers. J. App. Pol. Sci., 78: 676-684.
60. Lakshmi, S., S.S.P. Kumar and A. Jayakrishnan, 2002. Bacterial adhesion onto azidated poly (vinyl chloride) surfaces. J. Biome. Mat. Res., 61: 26-32.
61. Lin, J., 2002. Bactericidal properties of flat surfaces and nanoparticles derivatized with alkylated polyethylene imines. Biotec. Prog., 18: 1082-1086.
62. Park, K.D., 1998. Bacterial adhesion on PEG modified polyurethane surfaces. Biomaterials, 19: 851-859.
63. Graveland, B.J.F. and C.G. Kruif, 2006. Unique milk protein based nanotubes: Food andnanotechnology meet. Trends Food Sci. Technol., 17: 196-203.
64. Lorenceau, E., A.S. Utada, D.R. Link, G. Cristobal, M. Joanicot and D.A. Weitz, 2005. Generation of polymerosomes from double-emulsions. Langmuir, 21: 9183-9186.
65. Phillips, K.S., J.H. Han, M. Martinez, Z.Z. Wang, D. Carter and Q. Cheng, 2006. Nanoscale glassification of gold substrates for surface plasmon resonance analysis of protein toxins with supported lipid membranes. Anal. Chem., 78: 596-603.
66. Siegel, R.W., 1991. Nanomaterials: synthesis, properties and applications. Ann. Rev. Mater. Sci., 21: 559.
67. Siegel, R.W., 1994. Physics of new materials. Fujita, F.E. (Ed.). Springer Series in Materials Science, 27: Berlin: Springer.
68. Uyeda, R., 1991. Studies of ultrafine particles in Japan: Crystallography, methods of preparation and technological applications. Prog. Mater. Sci., 35: 1-96.
69. Friedlander, S.K., 1998. Synthesis of nanoparticles and their agglomerates: Aerosol reactors. In R and D status and trends, ed. Siegel *et al*. (CITATION).

70. Boanini, E., P. Torricelli, M. Gazzano, R. Giardino and A. Bigi, 2006. Nanocomposites of hydroxyapatite withaspartic acid and glutamic acid and their interaction with osteoblast-like cells. Biomaterials, 27: 4428-4433.
71. Aksay, I.A., 1992. Hierarchically structured materials. MRS Proceeding, 255.
72. Bhainsa, K.C. and S.F. Souza, 2006. Extracellular biosynthesis of silver nanoparticles using the fungus Aspergillus fumigatus. Colloids Surfaces B: Biointerfaces, 47:160-164.
73. Bhattacharya, D. and R.K. Gupta, 2005. Nanotechnology and potential of microorganisms. Crit Rev Biotechnol, 25:199-204.
74. Bishop, J., 1990. Surface modified drug nanoparticles. U.S. Patent application. Docket 61894 Filed 9/17/90.
75. Suslick, K.S., T. Hyeon, and F. Fang., 1996. Sonochemical synthesis of iron Colloids. J. Am. Chem. Soc., 118: 11960-11961.
76. Sunstrom, J.E., IV, W.R. Moser, and B.M. Guerts, 1996. General route to Nanocrystalline oxides by hydrodynamic cavitation. Chem. of Mater. 8: 2061-2067.
77. Ping, L., J. Li, C. Wu, Q. Wu and J. Li, 2005. Synergistic antibacterial effecy of ß-lactum antibiotic combined with silver nanoparticle. Nanotech., 16: 1912-1917.
78. Vu, H. and H. Nikaido, 1985. Antimicrob. Agents Chemother., pp: 393-398.
79. Fontana, R., G. Amalfitano, L. Rossi, and G. Satta, 1992. Mechanisms of resistance to growth inhibition and killing by beta-lactam antibiotics in enterococci. Clin. Infect. Dis., 15: 486-489.
80. Jredget, E.E, H.A. Shankowsky, A. Groeneveld and R. Rurrell, 1998. Antibacterial nature of Ag used in infectious wound. J. Burn Care Rehabil., 19: 531-537.
81. Pirnay, J.P, D.D. Vos, C. Cochez, F. Bilocq, J. Pirson, M. Struelens, L. Duinslaeger, P. Cornelis, M. Zizi and A. Vanderkelen, 2003. Molecular epidemiology of *Pseudomonas aeruginosa* colonization in a burn unit: Persistence of a multidrug-resistant clone and a silver sulfadiazine-resistant clone. J. Clin. Microbial., 41: 1192-1202.
82. Batarseh, K.I., 2004. Anomaly and correlation of killing in the therapeutic properties of silver (I) chelation with glutamic and tartaric acids. J. Antimicrob. Chemother., 54: 546-548.
83. Hongwei Gu, Pak-lewingHo,Kenneth W.T. Tasang, Chun-Wing Yuand BingXu, 2003. Using Biofunctional magnetic nanoparticle to capture Gram-negative Bacteria at an ultra-low concentration. Chem. Communication. 1966-67
84. Rechards, W. T and A.L Loomis, 1927. The Chemical effects of high frequency sound waves, a preliminary survey. J. Am. Chemical Society; 49: 3056.
85. Tiwari D.K., J. Behari and P. Sen, 2007. (unpublished data).