ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Nanotechnology for Environmental Remediation.

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ABSTRACT

Environmental pollution is the major concern of developing as well as developed countries today. Extensive industrialization, as well as intensive agricultural activities, being carried out globally in both urban and rural areas, is the prime causes for this contamination of the land, water and atmosphere at all levels. Nonchalance for the ecosystem and indifference towards preservation of natural resources may cause long term damage, if not controlled at the right time. Nanotechnology has now emerged to provide a solution to this perennial problem and remediation procedures based on these techniques have been fairly successful to some extent in preventing further damage to the environment. However, more extensive research and development into efficiently utilizing nanotechnology based techniques to further this cause. This review explores the different types of nonmaterial's, including various types of metal nanoparticles, available today for remediation purposes and also the types of remediation which have been successfully attempted with the same.

Keywords: Remediation, Pollution, Nanotechnology, Nanomaterials, Metal Nanoparticles

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INTRODUCTION

Global industrialization during the last century has resulted in large scale damage to the limited natural resources available throughout the world. Unless serious measures are adopted to prevent their depletion and possible remediation for reuse, future generations will face a severe scarcity even for potable water. Intensive agriculture and land activities not only contaminate water and soil resources but also release toxic pollutants. Their remediation, in turn, may lead to the production of compounds which may have adverse health effects. For example, waste discharge from pulp, dyeing, petrochemical and textile industries and the partial degradation of phenoxy contaminants in various remediation processes produce phenolic components. These may have deleterious consequences on the health and well being of plant and animal biota.

Salvaging basic resources, along with remediating toxic pollutants and contaminants, by adopting latest technologies is a challenging priority and here nanotechnology is emerging to provide a state of art solution. Breakthrough research in nanotechnology, banking on a multidisciplinary frontier, is now being expected to solve the issue of environment detoxification, at least partially, within short periods of time. Nanoparticles, especially metal based ones, exhibit properties which are largely different from the respective bulk forms due to their large surface area to volume ratio, in addition to quantum confinement effects. The larger exposed area reflects in higher number of atoms being stationed at the surface and these are readily available for several reactions including catalysis. The possibility of this advantage being used for remediation of natural resources and detoxification of contaminants is currently a thrust area of research throughout the world. This technology achieves more importance due to the fact that even bioremediation processes like composting can generate compounds which cause undesirable ecological effects and seriously damage removal efficiencies [1].

Availability of clean water is one of the most important requirements for human life and for industries. The improvement of water quality is thus an important area of research globally for scientists. The nanosorbants, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes and nanoparticle enhanced filtration, which are the spin offs of nanoscience, have enormous applications in the field of water purification. They can also serve as high capacity/ selectivity / recyclable ligands for toxic metal ions, radionuclides, organic and inorganic solutes/anions in aqueous solutions. Due to their large surface area and their size and shape dependent optical, electronic and catalytic properties, they are currently being used to develop more efficient water purification catalysts and redox active media [2].

Nanomaterials also find applications in detecting and treating existing environmental contaminants and preventing new pollution. They can be used in the treatment of various contaminated media by chemically transforming contaminants or acting as a “super adsorbent” for many compounds. They also play a promising and vital role in the development of rapid and precise environmental sensors which can be used in the detection of pollutants at molecular levels and also for inactivating harmful bacteria [3].

Land contamination is a serious problem faced by our ever growing population. Emerging nanotechnology solutions for bioremediation and phytoremediation have proved to be extremely beneficial in the treatment of these contaminants. While one such technology is already commercially available for use in remediation, it is only inevitable that other similar applications, currently on the bench and lab scale will gradually and eventually move into field-scale trials [4].

Local environmental and public health agencies are most likely to face significant challenges in addressing nanotechnology risk issues, regardless of whether or not this is an ideal regulatory strategy. Downstream federal statutes, such as the CWA, CAA, and RCRA, are challenged by data gaps. Consequently, states and localities will likely be reacting to nanotechnology related environmental problems that may arise in the future [5].

The problem of remediation of soil and groundwater can be solved by using nanoparticles which due to their large surface area are effective in transforming environmental contaminants not conducive to detoxification. However, technical challenges, such as the delivery of the particles to the target area, have to be solved. Further, release of large quantities of manufactured nanoparticles into the soil prior to extensive human and ecological toxicity testing is a matter of concern. So far nano Zero Valent Iron (nZVI) is the only application of nanomaterials in soil and groundwater remediation that has been successfully commercialized - at least in the United States. The use of nanoscale calcium peroxide for remediation is expected to be common in a few years. Several nanomaterials have been tried for remediation applications and these were initially largely synthesized by physical and chemical methods [6, 7].These processes however, release toxic by products and also involve the use of drastic physical conditions. Hence the use of materials, prepared by these techniques, poses additional environmental hazard and are not be advisable for remediation. More recently, an alternative method of green synthesis of nanomaterials has been attempted successfully by several researchers. The process has been achieved from plant extracts as well as from microorganisms, *viz.*, mainly bacteria and fungi. This route of synthesis is however largely restricted to metal nanoparticles and involves a reduction process, making use of intracellular and extracellular enzymes secreted by the plants and micro organisms. The metal ions, reduced to nano forms by living organisms apart from serving as tools for cleaning up environmental resources, are also widely used in biosensors, bioprobes and other biosystems. Metal nanoparticles with desired shape and size can be obtained using the organisms ranging from simple bacteria to highly complex eukaryotes [8].

Iron Nanoparticles for Effective Remediation

Iron nanoparticles have always been extensively used in the chemical, electronics and other industries. Recently their applications have been extended to the treatment of toxic and hazardous wastes and also for remediating soil plus wastewaters. Iron is a strong reductant and nano iron has been accepted to have a core shell structure with Fe^0 as the core and oxide/hydroxide as the shell. In this form, it can degrade dyes, reduce aromatic nitro compounds and also dehalogenate organic compounds along with removing metal ions. It has been reported that zero-valent iron (Fe^0) nanoparticles are very efficient in scavenging chromium from soil with reduction of Cr (VI) being directly proportional to the concentration of metal particles [9]. Contact time, presence of stabilizers, humic acid and parameters like pH influence the reduction process. Higher contact time will naturally remediate more particles and so would the presence of stabilisers like carboxy methyl cellulose, since they would prevent aggregation of these particles and keep them in nano state. Hence a lower concentration would be required to remediate a given amount chromium as compared to unstabilised particles. This influence of stabilizers is seen in case of chromium remediation from ground water where it has been observed that starch stabilized particles are more effective than simple nanoparticles which may be again be due to the same reason of aggregation prevention[10]. Although iron is effective in chromium remediation, its presence in powder and filing forms show reduced efficacy of remediation as compared to its nano form probably due to reduced surface area. Stability of these nanoparticles in suspensions has also been achieved by modifying them with lactate and such particles are very useful in remediating dehalogenating organic pollutants, such as pentachlorophenol and dinitrotoluene, from various types of soil and ground water [11].

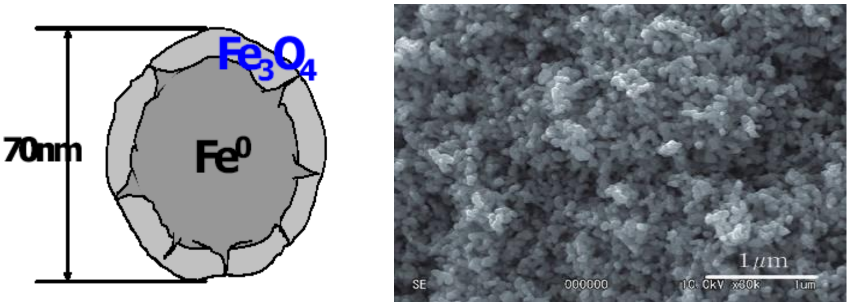

Figure 1: Structure and SEM image of Iron nanoparticles [11]

Nano Zero-Valent Iron is also an emerging option for *in-situ* remediation of contaminated soil and ground water as it facilitates the removal of chlorinated organic contaminants (e.g. PCB, TCE, PCE, TCA, pesticides, solvents) along with inorganic anions like (perchlorate) [12]. It has also been found to be efficient for the removal of polycyclic aromatic compounds from the contaminated soil and water sites. Conditions like particle size and number along with reaction time needs to be standardised for the same as reported for pyrene removal from affected sites [13]. Similarly magnetite Fe_3O_4 nanoparticles, synthesized from Fe (III) and Fe (II) by chemical co-precipitation with attached reactive amine groups on surface have been tested for their activity of sorbent removal of Cr (IV) ions and found to be effective [14].

The utilisation of zerovalent iron particles, *i.e.,* ZVI technology, for the decontamination of groundwater reduces both the chlorinated hydrocarbons and metal toxicity. Their reductive ability has also been exploited for the remediation of radio nucleotides like uranium [15].

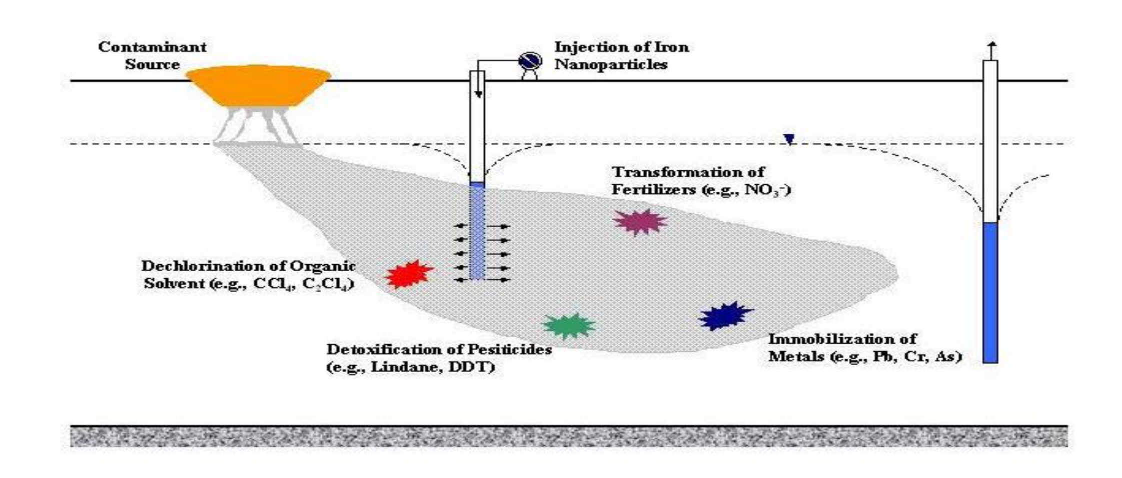

Figure 2: Potential remedial scheme using ZVI nanoparticles [15]

An electro exploding wire (EEW) technique has been proposed for the synthesis of iron nanoparticles which can be subsequently used for the removal of lead and cadmium ions from water [16]. The particles prepared by this technique have proved to be effective adsorbents with high adsorption capacities for the remediated metals at equilibrium. It is significant to note that at the initial stages, the absorption is rapid but decreases towards equilibrium. Removal is naturally directly proportional to the adsorbent dosage.

Metal hexaferrites are found to be more useful for arsenic remediation compared to simple magnetites. A distinct advantage of the former over the latter crystals is their separation after remediation which is much easier due to their stronger magnetic character and requires the application of a lower magnetic field. Solvothermal synthesis of magnetic nanocrystalline barium hexaferrite at 350ºC followed by annealing at 750ºC has been reported, which produces nanoparticles of <200nm capable of arsenic removal from waste waters [17]. Microbes can degrade toxic organics in the soil and iron nanoparticles can supplement their activity by several folds by increasing the microbial population as well as by enhancing the activity of soil enzymes. Enhanced degradation of 2, 4-dichlorophenoxyacetic acid in soil, especially in the presence of iron particles, in the nano range has been reported [18]. These special particles probably act by facilitating the growth of soil microbes and increasing the enzyme activity of urease, catalase and alkaline phosphatase in treated as compared to the untreated soil.

The removal of cadmium, lead, zinc and copper by nanohematite particles with high adsorption capacity has been investigated and the effect of pH, sorbent concentration and temperature has been studied. Here, it has been observed that while the adsorption of cadmium, lead and copper are endothermic processes, zinc adsorption is exothermic. Lead shows a spontaneous adsorption reaction [19].

Water soluble L-arginine capped super paramagnetic ferric oxide nanoparticles, having saturation magnetization upto 49.9 emu g-1, has been synthesized by using a one-pot and green method. The average diameter of particles was found to be 13 nm with negligible coercivity [20]. Maghemite nanoparticles have been prepared using electrochemical method for removal of As(V) due to their inherent adsorption capacity and their thermodynamic and kinetics parameters studied. The nature of adsorption processes here was found to be spontaneous and endothermic [21]. Investigations have been carried out on zero valent iron nanoparticles which cause the removal of hexavalent chromium ions from contaminated ground water. To increase the longevity and reactivity of ZVI nanoparticles, the role of factors such as alkalinity, pH, hardness, dissolved oxygen, particle density, oxidation-reduction potential, age and ionic strength of groundwater agglomeration of nanoparticles, contaminant concentration and concentration of competing oxidants have been reported[22]. The applications of ZVI nanoparticles, for soil and groundwater remediation, have been compared along with the methods of treatments and other factors such as particle concentration, media treatment, etc [23]. The inhibitory effect of Humic acid on 2,4-dichlorophenol dechlorination has been illustrated. Humic acid works as an adsorbate for palladium-iron bimetallic nanoparticles and decreases the efficiency of dechlorination. Humic acid is mostly found in ground water and its dosage is indirectly proportional to the reaction rates [24].

Zeolitic tuff is a mixture of volcano deposit that contains zeolites and some magnetic products such as volcanic glass and aluminum silicate minerals. There are many methods for producing and stabilizing zeolitic tuff in the nanorange. Differential bead size mixture production and attrition milling are some methods which change a raw zeolitic tuff to the nanorange. The beads get ground and disperses a raw zeolitic tuff into powder particles. Surface area, absolute zeta potential and cation exchange capacity increases at the nanorange thus increasing its potential for immobilizing heavy metals. Hence zeolitic nanotuffs are also important supplementary materials for the soil remediation [25].

Organic halides can cause reductive dehalogenation with the help of zerovalent metals. ZVI and its bimetallic combinations have high surface area and reactivity. When the second catalytic metal (Pd, Pt, Cu or Ni) is mixed with zerovalent iron, they increase dehalogenation rate. Due to this property, ZVI is used in environment remediation application. Dechlorination rate can be increased in supported zero valent Fe/Cu bimetallic nanoparticles in comparison with supported nano ZVI [26].

Iron nanoparticles, coated with ferromagnetic carbon, have a stronger ability to remove Chromium (95%) from the water waste than simple iron nanoparticles. The iron group elements such as iron and cobalt have additional magnetic and chemical catalytic properties when they are used at nano level [27].

Iron nanoparticles have enormous potential for *in situ* applications. Research has shown that they are also effective for transformation and detoxification of environmental pollutants, like pesticide, PCBs etc. Nanoparticles can simply be transported from one place to another with help of flowing groundwater and the contaminated plume of nanoparticle-water slurry can be ejected under high pressure. This is useful in the treatment of water[28].Surface modified iron nanoparticles have more movement in porous media as compared to simple iron particles. Due to this increased movement, it acquires high potential for the removal of arsenic from water. Basically for this process, 2- 10 nm size particles are used [29].

Uranium sorption is very effective with magnetite nanoparticles in neutral solutions and the anionic species of uranium aids the same. The amount of Fe (III) contents are increased and U(Vl) reduction occurs. Hence with the help of magnetite nanoparticles, uranium can be removed from the pollutants [30]. Some specific enzymes can be immobilized on the surface of magnetic nanoparticles and then used in a nanodevices, nanosensors and biomedicines [31].

Nanoparticles are also harmful in some cases. The cytotoxic effects of Fe_3O_4, oleic acid-coated Fe3O4 (OA-Fe3O4), and carbon coated Fe (C-Fe) nanoparticles on human hepatoma BEL-7402 has been reported and the mechanism of toxicity has been elucidated. The report shows that the influence potency of magnetic nanoparticles observed in all experiments would be: OA-Fe3O4 < Fe3O4 < C-Fe[32].

A variety of contaminants have been removed with the help of nZVI particles. A cheap method for the removal of aqueous phosphate and other contaminants has been developed. In the phosphate removal technique, nZVI is used as a slurry material. Different concentrations of phosphate (1, 5, and 10 mg PO4 P/L with 400 mg NZVI/L) were removed to the extent of 96 to 100 % in 30 minutes and the efficacy of this method is 13.9 times higher than other microparticles [33]

The use of metallic iron (Fe^0) in subsurface reactive permeable barriers has been successful as a technology. In this technology, two different tools are used to optimize the efficiency of Fe^0 for aqueous contaminant removal. One involves reducing the particle size of Fe^0 down to the nanoscale (nano-Fe^0) and the other involves using bimetallic systems. So basically, this system is used for water treatment only [34].

Iron and nickel nanoparticles have been used in bioremediation for the removal of uranium. When these nanoparticles go through vacuum annealing processes, the efficiency of uranium removal is higher than the iron particles of larger size [35].

Metal /clays and aluminosilicates are the micro porous materials which are used as matrices for nanoparticle encapsulation and stabilization processes. These clays are thermo stable due to presence of the well-dispersed clay nanolayer. Thermo stable clays (aluminium oxide clay and iron oxide clay) are also used for treating simulated radioactive wastewaters [36] but in some cases, iron nanoparticles are encapsulated in alginate biopolymer. These types of alginate biopolymer encapsulated iron nanoparticles are used for trichloroethylene remediation. One reason for using alginate biopolymer is that it is biodegradable in nature [37]. The use of iron oxide nanoparticles (19.3 nm magnetite and 37.0 nm hematite) to remove arsenate and arsenite through columns has been studied. In the column experiment, it was noticed that 100% of arsenic is removed easily from the contaminated water [38].

NDSU scientists have recently invented a novel polymer-coated nanoparticle delivery system. It is a very useful and advanced technique in the area of environmental remediation processes. Many pollutants have been remediated using metal nanoparticles such as zero-valent iron (Fe°) nanoparticles (nZVI). This system has some positive useful properties like increased colloidal stability, reduced oxidation by non-target compounds, high affinity towards water/contaminant interface, etc. Due to all these properties, they show good results in the field of remediation[39].

Silica and Other Metal Nanoparticles as Bioremediators

It has been shown that ordered mesoporous materials (OMMs) comprise of thin films, spheres, monoliths, fibers and nanoparticles. OMMs are synthesized using different methods with structural properties and tailored surfaces which allow precise designing of these materials. OMM design and synthesis and their use in environmental applications which include removal of pollutants, both organic and inorganic, as well as heavy metal ions have been discussed[40].

SiO_2 particles in the nanometer range has been modified with 2,6 pyrimidine dicarboxylic acid, and used as a sorbent successfully for the separation and pre concentration of Hg(II) ions present in trace levels, from aqueous solution, before ICP-AES analysis. Better reusability and enhanced stability with respect to Hg ions was a positive aspect shown by the sorbent for the above purpose. The absorption equilibrium is fast, elution easy and the absorption capacity high with the procedure being rapid and convenient [41].

The interaction between immobilized nano Zirconium phosphate (ZrP) and host polymers has been illustrated. ZrP nanoparticles were encapsulated into three macroporous polystyrene resins with various surface groups like $-CH_2Cl$, $-SO_3$ -, and $-CH_2N\ (CH3)_3$. Three nano composite adsorbents (denoted as ZrP-Cl, ZrP-S, and ZrP-N) were fabricated, respectively for lead removal from water. It was shown that positively or negatively charged functional groups are more favourable on the host polymers than in neutral groups [42].Biogenic Pd nanoparticles, coated over the cathode of free microbial electrolysis cell (MCE) has been tested for the removal of water contaminants like Trihloroethylene and diatrizoate and it showed a 93± 4 % increase, in comparison to non- coated MCE[43].

The effects of geochemistry on Phlorochlorophenol (PCP) remediation by nanosized Pd^0/Fe^0 on smectite template has been studied and it was observed that the dehalogenation process of PCP was enhanced in presence of low pH and some anions like Cl^- [44].

It has been reported that bimetallic Palladium on-gold nanoparticles, reveal superior catalytic activity and improved deactivation resistance in comparison to normal palladium based materials[45].Bio-palladium, formed by deposition of Pd, on a bacterium, are actively used in the process of bioremediation through dehalogenation reaction[46].

TiO_2 nanoparticles have been employed for removal of Poly chlorinated biphenyl (PCB) from contaminated soil samples by the process of photo-catalytic degradation [47]. TiO MCM (Mesoporous molecular sieving) has been investigated for the photolytic degradation of endocrine disrupting compound, Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA) and it has been reported to be effected by the factors like catalyst, duration of light, amount of catalyst[48].Titanium dioxide nanoparticles (TiO_2-x) containing oxygen vacant sites have been synthesized using plasma discharge method and these increased mercury removal with increase in concentration of supplied oxygen. Moisture was found to be a competitive inhibitor for the binding of Hg to the oxygen vacant sites of TiO_2[49].The adsorption capacity of TiO_2 nanoparticles and bulk particles were compared and TiO_2 nanoparticles were reported to adsorb contaminant metals like Pb, Cu, Cd, Ni, Zn to a greater extent. The exhaustion was observed for bulk particles at pH 8 but not for nanoparticles[50].

Anti-parasitic activity of ZnO nanoparticles has been investigated against larvae of different parasitic species like cattle tick "*Rhipicephalus(Boophilus) microplus*", larvae of malaria vector*, "Anopheles subpictus"* Grassi; and filariasis vector*, "Culexquinquefasciatus"* Canestrini (Acari: Ixodidae) and head louse "*Pediculushumanuscapitis"* [51].

The problem of incomplete degradation of contaminants through sorption on metal oxide layers has been improved by employing acidic wash. Nickel nanoparticles have also been used for the sorption and degradation of 2,4-dichlorophenol (2,4-DCP) to 4-Chlorophenol, 2-Chlorophenol, and phenol under acidic conditions[52]. The application of Ni/Fe nanoparticles have been tested for the removal of 2, 4-dichlorophenol (2,4-DCP) from contaminated water in presence of humic acid and it has been found that the rate of removal of DCP reduced with the increase in the concentration of humic acid (HA) as it competed for the active site for adsorption on nanoparticles with DCP molecules [53].

A comparison of yeast cells with and without carbonized silver coating, showed that silver influences the adsorption of specific radio nucleotides, *viz.,*$^{239}Pu_{94}$ and $^{106}Ru_{44}$ from radio nucleotide liquid waste at very low levels. The silver nanoparticles were in the size range of 19 ± 9 nm and had no influence on the adsorption of $^{241}Am_{95}$. More detailed studies on optimization as well as the thermodynamics controlling this phenomena is required for elucidating the reasons behind this selective adsorption[54].

Role of Other Nanoparticles

There are some nanoparticles of Ag, CuO and ZnO which possess good antimicrobial properties against pathogenic bacteria. The bacteria play an important role in element cycling, pollutant degradation and plant growth. However, these particles act against beneficial soil microbes also, for example, against *Pseudomonas putida* KT2440[55].There has been increasing use of nanoparticles in everyday products used commercially as well as in research. These particles are expected to be released ultimately into wastewater streams [56].This is because nanotechnology finds application in various fields such as electronic, optoelectronic, biomedical, pharmaceutical, cosmetic, energy, catalytic and in materials. However it is difficult to assess the effect of nanomaterials on health and the environment because the methods and tools for such a task have not been well developed to a efficient extent [57]. It is very important that these processes be developed and investigated to ensure that nanomaterials are as safe as possible. Biofilters with long lifetime and high storage stability are very important for bioremediation processes to ensure the readiness at the time of occurrence of sudden contaminations[58]. Activated carbon is widely used for removing contaminants in public drinking system. Studies show that adsorption kinetics of activated carbon and its capacity of atrazine adsorption is reduced due to the presence of natural organic matter in water [59]. The use of zero-valent iron materials, singly or association with other technologies is very effective in the treatment of chlorinated solvent contamination. Iron seems to perform better if it is used singly. Due to its association with microbial dechlorination, it has been shown that the performance of nanoscale iron is significantly enhanced. This is likely due to the synergistic effect between the two processes[60]. It is proposed that the injection technology, instead, should be chosen according to the type of iron, the slurry concentration and the soil permeability. However, the injection technique by itself can also have a direct influence on the treatment efficiency. It suggested that zerovalent iron technologies for effective remediation warrants further application and exploration. The physicochemical and biological properties of the two kinds of biocomposites (n-CPC and m-CPC composites) have also been completely investigated[61].

FUTURE PROSPECTS

A technology develops only if it is cost effective, non-toxic and shows no accumulation in environment. The use of nanoparticles in the remediation schemes is limited by some factors like:

- Cost of synthesizing differently coated nanoparticles for larger sites.
- Lack of knowledge on the mechanism of interaction of nanoparticles and other normal constituents of a contaminated site and
- Lack of information on the final fate of nanoparticles used for the process

Research proposals for field work are not greatly encouraged as these involve the control of several variables. Research work needs to be directed towards field work and now many companies are working with nZVI for the remediation of contaminated soils and groundwater with several governmental agencies encouraging the research work, oriented towards developing remediation techniques in a cost effective way. Thus the use of nanoparticles in the field of bioremediation can boom in field practice by gaining more knowledge on the above mentioned areas.

ACKNOWLEDGEMENT

The authors thank VIT University for the support rendered in the preparation of this manuscript.

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