International Journal of Mathematics and Physical Sciences Research ISSN 2348-5736 (Online)
Vol. 3, Issue 2, pp: (143-150), Month: October 2015 - March 2016, Available at: www.researchpublish.com

Role of Nanotechnology As A Tool for Sustainability: Potential of Zerovalent Metal Naoparticles (ZVN) and Their Metal Composites in Environmental Remediation

[1]Priti Malhotra, [2]Arti Jain

[1]University of Delhi, Delhi-110007, India
[2]Department of Chemistry, Daulat Ram College

Abstract: **With the growing magnitude of environmental pollution, the focus on environmental remediation is also bound to increase and more so it becomes challenging task. With the advent of nanotechnology and the immense potential of nanomaterials, their role in cleaning the environment by efficiently removing the pollutants and biological contaminants becomes highly significant. This article is an overview of the nanoscaledzerovalentmetal (nZVm) particles in the field of various environmental contaminant remediation. Nanomaterials have given a new dimension to the environmental cleanup and have proved to be an effective alternative for site remediation. Among various other metals the potential of nanoscaledzerovalent iron(nZVI) in contaminant degradation has received considerable attention over the past decade and has been successfully utilized for the degradation of a wide range of pollutants including polyhalogenated compounds, chlorinated solvents, dyes, inorganic anions, heavy metals etc. Recent advances in exploring the potential of nZVI have led to modify them for enhanced stability and improved mobility. The high activity of nFeo is well preserved by stabilizing or supporting the particles either by another metal or by using some organic stabilizers. The bimetallic nanoparticles exhibit extraordinary reaction kinetics towards dehalogenation and thus decontamination processes. Stabilizers like carboxy methyl cellulose (CMC) and polyvinyl pyrrolidone (PVP) not only stabilized the nanoparticles but also result in the synthesis of smaller sized nanoparticles with higher surface area and greater efficiency.**

Keywords: **Zerovalent Metals, Nanoscaled, Adsorption, Environmental contaminant, Sustainability.**

I. INTRODUCTION

Nanotechnology has spurred significant interest in its approach for cleaning the environment. Burgeoning nanomaterials are being trapped by scientists to use them as a novel tool for environment sustainability. Nanomaterials can be engineered in such a way so that their characteristics properties can be harnessed for protecting the environment. In the recent past many researches have focussed on developing nanotechnology as more specific, cost effective remediation tool. For treating the toxic contaminants present in small amounts in air, water and soil, Naonomaterials are ideally capable of monitoring, recognising and removing them. For removing a particular pollutant nanomaterials can be fabricatedto decompose them even if they are present in micro levels. Nanomaterialscan also be engineered to develop highly miniature , accurate and sensitive pollution-monitoring devices: nanosensors which after detecting the pollutants may later interact with them and decompose them to less toxic species. Nanomaterials, when designed as catalyst, can be further aimed at manipulating such manufacturing processes which not only reduce the amount of material used, but also employ less toxic starting material and reduce the production of harmful wastes. Synthesis of various compounds which involves multistep processes can be catalyzed to minimize the number of steps and thus reduce the number of side products. This can further minimize the environmental hazards.

As the environment is ailing and horizons of nanotechnology is growing and it is being used in several applications to improve the environment. This includes cleaning up existing pollution, minimizing the pollution during manufacture of materials and making cost effective energy sources.

Two factors contribute to the nanoparticles capabilities as an extremely versatile remediation tool: the first is their small particle sizes (1-100nm) and second is their excellently high surface area which makes them an efficient remediation tool for both in situ and ex situ application. As compared to various other categories of nanoparticles, zerovalent metal nanoparticles like Zn^0, Cu^0, Fe^0, Mg^0, Pd^0etc have been reported to exhibit good reducing property leading to the removal of organic and inorganic contaminants from soil, sediments and ground water [1-6]. Recent advances in nanotechnology have allowed the synthesis of innovative superfine nanostructured Fe^0- particles which have shown tremendous potential to be utilized as remediation tool for treating waste streams [7-17]. The strong reducing capability of Fe^0 coupled with its nano size impact have been successfully applied as reductant to degrade chlorinated aliphatic and alicyclic compounds, chlorinated solvents, nitroaromatic compounds, textiles dyes, chlorinated pesticides and heavy metals [18-22]. Environmental toxins are best treated by zerovalent iron nanoparticles Fe^0 because of their abundance on earth crust and a highly reactive nature which makes them undergo rapid oxidation. Since nanoscalezerovalent iron has the most extensive contribution to the waste treatment as compared to other zerovalent metals, they have featured in many areas of environmental remediation. The massive potential of ZVIn is also reflected in their ability to adsorb a wide range of inorganic contaminants including nitrate[23]. Cr (VI)[24, 25], As(III) [26-28]and As(V) [29-31], Heavy metals and radionuclides [32-33]. Surface chemical analysis have revealed that the metals are converted to different oxidation states on the basis of their different in the reduction potential as compared to iron. As species having higher reduction potential than iron e.g. Cu(II) and Ag(I) are predominantly sequestered in their reduced state whereas those having reduction potential close to that of iron, the core Fe(0) acts as an electron source for reductive immobilization rendering nZVI to be an efficient adsorbent for metal cations.

Apart from Fe^0, nZVI/bimetallic technology has also proved to be efficient to subsurface remediation of chlorinated solvents and heavy metals [34,35]. Nanometals used for subsurface remediation at contaminated sites also include metals like Zn, Pd and Ni. However, role of nanoscaledzerovalent iron naoparticles has been largely recognized in the reduction of environmental burden of toxic wastes and this review is focussed on noble nZVI/bimetallic subsurface remediation.

Nanoscale bimetallic (Fe/Pd, 99.9% Fe) particle featuring large surface area and extremely high surface reactivity, are found to be among the vanguard of a new generation of remediation technologies. They could provide cost-effective remedial solutions to some of the most difficult contaminate sites and provide enormous flexibility for *insitu* remedial applications.

Metals like Cu, Zn and Sn have also known to possess catalytic ability in transforming and degrading halogenated organic compounds. Efficiency of Pd is manifested in complete dechlorination of many chlorinated aliphatic compounds to hydrocarbon by palladized iron [36, 37] nanoscalezerovalent copper supported on a cation resin was successfully synthesized to enhance the removal of carbon tetrachloride (CCl4) from contaminated water [38].

Iron based biometallic nanoparticles have further attracted a lot of attention because in combination with second metal their efficiency is enhanced. Fe^0 acts as the reductant and a second metal such as Pd, Cu, Ni or Pt act as the catalyst and together they shoe higher efficacy for transformation of various chlorinated compounds along with their predominant degradation mechanism, apart from enhancing the reaction rates, the second metal also increases the surface area of nanoparticles [39]. The second metal also on deposition creates many galvanic cells on the surface of iron thus enhancing its corrosion as well as the rate of redox reactions [40]. Due to the presence of second metal nFe^0acts as strong reductant for the dehalogenation of polychlorinated biphenyls [41], although the loading of second metal beyond a certain limit is not beneficial as it reduces the dechlorination efficiency [42] [Table 1]

Table 1: Bimetallic ZVIn in degradation of common contaminants

Nanoparticles involved	Contaminant removed	Proposed mechanism
nFe^0/Pd	Trichloroethene(TCE), and poly chlorinated biphenyl(PCB)	TCE dechlorinate to hydrocarbons And PCB to biphenyl
nFe^0/Pd	pentachlorophenol	Complete dechlorination to phenol
nFe^0/Pd	2,4-dichlorophenol	Catalytic dechlorination
nFe^0/Pd	2,2’,4,5,5’-pentachloro-biphenyl	Catalytic hydrodechlorination
nFe^0/Pd	Lindane	Complete dechlorination to cyclohexane
nFe^0/Ni	CCl_4 and $CHCl_3$	Reductive dechlorination
nFe^0/Ni	Poly-brominated diphenyl ethers (PBDEs)	Catalytic debromination
nFe^0/Ni	Aroclor 1242	Catalytic dechlorination to biphenyl
nFe^0/Ni	NO_3^-	Reduction
nFe^0/Ag	Tetrabromo-bisphenol A (TBBPA)	Reductive debromination
nFe^0/Ag	P	Reduction

Supported Zerovalent iron (ZVIn) for enhanced stability and mobility:

While ZVIn has substantial promise for environmental remediation, the high activity of nFe^0 also needs to be preserved for stronger and wider chemical action on various contaminants. Their synthetic approach may often ensure their narrow size distribution and low sedimentation rate. Different types of stabilizing agents are used who's potential depending upon their functional group, molecular structure and molecular weight. Some commonly used stabilizing agents are carboxyl methyl cellulose (CMC), polyvinyl pyrrolidone (PVP) and guar gum. It has been reported [43] that the efficiency of degradation of trichloroethylene by CMC stabilized Fe-Pd nanoparticles has 17 times enhanced reaction rates as compared to non stabilized ZVIn. CMC-Fe^0/Pd nanoparticles have also dechlorinated p-nitrochlorobenzene and 2,4-dichlorophenoxy acetic acid [44, 45]. Apart from being supported nFe^0 also gain long term stabilizing by immobilization on the supports. The supporting material helps to control the growth of nanoparticles and prevent their agglomeration, oxidation and hydrolysis in water. Moreover, the absorption capacity and overall reactivity of nFe^0 is also enhanced. Park et al [46] immobilized nFe^0 on an ion exchange resin discouraged agglomeration and reduced the amount of ammonia produced during nitrate reduction. Supporting agents like Kaoline [47], cellulose acetate, activated carbon, bentonite, resin etc have been used in the past as supporting agent for nFe^0 [48-52] and have proved to be efficient. Calcium alignate beads [53, 54] have also proved to be capable of preventing agglomeration and oxidation of nFe^0 while also retaining its activity. A wide range of contaminants which have been efficiently degraded by stabilized or supported $nFe^0$are listed in Table 2

Table 2: Supported ZVIn in degradation of common contaminants

Nanoparticles involved	Contaminant removed	Proposed mechanism
Cellulose acetate supported nFe^0	Trichloro ethylene	Dechlorination
CMC stabilized nFe^0/Pd	Lindane	Dihaloelimination and dehydrohalogenation under anaerobic conditions, oxidative degradation by dechlorination/dehydrohalogenationbunder aerobic conditions
CMC stabilized nFe^0/Pd	Trichloro ethylene	Complete Dechlorination
CMC-Cu/ nFe^0	1,2,4-trichloro-benzene	Sequential dechlorination
CMC-Pd/ nFe^0	p-nitrochloro-benzene	Dechlorination
CMC-Pd/ nFe^0	2,4-dichlorophenoxyacetic acid	Adsorption followed by reduction to 2-chloro phenoxyacetic acid and finally to phenoxyacetic acid
nFe^0/Cu with activated carbon support	*y*-HCH	Simultaneous adsorption and dechlorination
nFe^0/Pd-alginate	Trichloro ethylene	Complete Dechlorination
Bentonite supported nFe^0	Methyl orange	Adsorption followed by reduction
Resin supported nFe^0	Cr(VI) and Pb(II)	Reduction
CMC stabilized nFe^0	Cr(VI)	Reduction of Cr(VI) to Cr(III), and Pb(II) to Pb(0)
Calcium alginate entrapped nFe^0	NO_3^-	Reduction
Calcium alginate entrapped nFe^0	Cr(VI)	Reduction
Bentonite supported nFe^0	Cr(VI)	Reduction
Pillard Bentonite(Al-bent) supported nFe^0	Cr(VI)	Reduction

Dendrimers are a novel class of polymers used as templates or stabilizers to form relatively monodispersed organic/inorganic NPs and they play an important role in the synthesis of metal NPs. Although, the preparation of functionalized NPs using different methods still remains a challenge, one of the unique approaches used to prepare metal NPs. Dendrimers are highly branched nanoparticles with controlled composition and architectures and their sizes ranges from 1-100nm.Dendrimer encapsulated metal nanoparticles (DEMNs) have also been reported to be synthesized [55] by template approach in which metal ions are sorbed into the interior of the dendrimers and te subsequently chemically reduced to yield zerovalent metal particles having dimensions less than 4nm. The dendrimercomponent of these composites offer many advantages i.e they serve as a template for preparing nanoparticles, stabilize the nanoparticles enhance catalytic selectivity and control solubility. Apart from momometallic DEMNs, bimetallic materials have also been explored for their catalytic activity.

Nanosensors: Zerovalent metal nanoparticles as tools for synthetic biology:

Zerovalent metal nanoparticles offers a good amount of contribution in the area of synthetic biology as they act as efficient starting point in the form of quantum dots [56] (QD). QD's are class of novel compounds that are nanosized and emit light of specific wavelength depending on the size range of nanoparticle. Larger is the size of the np, higher is the wavelength of the infrared light emitted [57].These QD's are quite versatile in binding to proteins. An array of methods are available where CdSe:ZnS QD's emit light at 605nm and their location in the receptor cells are determined using an imaging microscope along with a 488nm laser [58].Such a method of sensing is applied to locate any protein of interest.

Similarly, it is also viable to use metal nanoparticles for detecting single proteins in situ in mammalian cells. 10nm gold nanoparticles have been produced which absorb a particular wavelength of laser light resulting in change in temperature. This further bring about a change in the refractive properties of the nanoparticles which is detected by second laser. A successful detection of gold nanoparticle labelled-protein mGluR5 (a neurotransmitter-receptor protein) within the cell membrane has been reported [59].There are also available examples of synthetic biology, being used to sense metal nanoparticles which would be further used for detection systems.

Due to the innovation of biological production of metal nanoparticles, these sensors can prove to be useful in engineering highly specific biological detection system where the purity of synthesized nanoparticles can also be assessed. For example the presence of arsenite is detected by engineering nanoparticles detecting systems using *Escherichia Coli* [60]Biological production of nanoparticles by bacteria is another lateral step towards environmental remediation as it reduces the toxicity of various metal ions because they are being reduced to zerovalent less toxic/soluble forms of metallic nanoparticles. Lots of research is going on in this area where both prokaryotics and eukaryoticsoraganisms are used to produce metallic nanoparticles as part of their defence mechanism fighting against toxic metals. One example of a eukaryotic nanoparticle producer is the fungus phoma, which produces silver nanoparticles as antibacterial agent also possessing catalytic efficiency utilized in oil industry and medical field [61]. ZVIn are known to be produced by bacterial strain Magnetospirillumgryphiswaldense and Shewanellasp [62]

which lead to the concept of novel nanoparticles known as nanowires used as contrast agent in MRI [63].Therefore biological synthesis of zerovalent metal nanoparticles can be used for wider applications such as contaminant identification, detoxification as well as specific production of nanoparticles from material found in water or soil so that their cleaning exercise can take place in situ. Nanosensors enables the atomic and molecular control of colloidal-metal nanoparticles as building blocks of advanced materials for environmental sensing applications whose immediate benefit will reduce human exposure to toxic metals in ground water, industrial effluents and run offs, thus improving human health.The potential of nanoparticles in environment monitoring is also extended as nanosensors for air borne volatiles [64-70], Alcohols, NH_3, NO_2, and CO. A Pd-Polyanilinenanocomposite has been developed as a selective methanol sensor [68].

II. CONCLUSION

The application of zerovalent metal nanoparticles and their supported nano composites provide greater sensitivity, lower cost, shorter turn-around times and smaller sample sizes for environmental remediation, real time analysis and higher portability. They can also be engineered to enhance their ability for removal of air and water pollutants. Through different degrees of functionalization of NPswth various chemical groups, selectivity in capturing the contaminants can be tailored. The environmental applications of polymer supported nanocomposites in photocatalytic/chemical catalysis degradation, the absorption of pollutants and pollutant sensing and detection can lead to a greener environment. However large scale production of polymer supportednanoomposites and their practical applications still remain open. Surface modification are still required for studying their high adsorption capacities, selectivitiesand process optimization. Sensors are being developed for sensing gases, chemicals and volatile organic compounds and for the detection and identification of bacteria. Dendritic nanopolymers is another zone where low pressure filtration can remove perchlorate and uranium from contaminated water and recover metal ions like copper, silver, nickel and zinc from industrial waste water. Since iron based nanomaterial have shown great promise, their dendritic nanocomposites can become the focus of many future research projects. Their long term efficacy, reusability, cost effective process optimization and diverse applications in biological systems can give rise to extensive environmental remediation.

ACKNOWLEDGEMENT

The authors greatly acknowledge University of Delhi for supporting and funding the innovation project.

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