Scholarly Research Journal for Interdisciplinary Studies,
Online ISSN 2278-8808, SJIF 2019 = 6.380, www.srjis.com
PEER REVIEWED & REFEREED JOURNAL, NOV-DEC, 2020, VOL- 8/62

ZERO-VALENT IRON NANOPARTICLES (NZVI) AND THEIR APPLICATIONS

Dr Yogendr Kumar Saraswat[1]

Department of Chemistry, B S A College Mathura

Dr Kaushal Kishor Singh [2]

Department of Chemistry, S V College Aligarh

Abstract

In 'Nanotechnology', a nanoparticle is described as "a particle having one or more dimensions in the range of 1- 100 nm." Nanoparticles are of great scientific interest because they effectively act as a bridge between bulk materials and atomic or molecular structures. The properties of materials change as their size approaches the nano-scale. An application of nanoparticles in the environmental cleanup is of great interest. Clean environment is essential for human sustenance and growth. The modern society is at crossroads of growing pollution and challenges it throws to researchers for finding the ways of its mitigation. Nanoparticles provide a powerful tool for detection and treatment of pollutants from the environment.

Key-words: *Nanoparticles, Zero-Valent Iron, Immobilizing, Photocatalysis, TCE.*

Introduction to Nanoparticles:

Zero-Valent Iron (ZVI) Zero-valent iron is a strong reducing material. It is capable of degrading or immobilizing a wide range of contaminants including organic chemicals and heavy metals. The use of nZVIs for environmental clean – up emerged when a small amount of it was used to destroy rapidly a group of recalcitrant ground water contaminants including trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) (Gillham et al., 2004; Wang et al.,2007). This seminal work led to the conceptualization of iron permeable reactive barriers (PRBs) which involves placing a vertical trench filled with granular ZVI materials in the flow path of an underground contaminant plume (Scherer et al., 2010). As contaminated ground water flows through the permeable wall bearing iron particles, the organic contaminants react with surface sites on iron particles thoroughly to form environmentally benign end products like hydrocarbons, chloride and water.

As a result, production and accumulation of some toxic and carcinogenic intermediate byproducts such as vinyl chloride (VC) and cis-1,2 – dichloro ethane takes place. Further, decreased permeability due to formation of secondary mineral products and microbial growth is a critical concern for the long-term effectiveness of PRB installation (Battelle, 2009; Liang et al., 2000). One of the primary parameters dominating the reaction rate is the number of active sites on the surface of ZVI particles presented to the ground water plume. Since the reaction on iron-based particles is a surface mediated process, the dechlorination rate strongly depends on the available surface area of the ZVI particles. In other words, increasing the fraction of active iron atoms located on the particles' surface would result in an increase in dechlorination activity. This can be achieved by decreasing the iron particle size. In order to enhance the dechlorination reaction rate and minimize byproduct formation, Wang and his co-researchers (Wang and Zhang, 2007) at Lehigh University investigated the application of zero-valent iron nanoparticles (nZVI) for the removal of TCE. He reported that nanoparticles, with a broad size distribution of 1-100 nm, showed much higher TCE dechlorination reactivity than that observed on micro zero-valent iron particles. Compared to conventional bulk iron, nZVI could potentially eliminate the need for PRBs, resulting in lower costs and greater remedial effectiveness. nZVI comprises a core, primarily zero-valent iron (Fe0) with a mixed valence oxide shell. The shell mainly consists of ferrous or ferric iron hydroxides which are formed from oxidation of the metallic iron through contact with oxygen or oxygenated water (Ghosh et al., 2012). The formed hydroxide or oxide layer can potentially reduce the reactivity of nZVI particles and thus decrease the effectiveness of the zero-valent iron particle and increase the possibility of harmful byproducts formation. Deposition of a second metal such as palladium (Pd), platinum (Pt) or nickel (Ni) prevents the formation of this oxide layer and enhances the dechlorination efficiency which consequently prevents the formation of toxic intermediates (Zhang et al., 2008).

A study conducted by Joia et al., during 1974-76, they picked up 140 samples of wheat flour from different flour mills and retail shops of various districts of Punjab and found more than 80% samples contained residues of DDT and HCH and their contamination level was far higher than the permissible limits. Cereal crops among others are contaminated most due to the extensive use various pesticides (Praveen Z. et al., 2017).

Eighty vegetable samples collected from different climatic regions of India during winter months of 1997-98 were checked and all of those found to contain pesticide residues and more than 30% of those contained pesticide residues beyond permissible limits (Beena Kumari, 2013).

As vegetables are consumed either raw or with least processing, the ingestion of pesticides into human body becomes more pronounced as an average Indian consumes about 150-250 g of vegetables per day. Organochlorine pesticide residues of DDT and HCH were reportedly present in the water samples of five lakes – Bhimtal, Sattal, Khurpatal, Naukuchiatal and Nainital of Nainital (U.P), India (Sharma V.P., 2007).

Further, the chemical analysis of branded packaged drinking water (commonly known as bottled water) conducted by Centre for Science and Environment, New Delhi, India has revealed that bottled water of all the major brands contain high doses of pesticide residues (Anon, 2003).

The problem is not endemic to India alone and rather has pervaded to other parts of the world also. Bottled drinking water samples in Mexico City were analysed and all of them were found to contain seven organochlorine pesticides (HCH isomers, heptachlor, aldrin and DDE) (Diaz et al., 2008).

Water samples collected from five water treatment facilities in Delhi were analysed and all of those found to have OCPs like lindane, endosulphan and DDT, but their concentrations were significantly low in the treated water (Thacker et al., 2008). Soil and ground water pollution by pesticides is the major concern to environmentalists. Pesticides in soil have become toxic to arthropods, earthworms, fungi, bacteria and protozoa which are vital to ecosystems. Andrade et al. (2007) reported and estimated the presence of lindane, DDT, dicofil and their degradation products at depths of 0 to 20, 20 to 60, and 60 to 100cm along 300m transect running between the land infill and a nearby river.

Pesticides are of great concern to not only Indian consumers but for the the entire world. No doubt, the use of pesticides in tandem with other agrochemicals has increased the food production all over the world, but at the same time it has contributed to many ailments in human beings including reproductive disorders in men and breast cancers in women. Advanced Oxidation Process Advanced oxidation process (AOP) is an attractive means for removing complex organics like pesticides and other environmental pollutants which were difficult to degrade chemically or biologically. In this process, the liquid phase organic compounds are degraded into their corresponding intermediates and mineralised further to carbon dioxide, water and mineral salts in the presence of a photocatalyst (Huete et al., 2006). About a decade and half ago, Augugliaro et al., (2006) focused on using semiconductor materials as photocatalysts for the removal of organic and inorganic pollutants from both aqueous and gas phase. Since then this method has been in vogue as a means of environmental clean-up due to its ability to oxidise the organic and inorganic substrates.

Techniques for production of hydroxyl radicals Hydroxyl radicals are very reactive due to their high oxidation potential i.e, 2.80 eV (Tchobanoglous et al., 2003). They are short-lived as their half-life is about one nano second (1 ns). These are therefore produced in situ by a variety of methods. Some of the frequently used methodsare O3/UV, O3/H2O2, O3/UV/H2O2, Fe2+/H2O2/UV, O3/TiO2, TiO2 / H2O2 / UV, ZnO / H2O2 /UV and photocatalysis. The chemical oxidizers used in these methods have their limitations which are –

1. The systems to be treated should be free from heavy metals.
2. Contaminants degradation efficiency may be reduced due to the presence of free radical scavengers.
3. Chemical oxidizers added into the system in excess may act as a scavenger.
4. Handling and storage of chemical oxidizers need special safety measures.

Photocatalysis Mechanism of α - Fe2O3:

When a photocatalyst is illuminated with radiations of correct energy, the electrons in the valence band jump to the conduction band and in the process create electrons and holes. These electrons/holes pairs start a series of redox reactions and ultimately degrade the target molecules. Both oxidation andreduction processes may proceed simultaneously and which process dominates depends on the chemical and adsorption properties of the targeted compound.

Material and Methods :

Reagents and Chemicals Anhydrous ferric chloride of analytical grade with purity more than 98% was obtained from Sigma - Aldrich, USA. Sodium borohydride of analytical grade with purity more than 95 % was obtained from Sigma - Aldrich, USA. Pectin from citrus peel was obtained from Sigma - Aldrich, USA. Palladium chloride (PdCl2) of analytical grade with purity more than 97 % was obtained from Sigma - Aldrich, USA. DDT of analytical grade was obtained from Sigma - Aldrich, USA. Ostracodtoxkit F was obtained from Micro-BioTests, Nazareth, Belgium.3-(4,5-dimethylthiazol-2-yl)-2,5 diphenyl tetrazolium bromide (MTT) was obtained from Merck. Hexane and acetone were obtained from SRL, India. Other general laboratory glasswares were arranged locally. All chemicals were used without further purifications. Double distilled water was used throughout the experiments for preparation and dilution of the solutions.

Synthesis of α–Fe2O3:

Pure hematite nanoparticles were synthesized by chemical co-precipitation method. In this method, an aqueous solution of ferric chloride of 0.05 M was prepared in a three necked RB flask. The solution was stirred magnetically for 30 min in an inert atmospheric condition to obtain a homogeneous solution. To this solution, 50 mL of aqueous solution of 2 M of NH4OH was added gradually as the precipitating agent. Base solution (NH4OH) was added drop wise to maintain a pH value of 11. The reaction vessel was then heated up to the temperature of 80 0C under magnetic stirring for 3 hour. The resulting precipitate was centrifuged, and then washed thrice with double distilled water and acetone for several times. It was finally dried in air at 80 0C for two hours and then calcined at 700 0C for four hours. The calcined hematite was preserved in vacuum.

Transmission Electron Microscopy (TEM) :

Transmission electron microscopy (TEM) is a type of characterization technique that gives information about morphology, size and crystallinity of different nanomaterials (Williams et al., 1996). In TEM, a beam of electrons is allowed to pass through the sample, and both the scattered and non-scattered (transmitted) electrons emerging out of the sample carry a lot of structural information of the sample. The working principle of TEM is very much similar to that of SEM except that the former detects transmitted electrons while the latter detects both back scattered and secondary electrons. The resolution power of this technique is far greater than the ordinary light-powered optical microscope and this can be used to measure specimens having size less than 0.5 μm in diameter.

Fe (II) extract from soil :

Following the incubation period of 7, 15, 21 and 28 days, about 0.5 g of soil was taken in a glass vial to which 5 ml of 0.5 M HCl was added and the entire content was mixed by swirling for 30 s. The whole mixture was then left for 1 hr at room temperature. Then 0.1 ml extract of the above mixture was added to 5 ml of ferrozine (1 g/L) in 50 mM HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid) and the solution was maintained at pH 7 by adding NaOH. The determination of Fe(II) content was done spectrophotometrically by measuring the absorbance of the supernatant at 562 nm. During the extraction process, Fe(II) was neither oxidized nor Fe(III) was reduced. Similarly, another soil sample of the same quantity was extracted by the above described method with the exception that the extractant was 5 ml of hydroxylamine hydrochloride (0.25M) in HCl (0.25M). Fe(III) is reduced to Fe(II) under acidic conditions by hydroxylamine. The calculated difference between the

Fe(II) obtained in the hydroxylamine and HCl extractions was taken as the amount of hydroxylamine-reducible Fe(III). A wide range of concentrations of Fe(II) (FeSO4), Fe(III) (FeCl3), nZVI and DDT were used to establish standard toxicity curves for ostracods to determine LC50 and EC50. Ostracods were exposed to soil spiked with DDT, zero valent iron nanoparticles, Fe(II) and Fe(III).

DDT extraction and analysis:

6g of dry soil sample was dissolved in a 100 ml mixture of hexane and acetone (1:1 ratio) in a 150 ml glass bottle and the suspension was incubated on a horizontal shaker, fixed at aconstant rpm, for 60 min. Then 30 ml of triple distilled water was added to it and the resulting emulsion was incubated for another 10 minutes. The emulsion was centrifuged (671×g, 5 min) to obtain phase separation. 2 ml aliquot of the upper hexane phase was taken into GCglass vials for analysis by GC-MS using a 0.2 mm x 50 m column and 1 ml/min He as carrier gas. A 2 µl sample was injected into a split/split less injector at an initial oven temperature of 75 0C, while the injector temperature was 240 0C and the column temperature was 300 0C. The total DDT recovery from the soil was 90.1±5.2 %.

Collembola tests:

The standard protocol (OECD guidelines 2008) was followed and accordingly 10 collembola were added to treated and untreated soil following the incubation of 7, 15, 21 and 28 days. About 30 g of soil samples from each category were taken in plastic cylinders of height 6 cm and inner diameter 4.2 cm. A small space in the cylinder cover was left for respiration of collembola. Dried baker's yeast weighing about 15 mg was added onto the top soil to serve as food for collembola. All these tests were conducted when soil's water holding capacity was about 50%. The test cylinders were maintained at 20 0C with an alternate light and dark cycle of16:8 hr at 400-800 lux. The test species' reproduction process took four weeks to complete.

Analysisand Results:

In this study, we synthesized well defined monodisperse α-Fe2O3 nanoparticles which were used to study the degradation of DDT in spiked soil. α-Fe2O3 nanoparticles are not properly studied before for their efficacy against DDT degradation in environmental remediation process. However, our study showed that the degradation rates of DDT in spiked soil by α-Fe2O3 nanoparticles were as good as to that of nZVIs capped with pectin. Hence, α-Fe2O3 nanoparticles could be a promising and effective material against soil pollutants like DDT. The ecotoxicity of α-Fe2O3 nanoparticles on soil biota was studied by taking collembola and ostracods as test species as these are predominantly sediment dwellers. The negative effects α-Fe2O3 nanoparticles on mortality and growth of both collembola and ostracods were quite severe, whereas the negative effects of DDT on reproduction of collembola and development of ostracods were very weak. It was also observed that prolonged incubation period led to diminishing toxicity of α-Fe2O3 nanoparticles on collembola and ostracods. More studies are required to study the effectiveness of α-Fe2O3 nanoparticles against DDT in different soil matrix of different agroclimatic regions.

REFERENCES

Ali, A.; Zafar, H.; Zia, M.; Ul Haq, I.; Phll, A.R.; Ali, J.S.; Hssain, A. Synthesis, characterization, applications and challenges of iron nanoparticles. Nanotechnology Science and Applications. 2016, 19(9), 49-67.

Cornell, R.M.; Schwertmann, U. The iron oxides: structure, properties, reactions, occurrences and uses. John Wiley & Sons. 2003.

Gavaskar, A.R.; Gupta, N.; Janosy, R.; O̓ Sullivan, D. Permeable barriers for groundwater remediation. Battele Press, Columbus, OH. 2008.

Ghosh, R.C.; Paria, S. Core/shell nanoparticles: classes, properties, synthesis mechanisms, characterization, and applications. Chemical reviews, 2012, 112(4), 2373-2433.

Gupta, P.K. Pesticide exposure-Indian scene. Toxicology. 2004, 198(1), 83-90. Gyliene, O.; Nivinskiene, O.; Pakstas, V. Use of metallic iron for decontamination of solution containing Ni (II)--citrate. Polish Journal of Environmental Studies. 2007, 16(3), 397-402.

Johnson, R.L.; Johnson, G.O.; Nurmi, J.T.; Tratnyek, P.G., Natural organic matter enhanced mobility of nano zerovalent iron. Environmental Science & Technology. 2009, 43(14), 5455-5460.

Kabra, S.G. Independent study on pesticide use and NTDs. Indian Institute of Health Management and Research, Jaipur, India. 2010.

Kalra, R.L.; Singh, B.; Battu, R.S. Organochlorine pesticide residues in human milk in Punjab, India. Environmental Pollution. 2014, 85(2), 147–151.

Kumari, B.; Kumar, R.; Madan, V.K.; Singh, R.; Singh, J.; Kathpal, T.S. Magnitude of pesticidal contamination in winter vegetables from Hisar, Haryana. Environmental Monitoring and Assessment. 2013, 87, 311-318.

Mishra, K.; Sharma, R.C.; Kumar, S.; Contamination levels and spatial distribution of organochlorine pesticides in soils from India. Ecotoxicology and Environmental Safety. 2012, 76(2), 215-225.

Nag, S.K.; Raikwar, M.K. Organochlorine pesticide residues in bovine milk. Bulletin of Environmental Contamination and Toxicology. 2008, 80(1), 5-9.

Prabu, D.; Parthiban, R. Synthesis and characterization of nanoscale zero valent iron (NZVI) nanoparticles for environmental remediation. Asian Journal of Pharmacy and Technology. 2013, 3(4), 81-184.

Puri, S.N.; Murthy, K.S.; Sharma, O.P. Pest problems in India-current status. Indian Journal of Plant Protection. 2009, 17(1-2), 20-31.

Singh, R.; Misra, V. Stabilization of zero-valent iron nanoparticles: role of polymers and surfactants. Handbook of Nanoparticles, Springer. 2015, 1-19.

Tiwari, G.; Sriwastawa, B.; Tiwari, R.; Bhati, L. Drug delivery systems: An updated review. International Journal of Pharmaceutical Investigation. 2012, 2(1), 2-11.