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# APPLICATION OF NANOTECHNOLOGY IN THE REMEDIATION OF CONTAMINATED GROUNDWATER: A SHORT REVIEW

Ashutosh Agarwal\* and Himanshu Joshi

Department of Hydrology, Indian Institute of Technology Roorkee, 247667, India

## Abstract

Nanotechnology is an emerging science that has shown promise in humanizing various life facets ranging from medicine to industrial materials. One such application of nanotechnology is for the remediation of contaminated groundwater. Groundwater pollution is becoming a major problem not only for the developing countries like India but also for most of the developed countries of the world. In this respect the application of nanotechnology may prove a boon to the mankind by providing an advance way for groundwater treatment. The status of groundwater quality, basic idea of nanotechnology for remediation and its practical applicability, ongoing projects and future scope in India has been reviewed through this article.

**Keywords:** Nanotechnology, Groundwater, Organochlorine, Organophosphorus

## Introduction

With the advancement of industrialization, agricultural and urban activities the levels of groundwater pollution have increased many folds in the last few decades. In India, this has led to the increase in the concentration of many organic and inorganic pollutants much more above the permissible limits of drinking water standards [1]. A vast majority of groundwater quality problems are caused by contamination, overexploitation, or combination of the two. Soil and groundwater quality is slowly but surely declining everywhere. Direct dumping of untreated effluents into the wells is becoming one of the major causes of groundwater pollution. Moreover extensive use of pesticides in India has also led to the increase in the pollutants concentrations in groundwaters [2]. The most harmful compounds that are finding their ways in groundwaters through various illegal industrial and agricultural activities includes various organochlorine & organophosphorous pesticides, heavy metals and other carcinogenic compounds.

The application of nanotechnology for the remediation of contaminants may give promising results in future. The search for new and advanced materials is an important task of contemporary research in the environmental protection. In recent years, a great deal of attentions has been focused onto the application of nanostructured materials as adsorbents or catalysts to remove toxic and harmful substances from wastewater and air [3, 4]. Reactive nanoparticles appear to be useful in remediating groundwater and thus may prove useful in removing pesticides and herbicides in the environment [5]. Nanoparticles also may provide a more efficient and

controlled delivery/release method for the application of pesticides and fertilizers. Increasingly wide practical application of iron nanoparticles has been achieved in various hazardous waste site remediations. Since 1996, after it was proposed for the first time, the iron nanoparticle technology is at a crucial stage of its developmental process. Important research innovations have been accomplished in terms of synthetic methods, surface property amendments, and augmentation for field delivery and reactions. It has been demonstrated by various laboratory studies that iron nanoparticles are valuable for the treatment of a wide array of common groundwater contaminants such as chlorinated organic compounds like pesticides and polychlorinated biphenyls (PCBs), organic dyes and various other inorganic compounds.

## Status of groundwater contamination in India

Man's activity at ground surface, unintentionally by agriculture, domestic and industrial effluents, unexpectedly by sub-surface or surface disposal of sewage and industrial wastes has led to adverse effects on soil and groundwater quality. Since 1954 the dominant group of pesticides called organochlorine insecticides have been extensively used in India for agriculture as well as in public health sector [6]. Almost every organochlorine which includes notorious pesticides like DDT, endosulfan, dioxin, HCH (hexachlorocyclohexane) and aldrin has been found to cause some environmental or human health hazard. The use of organochlorines which are banned or restricted in most developed countries are still being used in this country. As a result of the effects of intense agricultural activities, the studies conducted on the contamination of soil and groundwater quality of

\* Corresponding Author, *Email:* [wheland@rediffmail.com](mailto:wheland@rediffmail.com)

Roorkee area, district Haridwar, India indicated the presence of 17 organochlorine and 9 organophosphorous pesticides which were found to be much above the permissible limits of Indian drinking water standards [2]. Their accumulation in low concentration in the body fat of mammals may pose health problems in long run [7] and it has been reported that most Indians accumulate about 26 mg DDT in their body through food items. The persistence of toxic pesticides in soil and water adversely affected soil health [8], aquatic life and quality of drinking water [9]. Cypermethrin residues in groundwater samples from Guatemala used for human consumption exceeded safe levels of  $0.5 \mu\text{g l}^{-1}$  in most of the cases. Contamination of soil and groundwater has been reported globally [10 – 14]. The concentration of various organochlorine pesticides like endosulphan, DDT and lindane in the groundwater samples of Hyderabad city, India has been found to be of the order of 0.5 to  $1.3 \mu\text{g l}^{-1}$  [15]. In the heart of India's green revolution belt, local farmers extensively use several banned and restricted pesticides. When fifty samples of soil, groundwater and vegetables were collected from various locations of the district Meerut, India and analyzed for pesticides contamination; the presence of extensive amounts of pesticides was reflected both in the soil surface as well as in groundwater bodies [16].

Ground is not only contaminated by organic pesticides but also the presence of huge concentrations of inorganic toxic metals and non metals have been reported. Among them the problem of arsenic is most prevalent. Arsenic contamination in groundwater and consequent human suffering in West Bengal, India has been a major problem which was first reported in December 1983 when 63 arsenic patients from 3 villages were identified. At present 3000 villages are arsenic affected. According to the WHO recommended value of arsenic in drinking water is nearly 10 mg/L which is much high then the permissible limits off drinking water standards. In a study, 95,000 people were clinically examined from arsenic affected districts of West Bengal and 10,100 people (9.4% including 2% children) were registered with arsenical skin lesions. Studies reveal the presence of elevated level of inorganic arsenic in food chain and in those consumer products where groundwater is used in affected villages [17]. In view of increasing groundwater pollution in the modern world there is an immense need to modify the existing technology for their remediation which not only works on small scale but can be employed on a large scale in nature to get the results in bulk. Application of reverse osmosis and other water purification systems works on a confined scale and their applications are limited to the user only. In order to look in a broader way, nanotechnology provides a very recent and better way to remediate soil and groundwater in nature.

### Nanotechnology an emerging technique

The solutions to most of the groundwater quality problems are difficult to detect and hard to resolve moreover they are quite expensive, tedious and not always efficient. In the field of environmental protection one of the important task of modern research is to find some new and advanced materials thereof. In recent years, a great deal of attention has been focused onto the applicability of nanostructured materials as adsorbents or catalysts in order to remove toxic and harmful substances from air and wastewater [3, 18]. 'Nanotechnologies are the characterization, design, production and application of structures, devices and systems by controlling shape and size at nanometer scale'. Reactive iron nanoparticles were found to be useful in remediating groundwater and thus also may prove useful in removing pesticides and herbicides from the environment [5].

In the field of nanotechnology the production of nanomaterials and products containing them are rapidly developing fields which provides many opportunities for new innovation. For the abatement of pollution production the application of nanotechnology is just beginning to be explored which could dramatically catalyze the most radical changes in the field of environment [19, 20]. The major factor which defines the capability of nanoparticles as an extremely versatile remediation tool includes their very small particle sizes (1–100 nm) in comparison to a typical bacterial cell which has a diameter on the order of  $1 \mu\text{m}$  (1000 nm). Hence nanoparticles can be transported effectively by the groundwater flow. Despite their minuscule status, nanoscale particles may hold the potential to cost-effectively address some of the challenges of site remediation [19, 21, 22]. Moreover the nanoparticles can also remain in suspension for ample periods of time in order to launch an in situ treatment zone. As a result, nanoparticles can be anchored onto a solid matrix such as activated carbon and/or zeolite for improved water, wastewater, or gaseous process streams treatment.

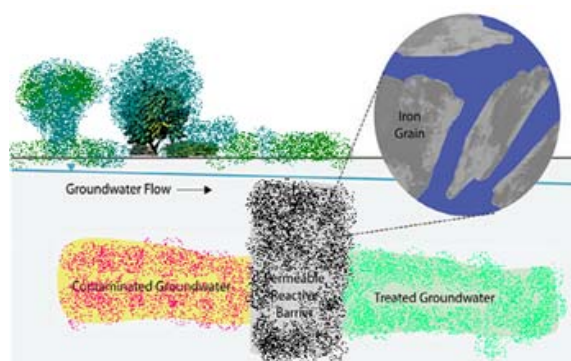
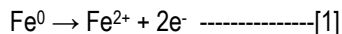


Fig. 1. Practical application of permeable reactive barrier for ground water remediation.

Over the past few years, the field of remediation has evolved continuously while developing and adopting new technologies so as to improve the remediation process. Among those new technologies the “pump and treat” [23] is considered to be one of the most established systems. The basic principle involved in the pump and treat systems is the ejection of contaminated groundwater from ground downstream of the contamination site and then treating it before returning it to the ground. However there are few drawbacks associated with this technology; for example the technology is tedious and expensive to operate and maintain while requiring continual energy input [23]. In the early 1990s with the examination for the reducing capabilities of metallic substances such as zero valent iron (ZVI) to treat a wide range of contaminants in hazardous wastewater, the most common employment of ZVI has been established in the form of permeable reactive barriers (PRBs) (Fig 1) designed to interrupt plumes in the subsurface and consequently remediating them.

In 1994, PRBs were first installed at the field scale to offer a proxy for the more established pump and treat systems. This technology was restricted only to the shallow plumes up to a depth of 50 ft due to their small depth installation capabilities. Moreover to prevent contaminants from circumventing the PRB, plumes had to be carefully differentiated and demarcated [24]. Problems occur from a decrease in iron reactivity caused by the precipitation of metal hydroxides and metal carbonates onto the surface of the iron [25]. The low reactivity of ZVI toward lightly chlorinated compounds resulted in the formation and determination of hazardous byproducts. Just as PRBs were designed to provide a better option to the pump and treat technology, new technologies are now available to compete with PRBs. Iron nanoparticles and their derivatives provide a potential for more effectual and inexpensive substitute to many remedial technologies [26]. The particle small size of the iron nanoparticles (1-100 nm) facilitates a very high level of remedial flexibility.

The use of nano ZVI, bimetallic nanoparticles, and emulsified zerovalent nanoparticle forms the whole sole for both soil and groundwater remediation. Besides these the most latest research also indicated that carbon nanotubes may also prove to be a most effective tool in remediating contaminated waters [27]. The most basic form of the nano iron technology encompasses nano ZVI and reactive nanoscale iron product (RNIP) [26, 28]. The practical applicability of these nano zero valent iron ( $\text{Fe}^0$ ) particles lies in the fact to get oxidized into +2 and +3 oxidation states thereby reducing other organic as well as inorganic impurities. Metallic iron ( $\text{Fe}^0$ ) serves effectively as an electron donor:



Chlorinated hydrocarbons on the other hand accept the electrons and undergo reductive dechlorination [29, 30]:

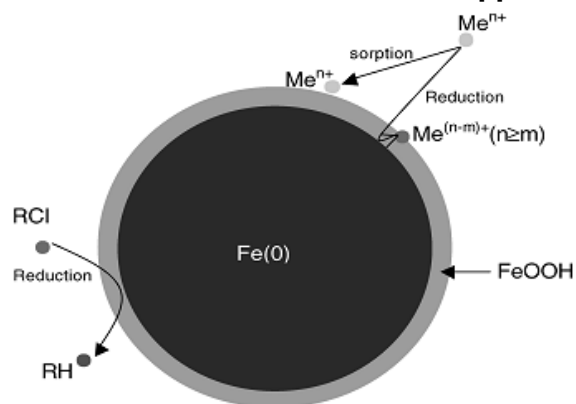
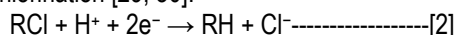
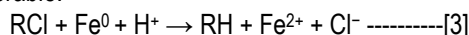


Fig. 2. Core shell model of nano zerovalent iron showing various chemical mechanisms

From a thermodynamic perspective, the coupling of the reactions [1] and [2] is often energetically highly favorable:



The standard reduction potential ( $E^\ominus$ ) of ZVI ( $\text{Fe}^{2+}/\text{Fe}$ ) is  $-0.44$  V, which is lower than many organic compounds like chlorinated hydrocarbons and metals such as Pb, Cd, Ni, and Cr hence these organic compounds and metals are thus prone to reduction by ZVI nanoparticles. Over the last few years, nano ZVI has been extensively used in the degradation of toxic and hazardous organic pollutants like lindane and atrazine [31], pentachlorophenol [32], 4,4'-dinitrostilbene-2,2'-disulfonic acid [33] etc. The study for the reductive capacity of zero valent metals have focused not only on halogenated (chlorinated) hydrocarbons e.g. DDT, DDD, DDE [34], but also on contamination of water due to nitrate [35], arsenic [36, 37], Cr(VI) and Pb(II) [38, 39], s-triazines [40], RDX [41, 42] and perchlorate [43].

Several recent studies provided precious approach into key nano ZVI properties associated with the potential to transform metal ions such as Cd, Ni, Zn, As, Cr, Ag, and Pb, as well as infamous inorganic anions like perchlorate and nitrate [44 – 48]. ZVI nanoparticles have been found to possess relatively higher capacity than conventional sorptive media and granular iron particles for the removal and/or reduction of these inorganic ions. Moreover several studies have predicted that bimetallic iron nanoparticles (Pd-Fe, Pt-Fe, Ni-Fe, Ag-Fe) can achieve relatively higher degradation rates and prevent or reduce the formation of toxic byproducts [26, 49]. Bimetallic iron nanoparticles involve a second and often less reactive metal such as Pd, Ni, Pt, or Ag along with iron nanoparticles. As with the addition of metal catalysts to

nano ZVI particles, the formation of emulsified zero valent iron (EZVI) also represents an enhancement to the existing nano ZVI technology. Emulsion droplets can be created using a food grade surfactant, biodegradable vegetable oil, water, and nano ZVI, where a surfactant-stabilized oil-liquid membrane forms around the iron particles in water [50].

With respect to remediation of environmental contaminants, the range of nanotechnology applications mirrors the spectrum of 'nonnano' strategies for contaminant remediation. Two of the major distinctions that define types of conventional remediation technologies also apply to nanotechnologies for remediation: in situ versus ex situ. In situ technologies involve treatment of contaminants in place, whereas ex situ refers to treatment after removing the contaminated material to a more convenient location (e.g. pumping contaminated groundwater to the surface and treatment in aboveground reactors). Various types of nanostructured adsorbents are most likely to be applied ex situ, where they can be recovered with the concentrated hazardous material that they adsorb. Particles of iron can be used in ex situ slurry reactors to treat soil, sediment [51], and solid waste. In cases of water and/or wastewater treatment, anchoring nanoparticles onto a solid matrix, such as activated carbon, can prove extremely effective. On the other hand the injection of nano iron into the ground represents the most common deployment of this technology thus far. Overall the process provides a number of remedial benefits. In comparison with PRBs, nanoparticle injection allows remediation at greater depths and in areas unreachable by PRBs (i.e. land covered by a building). Most importantly, this technique facilitates source zone remediation, a clear benefit for site cleanup. Nanoparticles can be mixed with water to form slurry that can be injected using pressure or gravity into a contaminated plume. Once injected, the particles remain in suspension, forming a treatment zone. Nano scale iron product (NIP) injections only work for aqueous phase source zone treatment and while they can enhance dense non aqueous phase liquids (DNAPL) dissolution, NIP injections cannot directly treat DNAPL. Emulsified zero valent iron offers a solution to this problem in the form of an external oil membrane [52].

Since 2000, several in situ field demonstrations employing the use of the nano ZVI technology have been conducted in contaminated groundwater site, including the first field pilot test [53] in Trenton, New Jersey, from May 8 to July 18, 2000. Numerous pilot tests undertaken by Golder Associates (between 2003 and 2005) in North America (United States and Canada), Europe, and Australia have been used to collect a large amount of field data that was interpreted together to establish the first cross comparison between various field applications. The involvement of iron nanoparticles for many academic and commercial

field scale tests are in progress or have reached completion along with many more sites yet to be scheduled for various other field studies. Some of them are as follows: Naval air engineering station, Lakehurst, New Jersey; Naval air station, Jacksonville, Florida [53]; Public service electric and gas company (PSE&G), Klockner road site, New Jersey etc. sites for the remediation of groundwater in shallow aquifer against various chlorinated hydrocarbons have already been completed by the injection of bimetallic iron nano particles in 2005. In addition to this many other nanotechnology applications for wastewater treatment and site remediation are currently in the research and development stages.

## Conclusions

There is no doubt in saying that the quality of groundwater is decreasing day by day and there is an immense need for adopting a new and advanced technique for the remediation of groundwater as a whole. Indian scientists are also actively working on the synthesis of various types of nano particles. It has been reported that halocarbons undergo catalytic destruction and mineralization with silver and gold nanoparticles in solution forming metal halides and amorphous carbon [54]. Jain et al., [55] suggested that silver nanoparticles coated polyurethane foam works as an antibacterial water filter which can be extensively used for practical purposes. Also Gold and silver nanoparticles have been used in the detection and extraction of endosulfan, an important pesticide in the developing world, from water solutions in sub ppm concentrations suggesting potential applications [54]. Even a porous thin film of TiO<sub>2</sub> has been found to be highly efficient for the degradation of naphthalene and anthracene. The rate constants are high and the reactions mostly follow the first order kinetics [56]. A team of researchers from IIT Chennai has developed nanoparticles that can abolish organochlorine pesticides. The quantitative removal of chlorpyrifos and malathion have been effectively achieved by gold and silver nanoparticles in solution state as well as in supported form over activated alumina. It has been observed that complete removal of these pesticides occurs when contaminated water is passed over nanoparticles supported on alumina [57]. Thus nanotechnology has been able to show promising results in this way. In India, there is a great need for adopting such a technique to remediate groundwater and a lot of further scope in research and development is still there to be worked on.

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