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*Original Research*

# The Application of Nanoscale Materials in Groundwater Remediation

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### Abstract

This review article summarizes the current situation in the application of nanotechnology to contaminated site remediation. Many types of nanomaterials and nanoparticles have been produced since their discovery. As remediation tools, carbon-based nanomaterial (CNM) sorbents and nanoparticles of zero-valent iron (nZVI) are at the forefront of scientific interest. The most often used CNM sorbents are multiwalled and singlewalled carbon nanotubes (MWCNTs and SWCNTs), which are only examined under laboratory conditions. nZVI has already been applied to real contaminated sites as an *in situ* technology through direct injection into aquifers. CNM sorbents can remove both organic contaminants – aliphatic and mono and polycyclic aromatic hydrocarbons and their derivatives, plus inorganic contaminants – such as divalent metal ions ($Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$) from polluted water. Zero-valent iron nanoparticles have been used for the removal of TCE, VOC, nitrates, and uranium. This review shows that these nanomaterials are a promising solution in the field of groundwater remediation, but there are also many unanswered questions regarding the environmental risks of nanoscale materials, which are outlined as well.

**Keywords:** remediation, carbon nanotubes, nZVI, nanotechnology, groundwater

## Introduction

Contaminated sites present serious problems not only for their owners but also for society as a whole. Many types of chemical substances (e.g. heavy metals, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, or petroleum products) are released from abandoned industrial sites, unprotected hazardous waste, former military bases, mining sites, old dump sites, agricultural-related sites, etc. Water represents a medium through which pollutants become mobile in the environment. Therefore, groundwater remediation is an important part of site remediation as a whole.

Groundwater remediation methods can be divided into two basic categories: *in situ* and *ex situ* technologies. *In situ* technologies include the decontamination of water underground by methods such as biodegradation, bioventing, air sparging, etc. *Ex situ* technologies refer to treatment after removal of the contaminated groundwater from the aquifer to a more convenient location. In most cases this means "pump-and-treat" methods, where contaminated groundwater is pumped to the surface and then conventional methods such as adsorption on activated carbon (AC) are used, as well as stripping to capture pollutants, chemical precipitation, biological treatment, or membrane filtration.

When choosing a remediation method, it is important to properly define the site-specific conditions such as the hydrogeology and geochemistry of the site, the types of contaminants, and their concentrations and distribution. The main goal of site remediation is to reach an appropriate water quality that meets specific national legislative standards.

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Therefore, the most economical technology for achieving the standards is the main criterion for selecting a remediation procedure [1, 2].

A number of remediation methods aimed at reducing the negative impacts of contaminated sites on all components of the environment have already been developed. However, the research and development of new remediation technologies are still the focus of scientists, and can lead to greater efficiencies.

## Nanotechnology for Site Remediation

In recent years the use of nanotechnology in the field of environmental protection has become increasingly popular, especially for cleaning contaminated wastewater and groundwater. The removal of metals is the most popular, although a lot of work relates also to the use of nanomaterials for the elimination of persistent organic pollutants.

Nanomaterials are defined as having at least one dimension of 1 to 100 nm. They are divided into natural and man-made materials. Natural nanomaterials can be of biogenic, geogenic, atmospheric, or pyrogenic origin, whereas man-made materials can be engineered or unintentionally produced as by-products. Due to composition, all of these nanomaterials are classified into inorganic and carbon-based nanomaterials [3, 4].

Among the nanomaterials tested for possible application in remediation processes are engineered carbon-based nanomaterials (CNM), metal nanoparticles (such as nanoparticles of zero-valent iron (nZVI) [5, 6]), bi-metallic nanoscale particles, nanoscale semiconductor photocatalysts (which have the ability to oxidize organic pollutants into nontoxic materials), or titanium dioxide nanotubes [7, 8]. Carbon-based nanomaterials include fullerenes, carbon nanotubes, both single and multiwalled carbon nanotubes (SWCNTs and MWCNTs), or graphenes. The SEM image of MWCNTs is shown in Fig. 1. All of these materials can be modified by different processes (oxidation, acidification, etc.) to create new useful properties.

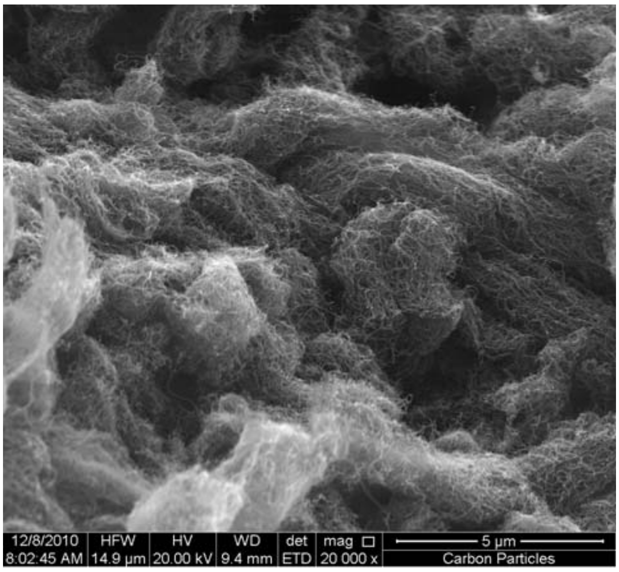

Fig. 1. The SEM image of MWCNTs (courtesy of Geotest a. s).

Researchers are developing a variety of nanomaterials for potential use to adsorb or destroy contaminants as part of either *in situ* or *ex situ* remediation. A lot of examples of nanomaterial applications in site remediation are described in a fact sheet "Nanotechnology for Site Remediation," which was prepared by the U.S. Environmental Protection Agency's Office of Superfund Remediation and Technology Innovation [8, 9]. However, most of the remediation projects using nanoparticles are just beginning or are ongoing, so there are limited data at this point. The advantages of *in situ* and *ex situ* applications of nanomaterials for environmental cleanup were compared by Tratnyek and Johnson [3]. *Ex situ* processes can include, for example, photooxidation with nanostructured semiconductors or adsorption on self-assembled monolayers on mesoporous supports (SAMMS). The good adsorptive properties of SAMMS can be useful for contaminants such as mercury, chromate, arsenate, pertechnetate, and selenite. Dendritic polymers are another type of nanostructured material that has the potential for use in remediation (for the removal of $Cu^{2+}$ or $Pb^{2+}$). Both of these types of nanostructured adsorbents are likely to be applied *ex situ*, where they can be recovered with the concentrated hazardous material they adsorb. The above-mentioned photooxidation is primarily an *ex situ* strategy because, in this case, effective illumination usually requires that treatment be done in a reactor that is designed for the purpose [3].

### Carbon-Based Nanomaterials as Sorbents

Currently, a variety of adsorbents are being used in remediation; the most widely applied adsorbents are activated carbon, polymeric resins, aluminosilicates, etc. Adsorption using granular activated carbon is an effective technique for removing low solubility organics and some metals and inorganic species. Despite its many advantages, adsorption is simply a separation process in which residual contaminants are removed from the water, but the contaminants are not destroyed. Capacity of the adsorbent runs out after a certain time and the adsorbent must be regenerated or replaced. Regeneration of adsorbents or its replacement may increase the cost of the water treatment [1].

The sorptive capacity of conventional CNM sorbents is limited by the density of surface active sites, the activation energy of the sorptive bonds, the slow kinetics and nonequilibrium of sorption in heterogeneous systems, and the mass transfer rate to the sorbent surface. The large dimensions of traditional sorbents also limit their transport through low porosity environments and complicate efforts in subsurface remediation. CNM sorbents, with their high specific surface area, controlled pore size distribution, and manipulatable surface chemistry, overcome many of these intrinsic limitations. Sorption studies using carbon-based nanomaterials report rapid equilibrium rates, high adsorption capacities, effectiveness over a broad pH range, and consistency with BET, Langmuir, or Freundlich isotherms [10]. In a comparative study by the Department of Chemistry at Warsaw University, the $Cu^{2+}$ sorption capacity of carbon nanotubes was 2.08 mg/g and

Table 1. Examples of engineered carbon nanoparticles used for the removal of heavy metals from water by adsorption.

| Nanomaterial | Pollutant | The main tested effects | Reference |
|---|---|---|---|
| CNTs grown on $Al_2O_3$ particles | $Pb^{2+}$, $Cu^{2+}$, $Cd^{2+}$ | adsorbent amount, pH | [16] |
| Exfoliated graphitic nanopelets | $Pb^{2+}$ | adsorbent concentration, contact time, surface morphology, pH | [17] |
| Carbon-encapsulated magnetic nanoparticles, CNTs | $Cu^{2+}$, $Co^{2+}$, $Cd^{2+}$ | functional groups, pH | [18] |
| CNTs | $Pb^{2+}$ | adsorbent amount, agitation speed, contact time, pH | [19] |
| Four kinds of CNTs | $Pb^{2+}$ | functional groups, surface morphology | [20] |
| Oxidized CNTs (with $H_2O_2$, $KMnO_4$, and $HNO_3$) | $Cd^{2+}$ | adsorbent amount, functional groups, pH, surface morphology | [21] |
| CNTs | $Pb^{2+}$ | thermodynamic parameters | [22] |
| MWCNTs, SWCNTs | $Zn^{2+}$ | contact time, pH, surface morphology | [23] |
| MWCNTs | $Cu^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Pb^{2+}$ | metal ions concentration, pH | [24] |
| Acidified MWCNTs | $Pb^{2+}$ | functional groups | [25] |
| Oxidized MWCNTs | $Ni^{2+}$ | contact time, competitive ions, absence and presence of polyacrylic acid (PAA), pH | [26] |
| Synthesized carbon nanomaterials | $Cd^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ | contact time, surface morphology | [27] |
| As-grown and modified CNTs (with $H_2SO_4$, $H_2SO_4/KMnO_4$) | $Cu^{2+}$ | functional groups, temperature, pH, zeta potential | [28] |

just 0.316 mg/g for activated carbon [11]. Maximum $Ni^{2+}$ sorption capacities of SWCNTs, MWCNTs, and granular-activated carbon were 47.85, 38.46, and 26.39 mg/g, respectively [12].

Although there is much research illustrating the promising sorption properties of carbon-based nanomaterials, their applications in real environmental samples are scarce [13]. Thus, a major challenge will be to develop a groundwater treatment system that is cost effective, environmentally friendly, and where CNM sorbents can be easily integrated. Savage and Diallo believe that nanosorbents could be readily integrated into existing water treatment plants [14]. One of the examples of a practical application (for water treatment and desalination) is a demonstration that carbon nanotubes (CNTs) can be readily immobilized into the pore structure of a polymeric membrane, which can dramatically improve its performance [15].

### *CNM Sorbents for Removing Heavy Metals from Water*

The whole adsorption process of heavy metals is mainly affected by the properties of the solution and by the properties of the adsorbent (carbon nanomaterial). Among the properties of the adsorbent, especially surface morphology (such as amount and type of functional groups), pore size distribution and specific surface area are most important. Moreover, effects of adsorbent amount, pH, initial concentration of metal, contact time, agitation speed, temperature, competitive ions, ionic strength, etc. significantly influence the adsorption process. Effects of both solution properties and adsorbent properties were studied by the scientists listed in Table 1.

Unfortunately, the adsorption properties of carbon-based nanomaterials were in most cases investigated under laboratory conditions only. Another drawback was the use of synthetic water for laboratory tests [29]. Application at actual contaminated sites or with real, highly contaminated water samples will be more complicated.

Ruparelia et al. [27] studied heavy metal sorption on synthesized carbon nanomaterials, which were prepared by a chemical vapour deposition process (CVD) under various conditions (a cobalt catalyst in $N_2$ atmosphere or a silica catalyst in $H_2$ atmosphere). The adsorption of cadmium, lead, zinc, and nickel onto the two prepared nanomaterials was compared with the adsorption onto commercially activated carbon. Nanoporous carbon (NPC), prepared using the silica catalyst, exhibited superior adsorption of heavy metals compared to both the activated carbon (AC) and the nanomaterial prepared using the cobalt catalyst (e.g. $Zn^{2+}$ sorption capacities of NPC and AC were 2000 μeq/g and 625 μeq/g, respectively). It was found that activation plays an important role in enhancing maximum sorption capacity. Activation causes a modification in the surface morphology as well as the removal of amorphous carbon. During activation, the metallic impurities and catalyst support materials are dissolved, and the surface characteristics are altered due to the creation of new functional groups. Removal of the amorphous carbon increases the adsorption ability of CNTs [30]. Activation of CNTs is usually performed under oxidizing conditions using, for example, $HNO_3$, $KMnO_4$, $H_2O_2$, NaOCl, $H_2SO_4$, KOH, or NaOH [27].

Carbon-encapsulated magnetic nanoparticles (CEMNPs) were studied as mobile sorbents for the removal of the ions $Cu^{2+}$, $Co^{2+}$, and $Cd^{2+}$ from aqueous solutions [18]. The conclusion of this study was that CEMNP-based sorbents are fully mobile and have excellent sorption capacities that substantially exceed the capacities of carbon nanotubes and activated carbons (the ion uptakes achieved were at least 80% at pH 9).

Rao et al. reviewed the adsorption of divalent metal ions ($Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Pb^{2+}$, and, $Zn^{2+}$) on both untreated CNTs and oxidized CNTs [31]. Functional groups on CNTs were formed by oxidation with NaOCl, $HNO_3$, and $KMnO_4$. They concluded that the sorption capacities of CNTs remarkably increased after oxidization. In 2007, Hsieh and Horng reported results from their study of the adsorption of the ions $Pb^{2+}$, $Cu^{2+}$, and $Cd^{2+}$ on as-grown CNTs/$Al_2O_3$ [16]. These CNTs were created on the surface of $Al_2O_3$ particles in a $CH_4$ atmosphere at 700ºC under the catalysis of Fe-Ni nanoparticles. The adsorption capacity of these CNTs was then compared with active carbon powders (PAC), commercial CNTs, and $Al_2O_3$ particles. They found that as-grown CNTs/$Al_2O_3$ showed an exceptional adsorption capability and the adsorption capacity was superior to the other adsorbents. $Pb^{2+}$ adsorption capacities of CNTs/$Al_2O_3$, PAC, commercial CNTs and $Al_2O_3$ particles were 67.11 mg/g, 33.78 mg/g, 11.23 mg/g, and 8.92 mg/g, respectively.

The removal of $Pb^{2+}$ from aqueous solution using adsorption to carbon nanotubes also was investigated [19]. The adsorption process was studied under various conditions to estimate the effect of pH, agitation speed, CNT dosage, and contact time. The results indicated that the use of CNTs is promising for water and wastewater treatment. Lead removal also was in the spotlight of Li et al. [20], who compared four kinds of CNTs with different morphologies produced by CVD and oxidized with concentrated nitric acid. The maximum adsorption capacity (82.6 mg/g at the lead equilibrium concentration of 10 mg/l) was reached by using CNT sample Methane-Ni-650-C-Vert. The adsorption results indicated that the CNTs with poor quality and morphology had higher lead adsorption capabilities [20]. In addition, Wang et al. [25] studied the adsorption of $Pb^{2+}$ on MWCNTs and the effect of the presence of carboxyl, carbonyl and hydroxyl functional groups on the MWCNTs surface. He compared untreated CNTs and CNTs oxidized with concentrated nitric acid and concluded that the functional groups formed by oxidation on the surface of the CNTs play a significant role in the adsorption of $Pb^{2+}$. In addition, optimized ethylenediamine-grafted MWCNTs were studied for using in analytical chemistry and applied as solid phase extraction (SPE) absorbents to extract $Pb^{2+}$ from river water samples [32].

Li et al. [21] compared the $Cd^{2+}$ adsorption ability of both as-grown CNTs and CNTs oxidized with $H_2O_2$, $KMnO_4$ and $HNO_3$. He found that CNTs oxidized with $KMnO_4$ had the greatest adsorption capacity for cadmium, namely 11 mg/g. The adsorption capacity strongly depended on pH and the amount of CNTs. The ability of the CNTs to remove $Cd^{2+}$ increased with increasing doses from 0.03 to 0.08 g/100 ml, while at a dose of 0.08 g/100 ml the efficiency reached 100%. Optimum pH was determined to be 5.5 (as this pH value has the largest amount of cadmium present as $Cd^{2+}$).

Other divalent ion adsorption studies include, for example, the report of Lu and Chiu [23], who studied $Zn^{2+}$ adsorption on SWCNTs and MWCNTs; the study of Kuo [28], who compared aqueous $Cu^{2+}$ adsorption onto as-grown and modified CNTs; and adsorption experiments with $Ni^{2+}$ [26]. Yang et al. studied the adsorption of $Ni^{2+}$ onto oxidized MWCNTs as a function of contact time, pH, and competitive ions, both in the absence and presence of polyacrylic acid [26]. The main result was that the $Ni^{2+}$ adsorption increased with increasing pH, and that in the presence of polyacrylic acid, the adsorption increased at low pH and decreased at high pH values. Kuo found that the adsorption capacity of copper onto CNTs modified using $H_2SO_4$ and $H_2SO_4$/$KMnO_4$ was greater than onto as-grown CNTs [28].

In addition to CNM sorbents, other nanoparticles can also be used as a sorbent for heavy metal removal. Among these are, for example, magnetic iron-oxide nanoparticles (NPs), which are used to remove As ions (both $As^{3+}$ and $As^{5+}$) from drinking water. The As ions spontaneously adsorb onto the iron-oxide NPs and the complex is removed using weak magnetic fields [33]. Arsenic adsorption to magnetite nanoparticles also was examined [34, 35]. Other examples are the adsorption of Pb, Cd, Cu, Ni, and Zn ions to titanium dioxide nanoparticles [36], the adsorption of $Pb^{2+}$ and $Cd^{2+}$ onto Fe and Ag nanoparticles [37], and the removal of mercury from drinking water using gold nanoparticles [38].

### *CNM Sorbents for Removing Organic Pollutants from Water*

The adsorption of organic compounds by CNM sorbents is influenced by a number of factors. The success of an adsorption process depends mainly on the correctly designed conditions, such as contact time, amount of adsorbent, initial concentration of adsorbate, method of mixing, etc. The proper selection of conditions depends on the type of the organic compounds and on the type of nanomaterial used. The effect of pH and ionic strength is almost always insignificant in contrast to heavy metal adsorption. Table 2 gives examples of various researched pollutants adsorbed on various carbon nanomaterials and the main tested factors that affect their adsorption.

According to Shao et al. [44], MWCNTs have a high adsorption capacity for removing organic compounds from water. This claim was supported by research into the adsorption of polychlorinated biphenyls (PCBs) onto carbon-based nanomaterials in aqueous solution. For this study, special MWCNTs (MWCNT-g-CD) were prepared. β-cyclodextrin (β-CD) was grafted onto the surfaces of MWCNTs using plasma techniques because of the strong interaction between β-CD and PCBs. The results showed that the MWCNT-g-CD had much higher adsorption capacities (261 mg/g and 235 mg/g) for PCBs (4, 4'-DCB and 2,

Table 2. Examples of engineered carbon nanoparticles used for the removal of organic pollutants from water by adsorption.

| Nanomaterial | Pollutant | The main tested effects | Reference |
|---|---|---|---|
| As-grown CNTs, graphitized CNTs | 1,2-dichlorobenzene | contact time, pH, thermodynamic parameters | [39] |
| Six carbon nanomaterials: fullerene, MWCNTs, SWCNTs | phenanthrene, pyrene, naphtalene | surface area, micropore volume, mesopore volume | [40] |
| Purified MWCNTs | trihalomethanes | pH, surface properties, contact time | [41] |
| MWCNTs | phenanthrene, pyrene, naphtalene | competitive pollutants, initial concentrations of organic pollutants | [42] |
| Fullerene C60 | naphtalene | dispersal of C60, mixing | [43] |
| β-cyclodextrin grafted MWCNTs | PCBs | properties of MWCNTs | [44] |
| OH-functionalized MWCNTs | phenanthrene, lindane, atrazine | surface area, meso- and macropore volumes, functional groups | [45] |
| SWCNTs | benzene, toluene, chlorobenzene | functional groups, pH, temperature | [46] |
| NaOCl-oxidized MWCNTs | benzene, toluene, etylbenzene, p-xylene | contact time, functionalization, initial adsorbate concentration, ionic strength, pH | [47] |

3, 3'-TCB) than the unmodified MWCNTs. Moreover, it was found that the pH through the range 2.5-10 had no effect on adsorption. The contact time in these experiments was chosen to be 50 h [44].

Yang et al. [40] tested the adsorption of three PAHs (naphthalene, phenanthrene, and pyrene) onto six different types of CNM (fullerenes, SWCNTs, and MWCNTs). At a given equilibrium concentration, adsorption affinities increased in the order naphthalene-phenanthrene-pyrene. Yang et al. [42] also tried competitive sorption of these three PAH representatives onto the MWCNTs, and evaluated the results on the basis of the Polanyi theory. They concluded that the sorption models based on Polanyi's theory did not describe the competitive sorption in this case. Among other similar studies the adsorption of hydrophobic organic compounds (HOCs) (phenanthrene, lindane and atrazine) by original and OH-functionalized MWCNTs examined by Wang et al. can be mentioned [45]. In this study the time to establish adsorption equilibrium was determined to be four days. Phenanthrene adsorption from ethanol solution was examined in the work of Gotovac et al. [48].

Peng et al. [39] used the as-grown CNTs and graphitized CNTs as adsorbents to remove 1,2-dichlorobenzene from water. Experiments showed that it takes only 40 minutes to establish adsorption equilibrium. The adsorption capacity of as-grown and graphitized CNTs was 30.8 and 28.7 mg/g, respectively, from a 20 mg/l solution. CNTs have been successfully tested in the pH range 3 to 10. The adsorption and desorption of 1,2-dichlorobenzene and naphthalene with the fullerene C60 also was reported [49], and compared with activated carbon, a common sorbent.

Trihalomethane (THM) adsorption from water onto CNTs purified by acid solution was carried out by Lu et al. [41]. CNTs have a high adsorption capacity, and the contact time required for establishing adsorption equilibrium was set for only three hours. The properties of CNTs were greatly improved after acid treatment, which made the CNTs more hydrophilic and suitable for the adsorption of low molecular weight and relatively polar THM molecules. A comparative study between CNTs and powdered activated carbon (PAC) for the adsorption of THMs from water was also conducted. The adsorption capacities of CNTs and PAC (for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$) reached 0.11, 0.06, 0.05, 0.05 mg/g and 0.063, 0.089, 0.108, 0.119 mg/g respectively, for initial concentration 0.2 mg/l [41]. The smallest molecule, $CHCl_3$, is the most preferentially adsorbed onto CNTs and the largest molecule, $CHBr_3$, is the most preferentially adsorbed onto PAC [41].

Two kinds of CNTs, vertically aligned CNTs (VACNTs), synthesized by the floating catalyst method using ferrocene as the catalyst precursor, and agglomerated CNTs were used for oil adsorption [50]. It was concluded that oil sorption by CNTs does not depend on the surface area of the carbon materials. The high sorption capacity of VACNTs was caused by the intertube space with large-sized macropores. VACNTs had a high oil sorption capacity and also excellent recycling performance by both the heat treatment method and squeezing method [50]. In addition, CNTs and nanofibers on the surface of expanded vermiculite were synthesized using the chemical vapour deposition process for removing oil spilled on water [51].

The adsorption of benzene, toluene, and chlorobenzene onto SWCNTs (with and without modification by nitric acid oxidation) was examined in the pH range from 3 to 11 with a contact time of 28 hours [46]. It was found that the morphology, specific surface area, micropore volume, pore size distribution, and purity of SWCNTs remained the same after acid oxidation. Thus, acid oxidation influenced only the surface chemistry by introducing oxygen-containing surface groups. In consequence, these functional groups introduced on the surface of SWCNTs resulted in a decrease in the adsorption of benzene, toluene, and chlorobenzene. Similarly, Su et al. [47] researched the adsorption of benzene, toluene, ethylbenzene and p-xylene (BTEX) in aqueous solution onto MWCNTs oxidized by a sodium hypochlorite (NaOCl) solution. In contrast to the previous case, the oxidation improved the physicochemical properties of CNTs such as increasing purity, surface carboxylic groups and structure and significantly enhanced BTEX adsorption capacity. The adsorption capacity of the MWCNTs increased with contact time (equilibrium contact time was 4 hours) and initial adsorbate concentration. A comparative study of CNTs and granular activated carbon revealed that the MWCNTs showed superior adsorption performance (e. g. the maximum adsorption capacities of MWCNTs were 247.87 mg/g for benzene, 279.81 mg/g for toluene, 342.67 for ethylbenzene, and 413.77 for xylene) [47].

Graphene is another type of CNM with potential application as a sorbent. For example, graphene sheet nanocomposites with great potential as an effective absorbent for removing aromatic compounds were fabricated at Lanzhou University in China [52, 53].

## Nanoscale Iron for the Remediation of Aqueous Contaminants

Although a variety of nanoparticles might be applicable to *in situ* remediation, by far the greatest interest is currently in nanoparticles that contain nanoscale iron. For many years, iron has been used for remediation of contaminated groundwater [54-56]. For example, iron granules or other iron-bearing minerals may be used in a permeable reactive barrier (PRB) to treat an intercepted groundwater plume. However, nanoscale zero-valent iron (nZVI) may prove more effective than macroscale zero-valent iron under similar environmental conditions because of their different properties [9]. Nanoscale iron particles represent a new generation of environmental remediation technologies. An overview of practical experiences with nZVI applications is given by Mueller et al. [57]. They presented an example of the application of nZVI for groundwater remediation in Europe and compared it with the situation in the USA, where this method is more widespread and the application of nZVI is an established treatment method.

The most frequently used method of application of nZVI is injection of an nZVI suspension directly into an aquifer. Injection techniques include infiltration wells, sleeve pipe, push infiltration, or gravity infiltration. Another method of application is using a permeable reactive barrier [57].

*In situ* use of nanoscale iron particles for remediation has been applied since their introduction in 1994 by Gillham and O'Hannesin [58]. Since then, many scientists have dealt with this issue [3, 6, 59, 60]. The advantages of the use of nanoscale iron particles include large surface areas, high surface reactivity, enormous flexibility for *in situ* applications, efficiency for the transformation and detoxification of a wide variety of common environmental contaminants such as chlorinated organic solvents, organochlorine pesticides, inorganic anions and a range of heavy metals, including Pb, Cr, Cu, As, Ni, Zn, Cd, and Ag [61, 62], polychlorinated biphenyls or vinyl chloride [9]. The greater reactivity that is often ascribed to nanoparticles may be the result of the larger overall surface area, greater density of reactive sites on the particle surfaces, or higher intrinsic reactivity of the reactive surface sites. In comparison with iron, nZVI can degrade contaminants that do not detectably react with larger particles of similar material (e.g. polychlorinated biphenyls). However, also in the case of contaminants, which already react at useful rates with larger particles, degradation of contaminants is even more rapid [3]. The possibility of straight injection of nanoparticles into aquifers is also very important. Last but not least, nZVI could provide cost-effective solutions to some environmental clean-up problems. For example, iron nanoparticles could be used for remediation purposes in permeable reactive barriers, by straight injection where nZVI can be readily placed in the subsurface in slurry form even by simple means, e.g., via monitoring wells [60, 63].

Literature reviews give a number of examples of the experimental use of nanoscale iron. Yang and Chang [64] evaluated the treatment efficiency of a trichloroethylene (TCE)-contaminated soil by the combined processes of the injection of emulsified nZVI and electrokinetic remediation. The experimental results showed that electroosmotic flow played a key role in removing TCE from the soil matrix to the cathode reservoir. Therefore, the injection of emulsified nZVI into the cathode reservoir could enhance the degradation of TCE therein [64]. The application of nZVI and magnetite nanoparticles for the removal of uranium from carbonate-rich natural water from the Lisava valley (Banat, Romania) was investigated [61]. In this case, uranium was removed to <2% of its initial concentration (0.484 mg/l) within the first hour of the reaction period in both oxygen-rich and oxygen-poor conditions, and remained stable on the surface of the nZVI for 48 h. Zerovalent iron nanoparticles also were investigated as a remediation strategy for the removal of uranium from a chemically complex solution using industrial contaminated waste effluent from the Atomic Weapons Establishment, Aldermaston, UK [62]. An analysis of the solution indicated that under both conditions (oxic and anoxic), uranium was removed to <1.5% of its initial concentration within 1 h of introduction and remained at similar concentrations for approximately 48 h. This case study demonstrated the potential application of iron nanoparticles as a low-cost remediation technology for complex uranium-contaminated solutions of industrial origin [62].

Acid mine water containing leached uranium (Straz pod Ralskem, Czech Republic) was treated by nZVI in laboratory-scale experiments. The laboratory batch experiments proved a significant decrease in concentration of all the monitored pollutants (i.e., Al, U, V, Cr, Cu, Ni, Cd, Zn, and As) due to an increase in pH and a decrease in oxidation-reduction potential related to the application of nZVI. Mechanisms of contaminant removal include the precipitation of cations in a lower oxidation state, precipitation caused by a simple pH increase, and co-precipitation with the formed iron oxyhydroxides [6].

Nanotechnology, especially the use of nZVI particles to treat volatile organic compound (VOC)-impacted groundwater, was tested during numerous pilot tests undertaken by Golder Associates between 2003 and 2005 in North America [63]. In general, chlorinated solvents can be completely reduced to nontoxic compounds such as ethene and ethane, as previously demonstrated by research conducted at the University of Waterloo (1991) [63]. In all cases, the pilot tests showed a dramatic decrease in the concentration of chlorinated solvents a short time after the injection of particles. However, based on various input parameters such as the volume/mass ratio of injected nZVI, type of nZVI, concentration of contaminants in the groundwater in the area of the injection wells, hydraulic parameters and type of aquifer, hydrochemical parameters of the aquifer, and competitors in the reduction process (e.g., sulfates, nitrates, etc.), the results of the tests vary widely [63].

Lindsay et al. [59] evaluated the possibility of using organic carbon mixtures amended by zero-valent iron to treat acid mine drainage (AMD). In this study laboratory batch experiments were conducted using simulated mine drainage water to evaluate $SO_4^{2-}$ reduction, metal removal, and acid neutralization associated with five reactive mixtures.

The entrapment of iron nanoparticles in calcium alginate beads for groundwater remediation applications was studied [65]. The study demonstrated the potential use of this technique in environmental remediation using nitrate as a tested contaminant. Because of the smaller particle size and the relatively higher dispersibility, nZVI becomes mobile in the aquifer. Furthermore, if present in higher concentrations, nZVI tends to agglomerate due to magnetic and van der Waals forces and form larger particles that settle into aquifer media pores. The agglomerated particles have a decreased specific surface and hence lose the very advantage individual nZVI has. Entrapment of nZVI in a porous polymeric hydrogel was suggested to overcome these problems [65].

Early treatment remedies for groundwater contamination were primarily pump-and-treat operations. Because of the relatively high cost and often lengthy operating periods for these remedies, the use of *in situ* treatment technologies is increasing [8] and is now often preferred, where it is feasible. *In situ* methods of application of nanoparticles are site-specific and dependent on the geology of the contaminated site and the form in which the nanoparticles will be injected. The utilization of existing monitoring wells, piezometers, or injection wells is very frequent for injection of nanoparticles. Additional methods to inject the nanomaterials include direct push, pressure-pulse technology, liquid atomization injection, pneumatic fracturing, and hydraulic fracturing [9]. Before injection of nanoparticles, geologic and hydrogeologic conditions should be evaluated to determine whether the injected particles would have adequate subsurface distribution. Factors that affect the subsurface mobility of nanoparticles include the composition of the soil matrix, ionic strength and chemical composition of groundwater, hydraulic properties of the aquifer, and depth to the water table. Especially important are hydrogeochemical properties such as pH, dissolved oxygen, oxidation-reduction potential, and concentrations of nitrate, nitrite, and sulphate in the groundwater, etc.

## Potential Environmental Risks of Nanomaterials

The nanotechnology sector is currently expanding rapidly in many areas and as a consequence many research groups, organizations and institutions give attention to toxicological research and best practices for environmental health and safety [66]. Several studies about the behaviour, effects and toxicology of nanoparticles and some particular cases of nanotoxicology testing have been published [4, 68-70]. These studies give many examples of the possible effects of NPs in the environment and how the risks of NPs should be evaluated. The issue of detection of NPs in the environment was summarized [66]. They introduced the current techniques available for the detection of NPs and for the characterization of their properties. The overview describes analytical methods from microscopy and microscopy-related techniques, such as transmission electron microscopy (TEM) or atomic force microscopy (AFM) to chromatography, centrifugation, filtration, and spectroscopic techniques, e.g. size exclusion chromatography (SEC), hydrodynamic chromatography (HDC), ultracentrifugation (UC), or microfiltration [66].

In risk assessments of the nanoparticle applications in the environment, the entry of nanomaterials into the environment, the behavior and deposition of NPs, the determination of the concentration of NPs in all compartments of the environment (air, water, soil), their fate and bioavailability, their potential impact on food webs, the uptake and accumulation by organisms, their persistence, etc., are important issues that should be precisely described. For example, the potential risks of NPs in groundwater remediation *in situ* arise from the negative impact on bacteria useful for natural remediation, if nanoparticles are applied directly into the ground. What is more, if nanoparticles are used as adsorbents for organic or inorganic contaminants, nanoparticles with adsorbed contaminants (in the case of release to the environment) could be easily transported long distances due to their small size [58, 66]. Therefore, the transport and transformation processes of these NPs should be in the spotlight of scientific research as well as their controlled release into the ground. Grieger et al. [58] focused on the risks arising from *in situ* remediation techniques that use nZVI. In this paper there was an emphasis on the absence of data in environmental risk evaluations, and due to this absence, ‘best’ and ‘worst’ case scenarios for the evaluation of the potential environmental risks of nZVI were applied. The result of the evaluations indicated that at present there is no significant proof that nZVI poses a serious risk to the environment. But it was highlighted that the majority of the most serious criteria (i.e. potential for persistency, bioaccumulation, toxicity) are generally unknown [58]. Other questions that should be taken into consideration are whether potential transformation products of nZVI residues would be detectable in the environment, and how surface modifications of nZVI would alter its long-term environmental fate and effectiveness for remediation [3]. The ecotoxicity of inorganic NPs was also in the spotlight of authors [29].

Fate, transport and toxicity questions of nZVI are also of concern to the U.S. Environmental Protection Agency [8]. It is mentioned here that while increased mobility would allow more efficient remediation, it could also cause nanomaterials to migrate beyond the contaminated plume area, seep into drinking water aquifers or wells, or discharge to surface water during the remediation process. Moreover, in the U.S. the EPA paper [7] "Emerging Nanotechnologies for Site Remediation and Wastewater Treatment" describes toxicity and safety concerns for many kinds of nanotechnology used for remediation and wastewater treatment. There is an example of a study that demonstrated the negative impacts that nanotubes have on the respiratory tracts of rats and mice (the mice exposed to the nanotubes sustained significant lung damage). It explains that carbon nanotubes, especially, represent a cause for concern due to their similarities to asbestos [7]. Another example revealed the toxicity mechanism of nano-$TiO_2$ and indicated that nano-$TiO_2$ has some enzymatic impacts and might have impacts on natural immunity [71].

Not only the industrial sector and research groups are interested in nanotechnology. Many organizations, government agencies, and institutes in the USA and in the EU have multi-lateral cooperation to develop international documentary standards in nanotechnology. Since 2010, 31 new standards for nanomaterials have been published by ISO, including terminology, definitions, classifications, and categorization of nanomaterials and nanoobjects, methods of several nanomaterial characterizations, and also some propositions for risk assessment and toxicity testing (http://www.iso.org/). All the while it is supposed that rapidly developed processes will require reviewing certain methods or standards in the coming years [72]. However, methodologies of nanomaterial detection in the environment are still being developed.

Because of the need of existing nanomaterial registration some methodologies were proposed. Today, the evaluation of nanomaterials should be based on the European Commission [72] statement that according to currently available data nanomaterials are similar to normal chemical/substances in that some may be toxic and some may not. Possible risks are related to specific nanomaterials and specific uses. Thus, it is necessary to perform risk assessment on a case-by-case basis [72]. Nanomaterials become a part of the registration, evaluation, authorisation and restriction regulatory (REACH) as substances or mixtures, although the specific requirements will have to be proven.

## Conclusions

The choice of remediation technology is a site-specific complex process and no single technology is suitable for all contaminated sites, because conditions differ from site to site. Therefore, the development of new technologies is still topical parallel to the emergence of newly contaminated sites. The nanotechnologies for remediation discussed in this document are adsorption onto CNM sorbents and the *in situ* and *ex situ* application of nZVI.

This review shows that researchers in most cases use carbon nanotubes (MWCNTs and SWCNTs) as CNM sorbents. These sorbents can be either untreated or treated by oxidation with acids. Contaminants adsorbed from water include both organic contaminants, for example polychlorinated biphenyls, polycyclic aromatic hydrocarbons, 1,2-dichlorbenzene, trihalomethanes, oil, BTEX, and inorganic contaminants such as heavy metals, especially divalent metal ions ($Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$). The adsorption process is usually studied as a function of pH, contact time, agitation speed, dosage of adsorbent, temperature, or the presence of functional groups (carboxyl, carbonyl, or hydroxyl), which are synthesized on the surface of the carbon adsorbent by oxidation. Functional groups and pH usually play a significant role in heavy metal adsorption, in contrast to the adsorption of organic compounds, where pH and the presence of functional groups have little to no impact. Some researchers examined other common sorbents for comparison with nanosorbents, for example activated carbon, and found that CNM sorbents were more effective in these cases. In all cases, the removal of contaminants was carried out under laboratory conditions with one contaminant or one group of contaminants, but real site conditions are more complicated and real contaminated groundwater samples contain more kinds of contaminants.

Nanoscale zero-valent iron particles, in contrast to CNM sorbents, are used at real contaminated sites relatively frequently, because the straight injection of nZVI into an aquifer is possible and often successful. The *in situ* application of nZVI is widespread, especially in the USA, according to the list of sites in the U.S. EPA fact sheet [7]. However, most of the remediation projects using nZVI are either just beginning or are on-going. The contaminants removed by nZVI include, for example, TCE, VOC, nitrates, and uranium.

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