

Metallic Nanoparticles for the Treatment of Effluents Contaminated with Chlorinated Organic Compounds: a Review

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ABSTRACT

Nanomaterials are the core of a promising technology that can be used to accelerate and improve the transformation and detoxification of chlorinated organic compounds (COCs). Hence this review will cover topics such as efficient nanomaterials for COCs treatment, supports and stabilizers that improve the process, interactions of nanomaterials with the microorganisms involved, and emerging fields. The most common material used for treatment of waters polluted with COCs has been zero-valent iron (ZVI) because of its efficiency and low cost. However, there are concerns on the stability and long term durability of ZVI NP (NP). For this reason there are some works with other materials such as Pd, Zn or Ni and with combination of materials in the fabrication of NP. The bimetallic NPs allow for a lower cost of production, since one of the materials could be the most economic but not the most efficient whereas the second metal, the most expensive, provides a higher degradation capability. Alloyed and core-and-shell types of bimetallic NP have been tested. The process with NP can be made more efficient by using a support that prevents the aggregation of NP during reaction and in some cases can facilitate the recovery of the NP afterwards. Currently, the application of NP in bioreactors and *in situ* treatments is gaining momentum. Another significant issue especially for hybrid treatments is the interaction between NP and the microbial community harbored in bioreactors and devices, ranging from toxicity issues to biosynthesis of NP. There has been an attempt to incorporate metal NP onto the microbial cells for COC treatment, although more research is needed. Furthermore, there is increased interest on biosynthesis of NP with microorganisms in order to have true “nanoparticle-ized biomass” with increased degradation capability of pollutants. Among important emerging fields we can highlight the environmental impact assessment as well as life cycle analysis of the NP fabrication and use.

Keywords: nanoparticles, water treatment, chlorinated compounds



1. Introduction

The organochlorines compounds are part of persistent organic compounds, due of their physical chemical properties, degradation is slow and tends to accumulate in fatty tissues of various animals throughout the food chain. The use of these compounds in industrial processes start to mid twentieth century, such as plastics manufacture (vinyl chloride), aerosols, cleaning and degreasing metals (perchloroethylene, trichloroethylene), chemical manufacturing (dichloromethane, chloroform), additives paints and adhesives (dichloromethane, trichloroethane), pulp and paper industry (dioxins, furans), manufacture of pesticides (hexachlorobenzene and others), *etc.*

The organochlorine compounds also are used and are heavily used in agriculture, especially as pesticides for controlling pests. The main exponent of this group is DDT, manufactured in 1943 and used for decades until several investigations showed that its highly toxic [1], hormonal disruptor [2], carcinogenic [3] and exposure affects the nervous, respiratory and immune system [4],[5]. Other COCs belonging to this group are aldrin, chlordane, dieldrin, lindane, tozafeno, heptachlor, hexachlorocyclohexane, etc. Although the use of some of these compounds has been banned some years ago, the effect persists in the environment due their recalcitrance. For that reason is necessary to find technologies with efficient removal capability of COCs.

The metal particles and NP, particularly Fe particles, have been used for treating organochlorine compounds due to the ability of these metals to reduce chlorine compounds. The main chlorinated compound that has been removed using this technology is perchloroethylene (PCE) and its metabolites TCE, DCE, and VC. However because of the principle governing this removal, it's feasible to apply over other chlorinated compounds.

2. Nanoparticle as a technology for COCs treatment

One way to enhance the removal of chlorinated compounds is using nano-materials. The latter are characterized by their low size, ranging from 1 to 100 nanometers. Because of their small size, their properties are different compared to their millimeters counterparts, such as more surface contact and increased reactivity. Indeed, the changes in the crystal structure and chemical reactivity increase the catalytic activity.

The removal capacity of COCs by NP (NP) is often dependent on their size; some research suggests that with the use of smaller particles the removal is greater, as reported by Lin et al. [6] who used NP of 500 and 100 nm for the treatment of the dye acid black 24, and found that the decrease in particle size increased the removal by 90-fold. Nanoparticles are very efficient technology but expensive, the cost of 1 kg of supported NP is around 90 USD. The NP cost is variable depending of purity, size, support and the presence and concentration of catalyst (www.us-nano.com).

The reuse of NP can reduce the cost of the treatment. However the feasibility depends on solubility and stability of the compounds [7]. Regeneration of ZVI is difficult to achieve because of its reductive property is rarely recovered. Researches by Sun et al. [8] have tried to use acid wash to disrupt the iron oxide layer that passivated the removal of the contaminant. Wang et al. [9] regenerated NP of Fe/Pd by washing the NP in 0.4M of KBH_4 for 30 min. The wash caused the formation of active ZVI again. Another way to reduce the treatment cost is to reuse NP. Li et al. [10] used nZVI several times to remove a black dye BDE209: in the first five cycles the removal was high but in the sixth cycle the removal dropped to 23%. Another research with similar results of Li et al. [10] was performed by Velimirovic et al., [11]; they applied nZVI for the CACs removal and during the first five removal cycles the pollutant removal was 92% but in the sixth cycle the removal was under 22%.

3. Zero valent iron, a common nanoparticle used in COCs treatments

The ZVI is the material most used in the treatment of COCs compounds due to its low cost, abundance, ease handling and reactivity [7]. The nZVI technology has been tested in *in situ* remediation projects in US and Europe [12]. In most of these direct injection of nZVI, permeable barriers and small reactors were used [13, 14, 15, 16, 12]. The removal of COCs compounds by nZVI can be carried out mainly by abiotic reductive dechlorination that is a chemical reduction of the contaminant that requires direct contact between nZVI and the pollutant. The nZVI electrons are transferred to the chlorinated compound, generating lesser chlorinated compounds, oxides of iron on the surface of the ZVI NP, and release of chloride anion. A schematic chemical process is depicted below [15].



Under aerobic conditions



Under anoxic conditions



In both conditions (aerobic and anaerobic) there is a rise in the pH solution and release of reductants such as Fe_2^+ and H_2 that continues the dechlorination.

The application of nZVI directly to *in situ* remediation still faces challenges, like the longevity of NP activity and transport through aquifer. Nanoparticles tend to agglomerate and forms aggregates, resulting in decrease in the activity and mobility of nNZVI [17, 8]. Recent research carried out using nZVI has focused on using various stabilizers, surfactants and membranes for the NP (Table 1). Several studies have been used carboxy methyl cellulose (CMC) as stabilizing agent [18, 19, 20]. The stabilizing agents enhance steric or electrostatic repulsions between particles in order to inhibit nZVI aggregation and increase solution stability. The CMC it's a low cost material, very soluble and highly biocompatibility [21]. Bennett et al. [22] used CMC to stabilize nZVI in the treatment of sludge contaminated with PCE and its metabolites; they found that CMC was attached on the nZVI particles that adsorbed onto the sand of the aquifer. This effect of NP enhanced organic matter adsorption could improve the *in situ* bioremediation and the CMC provides additional carbon source to bacteria. Kaifas et al. [23] obtained nZVI NP with CMC. The CMC protected the surface of the nanoparticle and blocked their active sites. The authors discussed that this prolonged the life of NPs. Sunkara et al. [20] besides utilized CMC as stabilizer, also employed activated carbon granules of 1-3 mm size to prevent nZVI aggregation and to increase their adsorptive capacity. The final NP nZVI plus carbon were around 500 nm. They found that this relatively larger size facilitated the particle transport in groundwater. Roman et al. [24] compared a set of stabilizers of NPs: CMC, polyacrylic acid (PAA) and PAP. The results showed that the PAA-stabilized NP were more reactive and removed greater amounts of lindane in less time than those with PAP, followed by the NP stabilized with CMC. During the first 12 hours there was a difference of 25% between removals of PAA and PAP-treated NP, however, after 50 hours of contact, both types of NP removed all lindane. The decision of which stabilizer use will depend of other factors such as cost and easy handling.

While it is true that over the years researchers have tried various stabilizers, carriers and surfactants as dodecylsulfato sodico (SDS), tetrabutylammonium (TBA), poly-aspartate, methacrylic acid, methyl methacrylate, styrenesulfonate [8, 17, 25] and supports such as silica and activated carbon [26, 27], in order to prepare smaller, more reactive, more stable NPs, the research on these issues is still very active. As results of these investigations, commercial products are emerging, as reported by Chen et al. [28]. They evaluated Na-acrylic copolymer designed for the remediation of contaminated subsurface water. This product has the combination of a biodegradable organic and inorganic stabilizer. The results show that TCE degradation with Na-acrylic copolymer plus nZVI was faster than that with NP made of CMC plus nZVI. It was reported that some anions like NO_3^- , Cl^- , HCO_3^- and SO_4^{2-} inhibited slightly the TCE degradation.

4. Bimetallic Nanoparticles

Iron is an efficient metal in the chlorinated compounds removal but the addition of an extra metal like Pd, Pt, Cu, Ni or Ag usually enhances the stability of Fe due the second metal is a catalyst that avoids the iron oxidation and the formation of iron oxide coatings on the surface of the nanoparticle [29, 25, 30]. The incorporation of a second metal may increase the surface area and the number of potential reactive sites for interacting with the contaminant. Some authors suggest that catalysts like Pd and Ni could absorb the H_2 produced by iron corrosion into its lattice to form a transitional compound that can accelerate the reductive dechlorination of the COC [9, 31]. Other authors suggest that the removal mechanism by bimetallic NP is based on the attack of the hydrogen product of ZVI corrosion to the contaminant that is absorbed into the surface of the metal acting as a catalyst, resulting in the dechlorination of the COC (both the mother compound and its chlorinated degradation compounds) [32, 33, 30].

However the studies to elucidate the mechanism of bimetallic NP operation are still scarce or plainly lacking. Some researchers have used various combinations of bimetallic NP like ZVI/Ni, ZVI/Cu, ZVI/Mg and ZVI/Pt, ZVI/Zn [34, 35]. Also there have been efforts to use other metals besides iron. For instance, Lin et al. [36] synthesized NP of Pd/Sn (400 mg) of 50 a 100 nm with a BET de $5.9 \text{ m}^2\text{g}^{-1}$ for TCE treatment (7 mg L⁻¹). The results reported were encouraging; a removal of 2 and 1.56 h-1 was obtained. In turn, these results were higher than the removals obtained with more conventional bimetallic particles of Pd/ZVI [37]. Another example is the research by Li et al. [29] who synthesized NPs of Pd/Au y Pd/ Al_2O_3 of 4 nm with a BET of $200 \text{ m}^2\text{g}^{-1}$ to remove 8.5 mg/L of TCE. Their results show that these NPs were 10^5 x more reactive that commercial products NANOFER 25 y NANOFER25S.

The bimetallic NP commonly used in the treatment of chlorinated compounds is ZVI/Pd [38, 39, 40, 9, 41]. These bimetallic NPs were so efficient that they could treat aromatic compounds, as Yang et al. [42] reported. Indeed, they used NPs < 100 nm with a BET of $9.21 \text{ m}^2\text{g}^{-1}$ for monochlorobenzene treatment and achieved 97% removal of the pollutant. Furthermore they examined the effect of different concentrations of Pd in order to abate costs of NP fabrication (0.2%, 0.4%, 0.6%, 1%, 2% Pd on mass basis). The results indicate that 0.6% is the best concentration to stabilize iron and reach a removal similar to Pd 1%. When used a 2% proportion of Pd was used, the removal of pollutant was surprisingly lower.

Table 1. Recent research carried out using nZVI



Nanoparticle	Contaminant	Remotion	Size(nm)/BET(m ² g)	Supported	Ref.
nZVI	TCE	75%	50/25	Na-acrylic copolymer	[28]
Core/nZVI	TCE	ND	ND	Polyacrylic acid c.	[43]
nZVI	Chlorophenol	ND	80-120 nm	CMC	[18]
nZVI	TCE	100%	50 nm	CMC	[23]
nZVI	PBDEs	92%	50-80/35	Silica/microspheres	[26]
nZVI/Fenton	chloronitrobenzenes	ND	10-50 nm	ND	[44]
nZVI	Lindane	100%	ND	PAA/CMC	[24]
nZVI	Vinyl chloride	ND	80-120/55	surfactant	[45]
nZVI	PCE	99%	ND/15	ND	[46]
nZVI	TCE	80%	100-800 nm	carbon	[47]
nZVI	TCE	ND	500/320	CMC	[20]
nZVI	TCE	99%	5	alginate	[48]
nZVI	PCE, TCE,DCE	100%	15-40 nm	CMC	[22]

The authors suggested that a high Pd concentration such as Pd 2% could block some Fe active sites and inhibit the Fe activity and further corrosion. Other authors that used bimetallic nanoparticles for the removal of COCs also added various cations (Cu⁺, Ni⁺) hoping to find a stimulating effect on the removal of pollutant and also emulating the possible aquifers conditions. Shi & Chen, [38] used 12.5 g/L of Fe/Pd NP of 20-80 nm with 37 m²g⁻¹ and some cations (Fe⁺, Na⁺, Mg⁺, Cu⁺, Ni⁺) in order to remove pentachlorophenol (PCP).

They observed a removal of 98% of the pollutant. Addition of Na⁺ did not influence the pollutant removal, whereas addition of Mg²⁺ and Cu²⁺ cations were associated to an impaired removal of the pollutant. On the other hand the cations Fe³⁺ y Ni²⁺ enhanced the removal of the pollutant. Shih et al. [49] use NP Fe/Pd of 60-90 nm and cations in sulfate form, Na₂SO₄, CuSO₄, NiSO₄ and Fe₂(SO₄)₃ for the pentachlorophenol removal. The SO₄²⁻ inhibited the removal process but the Cu, Ni, and Fe cations enhanced the rate of contaminant removal. The Cu²⁺ and Ni²⁺ cations were added to the surface of the Fe/Pd NP.

The bimetallic NP can also be immobilized on carriers [9, 39, 50, 40, 51, 42]. In fact in recent years the majority of synthesized NP used some kind of medium support. Wang et al. [9] use a poly-vinylidene fluoride support with Fe/Pd NP of 50 nm for the removal of 5 mg/L of Trichloroacetic acid; it was possible to remove 96% in 30 min. because the use of the support increased the removal 6.8 times. Other authors have chosen to use organic compounds that may be able to be incorporated into the system. Kustov et al. [39] used chitosan with Fe/Pd NP to remove up to 276 mgL⁻¹ of PCE. The use of a support allowed for a smaller size of the NP as well as increased reactivity; the NPs were able to remove 99% of the pollutant in 5 hr. The NP were attached to chitosan surface via

-OH and -NH₂ groups. Cho & Choi [51] used CMC with Fe/Pd NP of 99 nm for removal of 13 mg/L of PCE, TCE and TCA. It was possible to remove 85% of the pollutant mixture; the use of CMC increased the removal 6-fold.

The use of polymers and membranes in bimetallic NP preparation and conditioning have improved NP properties such as decreased agglomeration, longer activity and increased pollutant removals.

5. In situ treatment with NP

The application of NP in organochlorine *in situ* treatments began in 2001 with the experiments of Elliott & Zhang. The first experiments focused on the application of filings of millimeter ZVI in the treatment of COCs (PCE, TCE, DCE, VC, CT). This generated knowledge and experience at laboratory and in situ levels, and paved the way to start using NP. Elliott & Zhang made bimetallic NP Fe/Pd, to prevent the rapid oxidation of Fe. Batch experiments tested various combinations of bimetallic NP Fe/(Pd, Ag, Cu, Co, Ni). The most efficient NP was Fe/Pd, this alloy enhanced the dechlorination of COCs by hydrogenation. The NP exhibited a size in the range 100 to 200 nm with a specific surface area of 33.5 m²/g. Removals of 99% of initial 4.6 mg/L pollutant (a mixture of chlorinated aliphatic compounds, i.e., PCE, TCE, DCE, VC, CT and CF) were observed.

Another well documented case study in which NP were used in the treatments of COCs was carried out by Quinn et al. [52] in the NASA's Launch Complex 34 (LC34). They applied a particular type of NP called EZVI because an oil-liquid membrane of Span 89 surfactant and corn oil surrounded the zero valent iron particle. The EZVI NP removed concentrations higher than 80% of TCE after 90 days of EZVI injection. The research on the action mechanism developed in the LC34 was continued by O'Hara et al. [53]. The results show that the EZVI technology can be an effective treatment for DNAPL zones, capable of treating dissolved phase besides even if the amount of ZVI is not enough to degrade all TCE, because then the vegetable oil and Span 89 surfactant can act as a slow release electron donor for improve the biodegradation processes. A removal of 86% of the whole DNAPL was reported, the mass flux decreased from 1826 to 810 mmoles/day. They found an increase in the



DCE and VC concentration indicating that there was an incomplete microbial degradation. One of the problems they faced during the research was the method of injecting the NP. The direct injection did not allow a homogenous distribution of the EZVI, so they tested different methods: pneumatic fracturing, hydraulic fracturing, and pressure pulsing and direct push injection. The best methods were pneumatic fracturing and direct push.

O'Hara et al. [53] also carried out batch experiments in order to show that pollutant degradation due to EZVI was mainly abiotic whereas the fast decrease in TCE concentration was due to a combination of sequestration of pollutant in the oily phase (solubilization) and abiotic degradation. He et al. [21]. used ZVI NP with Pd stabilized with carboxymethyl cellulose (CMC) for the removal of PCE (1.2-12 mg/L), TCE (1.6-23.8 mg/L), DCE (8.5-20 mg/L), VC (1.1-2.2 mg/L) and PCBs (6.9-97.7 mg/L) in the South of USA. The CMC avoided the nanoparticle aggregation, NP without a stabilizer could aggregate rapidly in water and form larger particles that could not travel through the soil matrix and become unavailable for further reduction of contaminants. Besides, CMC could be used as electron donor for microorganisms [54]. During treatment, two injections were performed separated by 596 days. After the first injection there was a 87% reduction of the DNAPL and a gradual reduction of DCE and VC by-products started, which were presumably generated by biological dehalogenation. At the end of the treatment, up to 70% of all injected iron was found in some wells.

Su et al. [55] also applied EZVI for CVOCs treatment in the site 45 MGRD, Parris Island, California. The site was monitored for two years and half. At the end a reduction of 86% of the whole CVOCs mass and a removal of 93% in the DNAPLs of PCE were achieved. The groundwater flow rate was from 0.046 to 0.055 m day⁻¹. After the first injection of EZVI there was an increase in the DCE and VC concentration, due that PCE and TCE degradation was carried out by the microorganism. Also they observed an increase in the concentrations of methane, ethene, ethane and acetylene. The increase in the DCE and VC concentrations started to decrease 220 days after the injection. The propionic, acetic and butyric acid concentrations increased from 1 mg/L-1 to 1700, 1300 y 420 mg/L-1 respectively. This release of VFA may have served as electron donor to microorganisms and stimulated the biological dehalogenation.

The information about the EZVI distance travel and the transformations to other minerals was discussed by Su et al. [56]. The travel distance from injection points was up to 0.89 m. for the direct injection and 2.1. m with pneumatic injection. The X-ray diffraction and scanning electron microscopy analysis showed that the EZVI nano was transformed to magnetite in the first 9 months; afterwards lepidocrocite started to appear, whereas after 2.5 years goethite and ferrihydrite appeared at the top of the aquifer.

Thus, NP began to be increasingly released into the environment in *in situ* treatments. Yet, there are some questions to be answered, such as the development of stronger NP that ideally will have very active sites, the study of some factors that inhibit the proper function of NP in uncontrolled conditions, etc..

6. Nanopartículas and Microorganism

The release of NP used in *in situ* treatments may have some effects on the indigenous microorganism. Although most of the NP are made of materials previously used in the removal of chlorinated compounds, due to their characteristics influenced by their small size, it is necessary to understand the interaction between NP – microorganism. Indigenous microorganisms also contribute to the removal of the compound besides to the ecological importance of them in the ecosystem they habit. For that reason it is necessary to know whether the NP – microorganism could affect positively or negatively the process of removing pollutants and the possible effect on the indigenous microorganism. Papers relating to elucidate these interactions and possible effects are scarce and clearly there is a need to foster research in this area.

Ma & Wu [57] treated PCE with 1 g/L of NP with the following treatments: ZVI, Zn, and both types of NP combined with microorganisms (MO). The best results corresponded to NP ZVI+MO. They reported that the combination of abiotic-biotic tools did not negatively affect the pollutant removal rate but changed the dechlorination process; however they did not report on how this change took place. They suggested that perhaps the MO promoted the dissolution of the iron oxides, promoting a lasting activity of the NP. Xiu et al. [58] investigated the effect of 1 g/L of nZVI on dechlorinating microorganisms that participate in bioremediation of 20 mg/L of TCE. The methanogenic MO were stimulated by the presence of nZVI and by the hydrogen released from the iron oxidation whereas dehalogenatinn MO were inhibited and presented a lag period of 300 hours. Afterwards, the dehalogenating MO began to recover. The authors suggested that it is necessary to carried out batch studies before the direct injections to know if the indigenous MO will be able to recover from possible inhibition episodes.

On the other hand Kirschling et al. [59] investigated the effects of 1.5 g/L of nZVI mixed with biopolyaspartate. The studies were carried out in batch operation, with material of three different aquifers polluted with 100 mg/L of TCE plus microbial population of these aquifers. The NP addition was also associated to some environmental changes such as reduced redox potential, which decreased from 400 to 100 mV after 68 days. The pH increased from 7.8 to 8.5 and the concentration of sulfate and methane increased. Such geochemical changes would be capable of modifying the indigenous microbial populations. The DNA increased in the treatment nZVI plus polyaspartate likely because this polymer is biodegradable and may have been used by



the MO as carbon and nitrogen source or maybe the use of that polymer decreases the *NP* toxicity as suggests the research of Li et al. [10]. The polymer could have prevented the *NP* adhesion to the MO surface. After 250 days there was a positive change in the microbial populations as a result of the changes generated in the environment and the release of H^+ product of nZVI corrosion.

Barnes et al. [60] focused on knowing whether the exposure of indigenous MO for 36 days to 100 mg/L of nZVI and pollutant TCE was able to modify the diversity and structure of the microbial community. A decrease in the abundance of microorganism was found. The 100 mg/L of nZVI were not toxic to MO because after 36 days the latter showed a recovery. In another study of Barnes et al. [60] the biological TCE degradation decreased as the nZVI concentration increased from 10 to 100 mg/L; the microbial activity ceased when the NP concentration increased to 300 mg/L. That concentration also inhibited the dehalogenating MO activity and the viable number of bacteria. They suggested that the best option is to apply combined abiotic and biotic treatments in two steps: first, to stimulate the MO with a carbon source, and second, to use high concentrations of *NP* to remove the metabolites generated for the MO as DCE and VC.

Cullen et al. [61] investigated the effect of 10 mg g⁻¹ of nZVI on soil MO. They observed that addition of nZVI enhanced dehydrogenase activity and had minimal influence on hydrolase activity probably. These enzymes measured the activity of either the transfer of electrons or hydrogen from substrates via electron carrier proteins and oxidoreductases to the terminal electron acceptor in respiration. This increase in the enzymatic activity might have been due to H^+ released in the nZVI corrosion. While Fajardo et al. [62] applied molecular and optical tools to determine whether the addition of 34 mg g⁻¹ of nZVI had some impact on the activity of soil MO or not. They carried out a transcriptomic analysis of three genes, *narG*, *nirS* and *gyrA*. The first genes encode the denitrification enzymes nitrate reductase, the second encoded the cytochrome *cd1* that contains the nitrite reductase, and the quantification of the third gene made a good approach of the overall DNA replication capacity. The results did not show any changes in gene expression after the nZVI addition. Yet, other NP that penetrated the membrane bacteria caused damage and in the worst case, they caused cellular lysis. Changes were also found in the structure and composition of the bacterial community.

Tilston et al. [63] investigated the addition of 10 g nZVI kg⁻¹ with a polyacrylic acid coating on a soil contaminated with Aroclor 1242. The treatment lasted 28 days in a two phase soil operation. First, using nZVI and then using aerobic biodegradation, the nZVI removed low concentrations of Aroclor 1242. Physico-chemical changes associated to the *NP* (pH, oxide potential reduction) disrupted the bacterial community and decreased the rate of removal and mineralization of the contaminant. Other research such as Li et al. [10], Chen et al. [28] and Zhou et al. [18] suggested that nZVI coated with polyelectrolytes, natural organic matter or CMC reduced the toxicity and availability of *NP* to MO because the physical contact between NP and microorganism was impaired, via electrostatic repulsive force.

Therefore, the research presented so far suggests that the NP applied *in situ* treatments can have a variety of negative impacts on the indigenous MO. Yet, some researchers showed that some impacted microbial populations could recover over time. The negative impacts of the NP have been decreased using stabilizers and emulsifying agents that cover the NP and prevent some attached between NP and MO membrane; in addition these covers could be used as carbon source for the MO. In the treatment of COCs, MO are not the only potentially exposed to NP: for instance, the exposure of subsurface water that is used as a source of drinking water to NP is of concern. In this regard, there are recommendations regarding the use of NP in *ex situ* treatments, or to develop some technology that allows for the capture and recovery of the NP at the end of the treatment.

7. Health and environmental issues related to nanoparticles use in environmental remediation and treatment

Nanoparticles can be released into the wastewater and finally end in a treatment plant or be released after a nanoparticle treatment. However there is a broad range of environmental and human health impacts can arise from different exposure routes of NP. Due this is necessary understanding the environmental benefits and disadvantage of nanomaterials compared with conventional products. In order to investigate the possible effect of NP on human health have been used some animal models that will predict the possible effects of NP exposition. Fako & Furgeson [64] have suggested the Zebrafish as an efficient model for predicting nanoparticle toxicity in humans due to the homology of it is genome with the human genome. Choi et al. [65] investigated the liver toxicity of Ag NP in Zebrafish. There were cellular alterations like disruption of hepatic cell cords and apoptotic changes. DNA damage and alterations in catalase and glutathione peroxidase enzymes were found. Other animals like oysters have been good models because these animals are filtering and are in direct contact with wastewater for many industries. Ringwood et al. [66] observed that oyster in direct contact with NP increased the expression of a metallothionein levels and damage the embryonic development. Other animals that have been used as models in nanotoxicology are *Drosophila melanogaster*, *Caenorhabditis elegans* [67, 68, 69, 70].

There are some reports that NP can entry living organism through some routes like gut, lung and skin and attack target organs such as lung, liver heart and brain [71]. The NP can disturb the cells by chemical or physical mechanisms. The chemical mechanisms are: (i) the production of reactive oxygen species (ROS), that can cause cell damage because they are involved in



inflammatory processes and the free radical formation can impact the cell integrity and damage the DNA [72, 43, 73] (ii) Dissolution and release of toxic ions, (iii) Lipid peroxidation [74], and (iv) disturbance of the cell membrane transport activity [75]. The physical mechanisms of NP disturbance are related with size and surface properties of NP and affect (i) transport processes, (ii) protein folding/aggregation, (iii) membrane, and (iv) lysosomes [76, 77, 78, 79].

Due the high risk in the use of nanoparticle technologies it is necessary to evaluate the products that use NP in terms of the environmental and health impacts of all the processes involved. One way to evaluate the environmental impact could be using the life cycle assesment (LCA) methodology, defined in standardized guidelines under the International Organization for Standardization (ISO 14040 and ISO 14044). The LCA is a widely accepted methodology for the evaluation of the potential environmental impacts. However it is necessary some adaptations when the impact is about water treatment. The traditionally approach focus on the volume of effluent treated or water produced and the others compare the treatment alternatives. [80, 81]. Actually the application of LCA to NP studies is very scarce. The LCA includes some steps: scope and definition of system boundaries, inventory of material, energy requirements and environmental impact) analysis and improvement analysis. The LCA studies will provide the necessary information to develop regulations and legislation for themes like occupational health and safety, environmental protection and consumer protection also develop information for comparative purposes about designs, processes and materials for the use of NP technologies.

8. Summary and perspectives

Nanomaterials are the core of a promising technology that can be used to accelerate and improve the transformation and detoxification of chlorinated organic compounds (COCs). We have reviewed significant subjects such as efficient nanomaterials for COCs treatment, use of supports and stabilizers that improve the process, interactions of nanomaterials with the microorganisms involved, and emerging fields. The most common material used for treatment of waters polluted with COCs has been zero-valent iron (ZVI) because of its efficiency and low cost. However, there are concerns on the stability and long term durability of ZVI NP. For this reason there are some works with other materials such as Pd, Zn or Ni and with combination of materials in the fabrication of NP. The bimetallic NPs allow for a lower cost of production, since one of the materials could be the most economic but not the most efficient whereas the second metal, the most expensive, provides a higher degradation capability. Alloyed and core-and-shell types of bimetallic NP have been tested. The process with NP can be made more efficient by using a support that prevents the aggregation of NP during reaction and in some cases can facilitate the recovery of the NP afterwards. Currently, the application of NP in bioreactors and *in situ* treatments is gaining momentum. Another significant issue especially for hybrid treatments is the interaction between NP and the microbial community harbored in bioreactors and devices, ranging from toxicity issues to biosynthesis of NP. There has been an attempt to incorporate metal NP onto the microbial cells for COC treatment, although more research is needed because some adverse effect has been detected. Furthermore, there is increased interest on biosynthesis of NP with microorganisms in order to have true “nanoparticleized biomass” with increased degradation capability of pollutants. Among important emerging fields we can highlight the studies on health and environmental impact as well as life cycle analysis of the NP fabrication and application. We have found that in spite of its importance the research on this area is scarce and has to be increased to avoid future, unpleasant surprises in the use of NP.

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