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NANO-SCALE ZERO-VALENT IRON AGENT IN CONTAMINATED AREAS: A REVIEW[1]

NANO FERRO ZERO VALENTE COMO AGENTE DE DESCONTAMINAÇÃO EM ÁREAS CONTAMINADAS: REVISÃO

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ABSTRACT

Pollution has become a target for environmental policies and numerous research due to a large number of contaminated environmental areas. Many measures must be applied and new remediation methods have been developed, such as nanoremediation. Nanotechnology is an ally of environmental science and among the nanomaterials used, zero-valent iron in nanoparticles is the most used for nanoremediation of soils and aquatic systems, due to its properties, effectiveness on a great variety of contaminants, the reduction of costs, and a higher decontamination efficiency. The aim of this study is to discuss the application of nanovaliant zero-valent iron as a nanoremediation tool for devastated environmental areas, aquatic systems and soil contaminated by different polluting agents. We based the research in 33 articles, which provided diverse information on the application, development, ecotoxicity and other relevant subjects on these nanoparticles. Most publications indicated the effectiveness of the application of it for the treatment of soil and aquatic systems.

Keywords: devastated areas, nanomaterial, nanoremediation.

RESUMO

Devido ao grande número de áreas ambientais contaminadas, este se tornou um tema alvo para políticas ambientais e inúmeras pesquisas, medidas devem ser aplicadas e novos métodos de remediação têm sido desenvolvidos, como a nanoremediação. A nanotecnologia se mostra aliada da ciência ambiental, dentre os nanomateriais usados destaca-se as nanopartículas de ferro zero valente, o mais usado para nanoremediação de solos e sistemas aquáticos, devido suas propriedades, apresenta efetividade sobre uma grande variedade de contaminantes, promovendo reduções nos custos e maiores eficiências de descontaminação. Este estudo tem o objetivo de discutir a aplicação da nano ferro zero valente como ferramenta de nanoremediação para áreas ambientais devastadas, sistemas aquáticos e solos contaminadas por diferentes agentes poluentes. Através de uma revisão bibliográfica, onde foram selecionados 33 artigos para compor os resultados e a fundamentação teórica, fornecendo informações diversificadas quanto a aplicação, desenvolvimento, ecotoxicidade e outros assuntos relevantes sobre estas nanopartículas. Em sua grande maioria as publicações demonstraram a efetividade da aplicação do nano ferro zero valente para remediação de solo e sistemas aquáticos.

Palavras-chave: *áreas devastadas, nanomateriais, nanoremediação.*

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INTRODUCTION

Nanotechnology is linked to the creation and manipulation of materials at the nano scale, these nanomaterials (NMs) have a size between 1 and 100 nanometers in at least one of its dimensions (GARNER; KELLER, 2014).

The nanometric scale improves specific and differentiated mechanical, optical, electrical and structural properties, as well as an increased surface area compared to the original substance (GARNER; KELLER, 2014; MATHIAS; ROMANO; ROMANO, 2014).

As the size of these particles decreases, the proportion of surface and near surface atoms increases. These surface atoms tend to have higher surface energy and a strong tendency to interact, adsorb and react with other atoms or molecules to achieve stabilization (LI; ELLIOT; ZHANG, 2006).

Currently, the application of NMs is widespread in several areas, mainly in the automobile, aeronautics, electronics, communication, chemistry, pharmacy, biomedicine, health, cosmetics, energy, environment, defense and food sectors. (GONZÁLES; JIMÉNES; BORCHERT, 2013; KELLER *et al.*, 2013).

Recently, NMs are being used in the remediation of devastated environmental areas and this has led to the introduction of significant amounts of different types in all environmental compartments: soils, aquatic systems and air (ALBERGARIA *et al.*, 2013; AHAMED *et al.*, 2014). Maintaining and restoring the quality of air, water and soil is one of the great challenges of today. Numerous countries face serious environmental problems, such as the availability of potable water, waste treatment, air pollution and contamination of soil and groundwater (THAGHIZADEH *et al.*, 2013).

Nanoremediation is a highly feasible treatment method because of its relatively low cost compared to traditional methods and the high efficiency of NMs in converting toxic compounds to less hazardous compounds (THAGHZADEH *et al.*, 2013). Among the NMs used, the nano-valiant iron nano (NZVI) stands out as the most used decontaminant for soils and aquatic systems currently (MUELLER *et al.*, 2012; O'CARROLL *et al.*, 2013; DONG *et al.*, 2019). This study aims to raise and discuss the application of NZVI as a nanoremediation tool for devastated environmental areas, these being composed of aquatic systems and soils contaminated by different pollutants.

LITERATURE REVIEW

The search for innovations and development, based on different processes and materials, made the environmental balance to be left in the background, causing exaggerated extraction, the spread of contaminants and the disposal of materials in the environment without due precautions (CECCHIN *et al.*, 2016).

Many cases of environmental disasters have already been reported, the environment has become a relevant issue in governmental, industrial and especially public health areas, causing environmental projects and policies to be heavily invested in the recovery of these impacted sites (CECCHIN *et al*., 2016).

It is possible to analyze as an example the situation of Brazil, the processes of identification of contaminated areas are in the initial phase, with little data on the current contamination situation of the Brazilian territory, but in the state of São Paulo, the Sanitation Technology Company In May of 2002 presented the first inventory of contaminated areas in Brazil, demonstrating 255 impacted areas in the state of São Paulo, and this research is continuously updated and, in its last publication in 2016, showed the value of 5662 contaminated areas, of which 1631 are in the process of remediation (CETESB, 2013).

The contamination of these areas is due to the presence of several types of contaminants, such as the most diverse several organic halogenated contaminants, such as Pentachlorophenol, Trichlorethylene, Trichloroethane, Dinitrotoulene and Trinitrotoluene, are present in several places, and these contaminants are listed as priority pollutants because of their toxicity and carcinogenicity. Many of these contaminants are persistent in the environment and are transformed or degraded by an extremely slow natural process (THAGHZADEH *et al*., 2013).

Over the last decades, the occurrence of organic micro-pollutants, such as pharmaceuticals in aquatic ecosystems, have been considered as an important environmental and health problem, among them antibiotics, their sources include sanitary wastewater, effluents from pharmaceutical industries, animal waste and also solid waste. Prolonged exposure to antibiotics can cause serious disturbances in humans and pose serious threats to the environment, moreover, antibiotics in natural water systems can promote super-resistant microorganisms (LEILI; FAZLZADEH; BHATNAGAR, 2017).

The removal of antibiotics from the environment presents a high cost and of great importance, because the pharmaceutical industries must treat their waste water before dispense them in the environment (SHOKOOHI *et al*., 2018).

About 30 to 90% of the doses of pharmaceutical compounds consumed by humans or animals are not degraded by their organisms and remain intact and their active substances are excreted, many of these drugs present toxicity to environmental microorganisms with large long-term environmental impacts (FAZLZADEH *et al*., 2016; SHOKOOHI *et al*., 2018).

Chromium (Cr) is also frequently referred to as a pollutant in the environment, it is one of the most abundant heavy metals, causing pollution of groundwater and soil due to its large industrial application. It mainly occurs as chromium trivalent Cr (III) and chromium hexavalent Cr (VI).

Most of its adverse effects are caused by Cr (VI) due to its solubility, mobility and high oxidation potential and generally its toxicity causes health problems, such as liver damage and lung problems, vomiting and severe diarrhea, Cr (III) is less reactive and toxic Cr (NĚMEČEL; LHOTSK; CAJTHAML, 2014).

Among the productive segments, the textile and paper industries generally have a prominence in contributing to environmental contamination, since they generate large volumes of effluents, with high demand of organic and biochemical load, low concentrations of oxygen, strong staining and little biodegradability, these residues have great facility to change biological cycles, thanks to their toxicity and carcinogenic and mutagenic potential (PEREIRA; FREIRE, 2005).

The remediation processes most used by most industries are based on pre-treatment by physico-chemical systems followed by biological treatment, mainly by the activated sludge system, however NZVI stands out as an excellent option for the remediation of heavy metals like Cr (PEREIRA; FREIRE, 2005; NĚMEČEL; LHOTSK; CAJTHAML, 2014).

The widespread use of pesticides in intensive agriculture leads to severe contamination of soil and groundwater. Among these pesticides, the main environmental concern is the molinate, which is normally used in rice plantations, avoids the growth of weeds, the use of NZVI shows to be efficient for degraded areas with molinate and other similar pesticides (GOMES *et al*., 2014).

As many pollutants can be cited as phosphate, phosphorus, pharmaceutical contaminants (ALMEELBI; BEZBARUAH, 2012; LIU *et al*., 2013; LEILLI; FAZLZADEHB; BHATNAGARC, 2017).

For this reason, mitigating measures must be applied and new effective methods of remediation have been studied and developed, such as nanoremediation (THAGHZADEH *et al*., 2013).

Nanotechnology is expected to bring fundamental development in the industrial sector in the coming years, and has a huge impact on environmental science for the detection, monitoring and remediation of various pollutants (THAGHZADEH *et al*., 2013).

Remediation is the science of removing or reducing pollutants from the environment, using chemicals or biological media. Recent advances have made the control and reduction of contaminants in soil, sediments and water, which represent the main environmental problems (MEHNDIRATTA *et al*., 2013).

In soils, nanoparticles (NPs) can be introduced directly, such as through fertilizers and other related products, used to protect plants or liquid suspensions used directly in contaminated sites, or indirectly through land application of sludge or biosolids (AHAMED, 2014).

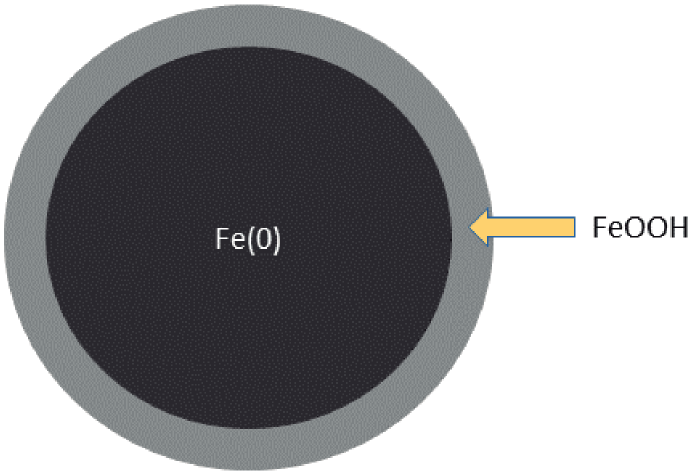
Nanotechnology offers a variety of NMs for this purpose, such as carbon nanotubes, nanoscale zeolites, dendrimers, bimetallic particles and metal oxides that can be used for remediation of the contaminated environment (MEHNDIRATTA *et al*., 2013).

We can highlight among the NMs used today, the zero-valent iron (NZVI) as the most used decontaminant for soils and groundwater (MUELLER *et al*., 2012; O'CARROLL *et al*., 2013; STEFANIUK; OLESZCZUK; OK, 2016). Being responsible for more than 90% of the works developed in the area, due to its low toxicity and cost of production (YAN *et al*., 2013; AHAMED, 2014; BARDOS *et al*., 2015; CECCHIN *et al*., 2016). The disadvantage of this NM is that after the decontamination the NPs are oxidized and can not be reused (MEHNDIRATTA *et al*., 2013).

This method of treatment is highly feasible due to its relatively low cost, compared to traditional methods such as filtering barriers or in situ treatment, and the high efficiency of these NMs in converting toxic compounds into less toxic and less toxic compounds (THAGHZADEH *et al*., 2013).

The NZVI particles exhibit a typical structure as shown in Figure 1. The core consists mainly of zero-valent iron or metallic iron while the surface is formed of Fe (II) and Fe (III) oxide and is the result of the oxidation of metallic iron. So far, its applications have focused mainly on electron donation properties. Under environmental conditions, NZVI is quite reactive in water and acts as an excellent electron donor, proving itself to be a very versatile material (LI; ELLIOT; ZHANG, 2006).

Figure 1 - Estruture of the nano zero-valente iron.



Source: Author's construction.

The major potential benefits of using NZVI, which led to its development on a nanometric scale, compared with the use of conventional (granular or microscale) zero-valent iron, is the high rate of potential degradation of the contaminant resulting from the larger area contact surface of nanometer-scale material (BARDOS *et al.*, 2015). NZVI demonstrate high efficiency because of their magnetic properties, small particle size and high reactivity rates (RAJA; PANDIAN, 2014).

These nanoparticulate iron compounds are materials with high adsorbent capacity of heavy metals and have gained prominence for the decontamination of waters and effluents, due to the ease of their application in situ and in a wide range of pH values, besides their low toxicity and the oxidation states that present (AHAMED *et al.*, 2013)

To guarantee the efficiency of NZVI NPs in situ, there are two major technical challenges: the high chemical reactivity of these particles, which consists of their ability to react with contaminants and the limitation of migrating through the surface, due to several processes, such as agglomeration, where the particles accumulate, and passivation, when the particles are chemically inactivated and there is their retention in aquifers (BARDOS, 2015; DONG *et al.*, 2019).

To assist in overcoming some of the problems encountered in the application of NZVI and increase its utility, several modifications have been made, including the stabilization, emulsification and anchoring of the same in an array, so bimetallic NPs have been developed, are variants NZVI NPs containing a small amount of a noble metal such as palladium (usually less than 1%), the added metal acts as a catalyst, increasing the reaction rates and range of treatable contaminants (O'Carroll *et al.*, 2013; Bards *et al.*, 2015).

According to Zhu *et al.* (2016) in recent years, bimetallic NPs, composed of Fe-Ni were used and efficient to reduce Cr (VI) of contaminated water.

Several studies show that interactions with NPs work quite differently when compared to soil with water, especially when we analyze the influence of the electronegativity of the soil colloids and with the stability of the particles, causing the efficiency of degradation to be reduced (CECCHIN *et al.*, 2016).

Methods for large-scale, cost-effective production of NMs are essential for the growth of nanotechnology, since environmental applications often require the use of significant quantities of remediation reagents for large volumes of contaminated water and soil. This may have been the main factor for the relatively slow adaptation of some environmental nanotechnologies (LI; ELLIOT; ZHANG, 2006).

DEVELOPMENT OF NZVI NANOPARTICLES

The ability to improve methods for the large-scale, low-cost production of NMs is essential for the growth of nanotechnology and its applicability. In general, the synthesis of NPs can be done through two different strategies: the top-down and bottom-up approaches, the first one producing the NPs starting from large size materials and generating NPs by mechanical or chemical methods; the second approach treats production in the opposite way, starting from nanostructures and generating larger structures, through syntheses (LI; ELLIOT; ZHANG, 2006; YAN *et al.*, 2013).

The methods generally used for the production of NZVI are: a) by decomposition of pentacarbonyl iron in organic solvents or in argon; from the reduction of iron oxides in a high temperature hydrogen atmosphere (200-600 ºC); b) or by reducing the Fe3 + or Fe2 + ions with sodium borohydride, the main advantage of the latter method being the simplicity, safety of the system and the use of simple reagents (LI; ELLIOT; ZHANG, 2006; YAN *et al.*, 2013).

The chemical reduction is the most used method to obtain NZVI mainly due to its simplicity, in addition, the product obtained is characterized by a homogeneous structure that exhibits high reactivity (STEFANIUK; OLESZCZUK; OK, 2016).

Methods that are currently not widely used, but which, due to their advantages, may soon become more popular, include precision grinding, carbothermal reduction, ultrasonic assisted production, electrochemical generation and green synthesis (STEFANIUK; OLESZCZUK; OK, 2016).

In general, the NZVI at nanoscale occurs in aqueous medium through a chemical process, involving oxidation and reduction reactions, the product of this reaction is the suspended iron NPs accompanied by the formation of metallic iron agglomerates (LI; ELLIOT; ZHANG, 2006).

An innovative synthesis process of NZVI, which is based on the production of extracts of natural products, such as green tea leaves, with high potential antioxidants due to the presence of polyphenols, has the capacity to react with Fe (III) and to produce NZVI, this method has advantages over others, because it reduces the toxicity, the use of natural products prolongs the reactivity of the NZVI and still this raw material can end up as secondary source of nutrients for complementary biodegradation (CHRYSOCHOOU; MCGUIRE; DAHAL, 2012; MYSTRIOTI; XENIDIS; PAPASSIOPI, 2014).

Leili, Fazlzadeh e Bhatnagar (2017) used the extract of thyme and nettle to synthesize NZVI particles and used them for the nano remediation of the antibiotic cephalexin in aquatic systems.

Currently, the synthesis of NZVI using polyphenolic compounds derived naturally from tea leaves and sorghum meal extracts has aroused much interest (YAN *et al.*, 2013).

In some experiments, NZVI NPs were commercially purchased. A stabilized suspension of water and polyacrylic acid may be used to stabilize the NZVI suspension against aggregation (GIL-DÍAZ, 2014).

The synthesis of bimetallic iron NPs occurs when another metal, generally less reactive, such as palladium (Pd), nickel (Ni), platinum (Pt) or silver (Ag), is added to the particle of NZVI, simply by dipping the NZVI freshly prepared in a second metal salt solution. It is believed that this second noble metal promotes the oxidation of iron and can act as a catalyst for the electron transfer and hydrogenation. It has been shown that bimetallic iron NPs (Pd-Fe, Pt-Fe, Ni-Fe, Ag-Fe) can reach significantly higher degradation rates and prevent or reduce the formation of toxic by-products (LI; ELLIOT; ZHANG, 2006).

This is a very well documented method of enhancing NZVI remediation properties, small amounts of these noble metals applied to the surface of the NZVI cause an increase in particle reactivity and provide good protection against passivation. Among the transition metals commonly studied as catalysts of the dehalogenation reaction, Pd proved to be the best (STEFANIUK; OLESZCZUK; OK, 2016).

The major challenge for the environmental applications of the reactive NMs is their great tendency of agglomeration, sedimentation and limited mobility, therefore, some studies look for the use of surfactants, the decrease of the average particle size, the reduction of the Zeta potential and the displacement of the point in NZVI to improve its effectiveness (SUN *et al.* 2006).

Stabilizers are coatings that provide greater surface area for the reaction. Among these coatings are guar gum and sodium carboxymethylcellulose (CMC-Na), which are polymers added to the NZVI by means of a post-synthesis process, or by synthesis in the presence of polymer, these polymers stabilize the particles (MUELLER *et al.*, 2012; O'CARROLL *et al.*, 2012). In order to avoid aggregation and deposition of these NPs, this would result in a lower remediation efficiency (MUELLER *et al.*, 2012).

Modification of surface properties was one of the main approaches aimed at increasing the dispersion in aqueous media and the mobility in pore media of NZVI. The surface coating causes a change in the surface charge of these NPs, which prevents the electrostatic attraction of molecules and reduces their aggregation, the natural and modified polymers, the anionic surfactants and other organic coatings have been tested, but the application of biopolymers is especially due to its bioavailability, low cost and environmental safety. Among these biopolymers, the use of starch, carboxymethyl cellulose (CMC) and guar gum proved to be particularly successful (STEFANIUK; OLESZCZUK; OK, 2016).

Chowdhury *et al.* (2012), demonstrated in their study the difficulty in the mobility of NZVI and experimented the use of the electrophoresis technique to improve the transport of the NPs and found an excellent in situ repair potential for a great quantity of chlorinated organic compounds and of heavy metals. The application of the external electric field increased the migration of the NZVI particles through the porous media, having good results in the soils with greater granulation, whereas in fine soils the permeability is still considered a challenge.

For the commercially available NZVI particles, the quality and efficacy of these available products can be highly variable and inadequate, quality control and characterization protocols exist to support the development of these products, since NZVI NPs produced with different methods can exhibit widely varying properties, as well as their reactivity and their surface properties can change rapidly, with the chemistry of the solutions and the environmental conditions (LI; ELLIOT; ZHANG, 2006).

The nature and morphology of these adsorbents can be characterized by equipment such as transmission electron microscope (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD) and Infrared Region Spectroscopy in Transmittance mode (FTIR) (LEILI; FAZLZADEH e BHATNAGAR, 2017).

Information is fundamental, such as pH, when it is about 8, iron oxides are positively charged and attract anionic binders, including environmental species such as sulfate and phosphate. When the pH of the solution is above the isoelectric point the oxide surface becomes negatively charged and can form surface complexes with cations, guaranteeing their action as excellent reducers or electron donors (LI; ELLIOT; ZHANG, 2006).

NZVI ACTION MECHANISM AND APPLICATIONS

Suggested pathways of NZVI particle removal for the removal of pollutants include adsorption, precipitation, reduction, oxidation and coprecipitation (LEILI; FAZLZADEH; BHATNAGAR, 2017). The application of NZVI can be performed with different methods, most field applications, the NZVI was applied by gravity feed or low pressure injection, it can still be by direct pressure (MUELLER, 2012).

According to Li, Elliot and Zhang (2006), data from some in situ tests indicate that NZVI NPs can migrate from a few centimeters to meters from the injection site and there are many factors influencing this mobility in the environment, such as size of the NPs, the pH of the solution, ionic strength, soil composition, soil water flow velocity, among others. Therefore, the method to be used, the distribution and the number of injection wells depend on the geology and geochemistry of the contaminated site.

Some studies have shown that for contaminated groundwater, the use of NZVI NPs is promising in the remediation of chlorinated organic contaminants, such as dichloromethane (DC), perchlorethylene (PCE), 1,1,1-trichloroethane (TCA), and trichloroethene (TCE), through oxidation reactions (MUELLER *et al.*, 2012).

The use of FeZ as a remediation agent in the treatment of groundwater was used in permeable reactive barrier systems (BARDOS *et al.*, 2015), where the water flows passively through a projected iron wall, while the contaminants are precipitated, adsorbed or transformed. Although these barriers may serve as remediation, there are significant challenges to this technology and may limit its practical application with a large amount of iron powder (LI; ELLIOT; ZHANG, 2006).

One promising method for decontamination of groundwater is a coupling of NZVI with anaerobic bacteria. First, the corrosion of NZVI could decrease the oxidation reduction potential, which could create a suitable reducing environment for the growth of anaerobic bacteria. Secondly, the hydrogen generated from this corrosion is able to provide electrons and together the bacteria act in the removal of pollutants. Third, and finally, the integrated treatment of NZVI and bacteria can completely degrade the contaminants in non-toxic or harmless substances (DONG *et al.*, 2019).

REMEDIATION OF ORGANIC CONTAMINANTS

The chemical foundations for the transformation of halogenated hydrocarbons have been well documented since these compounds are among the most common soil and groundwater contaminants. Iron (Fe0) serves effectively as an electron donor as shown below (LI; ELLIOT; ZHANG, 2006):

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

The Fenton reaction occurs in the presence of oxygen and strong oxidants are generated, such as hydroxyl radicals; however, this method presents some disadvantages, since their surface, energy and reactivity depend on the preparation conditions, they become easier to oxidize and are not suitable for practical applications, requiring surface agents to make them feasible (YAN *et al.*, 2013; RAJA; PANDIAN, 2014).

Chlorinated hydrocarbons, on the other hand, accept electrons and undergo reductive dechlorination:

$$RCl + H^+ + 2e^- \rightarrow RH + Cl^- \qquad (2)$$

For the dechlorination with NZVI, 3 mechanisms of potential transformations were proposed: (1) direct reduction on the surface of the metal; (2) reduction by ferrous iron at the surface; and (3) reduction by hydrogen (LI; ELLIOT; ZHANG, 2006).

The remediation mechanism consists of the direct transfer of iron electrons to the organic contaminants, turning these compounds into non-toxic or less harmful species (FU; DINYSIOU; LIU, 2014).

REMEDIATION OF INORGANIC CONTAMINANTS

They are basically composed of heavy metals. NZVI NPs can rapidly remove or reduce inorganic ions, such as Cd, Ni, Zn, As, Cr, Ag and Pb, as well as other inorganic anions, thanks to their properties. Iron NPs can also reduce some significantly stable inorganic compounds such as perchlorate and nitrate (LI; ELLIOT; ZHANG, 2006).

Nanotechnology and NZVI will have positive effects on the various fields of environmental technology. Still, the main limitation would be the lack of information on the toxicity of these NPs. Considering that nanotechnology may present a certain potential for undesirable human health outcomes and that it can not be ignored, to disseminate this technology, viable safety guidelines for the nanotechnology industry involving NP toxicity testing under environmental conditions should be applied (MEHNDIRATTA *et al.*, 2013).

The risks posed by the use of NZVI due to the release of NPs have led to a precautionary regulatory approach in many countries. However, a strict regulatory position is not supported by documented evidence already available. The processes that limit activity and mobility, combined with their high reactivity, result in the need to deal with NZVI with caution, how to prevent oxidation during the manipulation (for some products even combustion) of NZVI in the exposure to air, since high suspension density (BARDOS *et al.*, 2015).

Studies indicate that there is a possible impact of NZVI in bacterial communities and that this impact is dose dependent, so NZVI can be applied in soils, provided that its dosage does not exceed the level harmful to bacteria, on the other hand, the use of coated NZVI can improve environmental remediation, however, it is not certain that these coatings can allow the use of higher doses without causing a negative effect on bacteria. This is a theme that should be explored by more studies (AHAMED, 2014).

Considering the negative effects of NZVI, research based on laboratory studies has shown that the natural fate of these NPs used in an aquifer will be the conversion into larger particles of iron (II) and (III) oxides or hydroxides similar to natural minerals (O'CARROLL *et al.*, 2013; BARDOS *et al.*, 2015).

There are differences in the type of technology used in the application of NZVI between Europe and the USA, in Europe there are issues of economic and risk restrictions regarding the remediation of aquifers while in the USA NZVI is an established treatment method, with the use of NPs bimetallic and emulsified NZVI (MUELLER, 2012).

Monitoring the development of plants grown in polluted soil with NZVI can be considered as an indicator of soil quality (GIL-DÍAZ *et al.*, 2014).

Wang *et al.* (2014) observed that two plant species were significantly affected by Cr-contaminated soils and treated with short-term NZVI, but after 30 days both plants showed increased growth.

Previous studies have shown that the application of NZVI was effective for immobilization in soil samples and a decrease in soil phytotoxicity for barley and pea in germination tests (GIL-DÍAZ *et al.*, 2014).

The bactericidal action of NZVI was partially attributed to the oxidative stress caused by the generation of reactive oxygen species (ROS) and the direct interactions of NZVI with the cell membrane and the interruption of electron and ion transport. These results may suggest potential applications of NZVI as an antimicrobial agent (YAN *et al.*, 2013).

NanoRem is a research project, funded through the research program of the European Commission and seeks an international consensus in the European market between different stakeholders (regulators, site owners and service providers) on the proper use of NPs in nanoremediation. Its strategy to achieve this goal depends on three strands that function in an integrated way: Evidences that address crucial knowledge gaps; provide the right kind of evidence; communicate the evidence and develop shared conclusions (BARDOS *et al.*, 2015).

Despite these concerns, the results demonstrated with current applications of contaminant reduction are promising and no significant adverse impact on the environment has been reported (MUELLER, 2012).

Pilot tests are conducted to provide information on the amount of NZVI required for remediation and to raise possible contingencies, so accurate site investigations such as hydrogeology and site geochemistry are performed. Hydrogeology influences the transport of particles and geochemistry indicates substances that NZVI can react, reducing its useful life (MUELLER, 2012).

Aquatic invertebrates are usually affected by contaminants released into the environment. This is why these organisms are important for ecotoxicity testing to analyze the behavior and bioavailability of NPs in aquatic environments (AHAMED *et al.*, 2014).

Some recent field tests indicate that iron NPs may migrate only short distances from the injection site, this mobility of NPs in the underground environment depends on many factors, such as particle size, solution pH, ionic strength, soil composition, velocity of groundwater flow, among others. It is suggested that anionic surface charges can improve the transport of NZVI through the soil (LI; ELLIOT; ZHANG, 2006).

FUTURE PROJECTIONS

Significant progress has been made in the research and development of NZVI for soil and groundwater remediation. New research and development efforts should be directed at improving the performance of practical applications and minimizing potential economic and environmental risks (LI; ELLIOT; ZHANG, 2006).

The synthesis of these NPs represents the main foundation of this technology, several synthesis methods have been developed, but the cost of each is considerably different. The challenge is to expand production processes to generate large enough quantity to reduce values. Methods of control and quality assurance, such as particle size, reactivity, surface loading and mobility, should be established.

Other issues include the optimization or specification of the surface properties of NZVI for efficient underground transportation under site-specific conditions and for the degradation of contaminants (LI; ELLIOT; ZHANG, 2006).

There are many issues to be addressed in future chemical studies, such as prolonging the reactivity of nanoparticles and improving selectivity over target pollutants. In engineering, there is an urgent need to develop NPs with mobility in porous media and methods to avoid aggregation and other characteristics that prevent the transport of NZVI (YAN *et al.*, 2013).

Considering the environmental chemistry, a study of the reaction rate, mechanism and effect of environmental factors (pH, ionic strength, competing contaminants) on the transformation of specific environmental contaminants should be developed. As for geochemistry, this includes the reactions of NZVI with groundwater and the interactions with soil and sediments, settlement, aggregation and transport in porous medium. Assessing the long-term fate of NZVI represents another topic to consider, requiring research on the applications of NZVI technology and properly assessing its implications for the environment (LI; ELLIOT; ZHANG, 2006).

Another barrier lies in the difficulty of connecting laboratory studies to the practical application, since the interactions between NZVI and the natural environment are difficult to reproduce in a laboratory. To address these challenges, it is necessary to facilitate collaboration between the research community and the remediation industry for pilot testing (YAN *et al.*, 2013).

In a general assessment, NZVI has two major remediation benefits, based on efficient treatment processes, thanks to the wide range of types of treatable contaminants (BARDOS *et al.*, 2015).

MATERIALS AND METHOD

This study is characterized by a review. A total of 33 published articles were searched; the databases consulted were Science Direct and Periódicos Capes, in Portuguese and English. Being that of these, 18 studies were selected to compose the results of the research, demonstrating the effectiveness of NZVI, and the others were analyzed, based and added information to the work.

The following keywords were found for the search: "nano remediação", "nanoferro zero-valente" and their respective English descriptors: *"nano remediation"* e *"nanoscale zero-valent iron"*.

The articles included in this work were those that presented the delimited topic, nano remediation using NZVI, and may be associated with other metals on its surface, forming bimetallic NPs, but only to improve its properties and increase its efficiency for application in devastated areas of the environment, these being, soils and aquatic systems being able to present different contaminants.

RESULTS AND DISCUSSION

Due to population growth and the consequent increase in production activities, many environmental changes appear at extremely worrying levels, resulting in a significant reduction in soil, air and water quality.

With the objective of remediation of environmental contamination, many technologies are launched, among them, nanotechnology is highlighted, as it can be applied in the remediation of a wide variety of contaminants, while also reducing costs and obtaining greater remediation efficiencies. (KARN, KUIKEN; OTTO, 2009)

Among these NMs, one of the most used for environmental remediation is the zero-valent iron (NZVI), which has shown great prospects in the degradation of pollutants (STEFANIUK; OLESZCZUK; OK, 2016).

For the complete analysis of this has been selected the total of 33 articles were selected for this study, all of them presenting NZVI as a nanoremediation agent in devastated areas. Among these publications, 18 studies demonstrated the effectiveness of NZVI in experimental and original studies as a remediation agent in groundwater or in polluted soils as shown in table 1.

Table 1 - Summary demonstration of remediation articles with nFeZ, contaminants, treated site, presence of surface stabilizer and application efficiency.

Author / Year	Activity	Association	Poisoning	Treated Area
THAGHZADEH *et al.* (2013)	Effective		Organic chlorinated, Inorganic and Metals	Ground, Groundwater
CECCHIN *et al.* (2016)	Partially effective		Biodiesel	Ground
GOMES *et al.* (2014)	Effective		Molinate	Ground
FU, DINYSIOU e LIU (2014)	Effective		Chlorinated organic compounds, nitroaromatic compounds, arsenic, heavy metals, nitrate, dyes and phenol.	Groundwater and Wastewater
WANG *et al.* (2014)	Effective	Carboxyl cellulose	Chrome	Ground
CHOWDHURY *et al.* (2012)	Effective		Organics compounds and heavy metals	Ground
GIL-DÍAZ *et al.* (2014)	Effective		Arsenic	Ground
LEILI, FAZLZADEH e BHATNAGAR (2017)	Effective		Cephalexin	Water systems
LI, ELLIOT e ZHANG (2006)	Effective		Perchlorethylene, trichloroethene, carbon tetrachloride, nitrate, TNT, pesticides, Cr and Pb	Ground, Groundwater
STEFANIUK, OLESZCZUK e OK (2016)	Effective		Several	Ground, Groundwater
NĚMEČEL, LHOTSK e CAJTHAML (2014)	Effective		Chrome (VI)	Groundwater
ZHU *et al.* (2016)	Effective	Copper	Chrome	Ground

ALMEELBI e BEZBARUAH (2012)	Effective		Phosphate	Contaminated water
LIU *et al.* (2013)	Effective		Phosphor	Contaminated water
RAJA e PANDIAN (2014)	Effective	Palladium	Metronidazole	Contaminated water
KIM *et al.* (2013)	Effective	Zeolite	Lead (II)	Contaminated water
MYSTRIOTI, XENIDIS e PAPASSIOPI (2014)	Effective		Chrome (VI)	Groundwater
FAZLZADEH *et al.* (2016)	Effective	Hydrogen peroxide	Sulfatiazole	Wastewater

Source: Search data.

Gil-Díaz *et al.* (2014), demonstrated the development of barley plants grown at NZVI treated sites, soils were monitored for 33 days and plants with 10% NZVI application in soil had the highest growth rate, higher than plants treated with 1% and although the plants did not, the decrease in the availability of contaminants in the soil induced a reduction in the soil phytotoxicity and allowed a better growth of the plant.

The results showed that the degradation of the molinate pesticide by NZVI NPs through an oxidative pathway can also occur in soils. The soil type was the most significant variable for transporting iron and molinate (GOMES *et al.*, 2014).

According to Leili, Fazlzadeh and Bhatnagar (2017), NZVI NPs developed from nettle and thyme leaf extracts as low cost adsorbents showed a high potential for the removal of cephalexin (antibiotic) and these materials could be considered as promising adsorbents for remediation of other antibiotics and organic pollutants in aquatic systems, as analyzed by HPLC, it was observed that there was no degradation of cephalexin, so the removal was by adsorption.

The NZVI has been shown to be more effective than FeZ microparticles because of specific properties acquired from the nanometer scale, as shown by Almeelbi and Bezbaruah (2012), where NZVI particles were used to remediate a wide variety of contaminants, reactivity due to high reactive surface area and was successfully used for the removal of phosphate. The efficacy of NZVI at nano remediation was 13.9 times greater than the FeZ microparticles, the same concentrations were applied as the sorption capacity is dependent on the surface area (ALMEEBI; BEZBARUAH, 2012).

According to Cecchin *et al.* (2016), the degradation process of NZVI NPs was effective in the first few hours of the test, but their degradation capacity was drastically reduced after 192 hours of testing. The best results obtained in the process of biodiesel degradation with the use of NZVI were given in the tests that used the mass of 4 grams of NZVI for a contamination content of 40 g / kg.

Few studies show the fate of NZVI NPs in the environment, their action on the microorganisms of aquatic systems and soil. Its degradation and / or removal of the treated site was also not mentioned in these studies. Only 4 of the articles surveyed made objective references on this issue, and one article raised the question of toxicity of NZVI clearly, as shown below.

Regarding the ecotoxicity behavior of NZVI, few studies were concluded; several research groups are currently in the process of analyzing their toxicity data. The release of NZVI as a remediation agent depends on several problems, one of the most relevant factors being the fate and impact of these NMs in the ecosystems to which they are applied. Current literature is insufficient and many studies point to toxic effects when some organisms are tested (AHAMED *et al*., 2014).

But the study results by Němečel ; Lhotsk; Cajatham (2014) documented the possibility of NZVI application, its use resulted in a rapid decrease in concentrations of Cr (VI) and total Cr in contaminated groundwater without any substantial effect on its chemical properties. No significant changes were observed in the density of cultivable psyllophilic bacteria and concentrations of phospholipid fatty acids in the groundwater samples during the experiment and the ecotoxicological test with Vibrio fischeri revealed no change in groundwater toxicity after NZVI application. On the other hand, the soil phospholipid fatty acid samples showed that the application of NZVI stimulated the growth of Gram positive bacteria and indicated a correlation between the number of bacteria and the concentration of Fe.

Many authors report in their experiments the need to add to the NP of NZVI another metal, thus forming a bimetallic NP, with the objective of improving properties, avoiding agglomeration, improving the mobility and degradation of NZVI. As can be seen in the publication of Zhu *et al.* (2016), in order to increase NZVI stability and avoid agglomeration of the particles, they synthesized and characterized NP by adding copper (NZVI / Cu) to treat contaminated soil, showing that the effectiveness of the reaction was spontaneous and endothermic.

In order to avoid aggregation and deposition of these NPs, which would result in a lower efficiency in the nanoremediation, several stabilizers have been tested and used effectively for NZVI, keeping the NPs in suspension for longer, avoiding contact between them and stabilizers may increase NZVI reactivity with (MUELLER *et al*., 2012).

According to Raja and Pandian (2014) bimetallic Fe-Pd NPs were synthesized using sodium borohydride as a reducing agent under a nitrogen atmosphere and using palladium as a protector of the surface layer, thus prolonging the life of the particles and improving their efficiency. The spherical shape of the NPs and the mean size of 42.6 nm showed an improved response to the remediation of Metronidazole from contaminated tributaries.

Still in this context, some research shows that modifications of the surface of NZVI can help in its stabilization and efficiency, in the reduction of aggregation and of toxicity. However, the improvement of these properties can simultaneously lead to the creation of other properties that can cause threats related to the application of NZVI and should be studied in agreement with Stefaniuk, Oleszczk and Ok (2016).

The specific properties of NZVI are of extreme importance for its effectiveness in nanoremediation, among the characteristics we can highlight pH as primordial for the specificity of the application, as demonstrated by the study of Leili, Fazlzadeh and Bhatnagar (2017), where for the removal of cefalexin (CEX), the pH value of NP determined the removal efficiency of the contaminant CEX. According to Liu *et al.* (2013) the effect of pH affects the result interestingly, generally the pollution removal capacity of NZVI is improved low pH, less than 4.

CONCLUSION

Understanding the NZVI synthesis methods, their structural characteristics, and their transport phenomena is critical to establishing their role in environmental remediation.

The aggregation and accumulation of NZVI has been reported as the major disadvantages for its application. The modification of NZVI can improve and improve its structure, mobility and application in the environment.

The use of NZVI as a remediation agent appears to be more promising than the conventional FEZ (microscale) process or other in situ remediation methods.

However, studies are needed to make this technology feasible, minimizing unexpected environmental impact and other potential risks, eliminating any risks of toxicity.

The studies presented suggest that NZVI is effective as a nanoremediation agent on aquatic systems and contaminated soils, as well as being able to remediate a wide variety of pollutants. The results indicate the need for a greater number of studies for the development of methodologies for the production and characterization of NZVI that makes its practical application in devastated areas feasible and safe.

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