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Critical evaluation of the use of different nanoscale zero-valent iron particles for the treatment of effluent water from a small biological wastewater treatment plant

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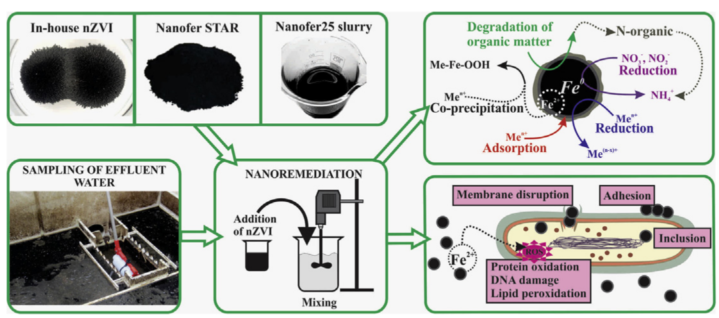
HIGHLIGHTS

- Different types of nZVI were used for the remediation of effluent water from SBWTP.
- Remediation depends on the reactivity of nZVI, iron load, mixing and settling times.
- In-house nZVI effectively disinfected effluent water, but contaminated it with B.
- Ammonium N was formed from organic N and by the reduction of nitrates and nitrites.
- Nanofer25 slurry the most effective removal of elements and inactivated pathogens.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanoremediation procedures are usually designed so that only one contaminant or similar class of contaminants is being considered. In the present work, a holistic approach was applied towards processes which simultaneously occur after the treatment of real effluent water from a small biological wastewater treatment plant (SBWTP) with different nanoscale zero-valent iron (nZVI) particles. Three different types of nZVI particles were tested: in-house nZVI, commercially available Nanofer STAR and Nanofer25 slurry, which differ in reactivity and their methods of synthesis. In order to optimise the conditions for the efficient removal of selected elements, nitrogen species, and pathogenic bacteria (Coliform bacteria, *Escherichia coli*, Intestinal Enterococci and *Clostridium perfringens*), effluent water samples were treated with different iron loads from each of the investigated nZVI at various mixing and settling times.

The results demonstrated that in-house nZVI, which is the most reactive of the nanoparticles tested, most effectively removed metals and inactivated pathogenic bacteria. However, the application of in-house nZVI is restricted, as it contaminates the remediated water with B, which originated from the reagents used in its synthesis. To a certain extent, all of the investigated types of nZVI reduced nitrates and nitrites to ammonium cations. The additional formation of ammonium nitrogen was

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the result of the interactions of the nZVI with the organic nitrogen present in the effluent water. At an optimised iron load, mixing time, and settling time, the most efficient removal of elements and disinfection of pathogens was achieved when Nanofer25 slurry was applied.

1. Introduction

Nowadays, the aquatic environment is globally polluted by various industrial or human activities, and water contaminated with pathogenic organisms is used by millions of people [2]. Apart from this, scientific evidence indicates that water scarcity will occur globally, even in regions which are now considered to be water-rich [28]. Thus, in order to ensure the availability of clean and safe water sources for humans and other living beings, it is necessary to make proper use of current technologies for wastewater treatment, as well as developing new technologies. The latter must be robust and available at low cost, with low energy consumption and minimal impact on the environment [27,37,13]. Most of the conventional water purification technologies have some drawbacks. For example, biofouling causes problems in membrane filtration, while the use of UV radiation for water disinfection is energy consuming. When chemical treatment using Cl_2 and O_3 is applied for disinfection, harmful secondary products, such as ClO_3^- and BrO_3^-, which are of environmental concern, may be produced [3,14,29].

Nanomaterials, including nanoscale zero-valent iron (nZVI) particles, known due to their distinctive chemical, catalytic, electronic, magnetic, mechanical and optical properties, are currently being intensively investigated for the remediation of contaminated wastewaters, waters, soils, and sediments [35,17,19,23,40]. Their synthesis on a laboratory scale via the reduction of ferric chloride by sodium borohydride in an aqueous solution under an inert atmosphere of nitrogen is relatively simple [44]. The commercially available nZVI is mostly produced by the hydrogen reduction of iron oxides at high temperatures [49]. In comparison to other nanoparticles, nZVI is among the cheapest, while the use of nZVI for remediation is low energy consuming. Nevertheless, environmental remediation by nZVI has not yet been extensively accepted, since there is still a lack of knowledge with regard to the technological limitations, environmental risks, and (eco)toxicological impacts of such applications. More comparable studies for different nZVI materials and deployment strategies are also needed [9].

Despite being differently synthesised, the composition of the nZVI produced is, in general, similar, although there are differences in the crystalline structure and in the size of the Fe^0 core and the iron (hydr)oxide shell. These characteristics have an important effect on nZVI reactivity [30]. Smaller nZVI particles have a higher proportion of atoms exposed on their surface, which increases their tendency to adsorb, interact, or react with other substances to achieve surface charge stabilisation [42,9]. In addition to contaminant removal processes which involve the surface reduction and complexation of intact nZVI, contaminants can also be co-precipitated with iron corrosion products [40,50].

Laboratory and full-scale applications of nZVI have demonstrated that they can be effectively used for the degradation of a wide range of organic pollutants, for the removal of trace elements, and for the inactivation of microorganisms. nZVI were extensively used for the adsorption and immobilisation of different elements [19,36,23,20] in various artificially prepared aqueous matrices.

Apart from other pollutants, water-borne bacteria, viruses, and fungi represent a severe threat to the aquatic environment [45,27]. The bactericidal effects of nZVI have been investigated from the viewpoint of their eco-toxicity, and their possible use for water disinfection [7,10,21]. The toxicity of nZVI differs within the same genus or even the same species of bacteria, and also depends on the growth phase of the bacterial cell [6,22]. On the other hand, iron oxide and hydroxide nanomaterials have no pronounced bactericidal effects [10,4]. The observed cytotoxic effects are the result of microbial cell membrane disruption or oxidative stress [22,39]. The adsorption of nZVI onto the microbial outer cell membrane increases the permeability of the biological membrane, and disrupt its lipid bilayer integrity to allow toxic Fe^{2+} (formed after the oxidation of nZVI Fe^0 core) to enter the cell [21,10,7]. Once internalised, Fe^{2+} could react with the H_2O_2 produced in the mitochondria and, via the Fenton reaction, release reactive oxygen species (ROS), thus exposing microbial cells to severe oxidative stress (OS). Manifestations of OS are the dysfunction of membrane lipids, proteins, and DNA. This alone can eventually lead to cell death [18,39].

The small biological wastewater treatment plants (SBWTP) are widely used for the purification of wastewaters from households. They remove most of the contaminants from wastewaters, but they are not effective in the inactivation of pathogenic bacteria. In order to prevent surface and groundwater contamination, it is important to reduce the release of the remaining contaminants and pathogenic bacteria into the aquatic environments.

Based on the above findings, the objective of the present study was therefore a holistic approach for the investigation of parameters which influence the efficiency of removal of toxic elements, nitrogen species, and pathogenic bacteria from effluent water from SBWTPs. For this purpose, nZVI particles, which differ in terms of their reactivity and synthesis pathways, were applied. In order to optimise the conditions for the efficient removal of contaminants by a particular nZVI, the effluent water was treated with in-house nZVI, or with two commercial products: Nanofer STAR or Nanofer25 slurry, by applying different iron loads and different mixing and settling times during the remediation procedure.

2. Materials and methods

2.1. Reagents and materials

The ferric chloride ($FeCl_3$) (98%) and sodium borohydride ($NaBH_4$) (98%) used for the synthesis of the in-house nZVI were supplied by Sigma-Aldrich (Steinheim, Germany). Samples of two types of commercially available FeNPs (Nanofer25 slurry; a stable water based dispersion containing 20 wt% of bare FeNPs, and Nanofer STAR; air-stable powder of FeNPs stabilized by inorganic stabilizers) were supplied by NANO IRON, s.r.o. (Rajhrad, Czech Republic).

Merck (Darmstadt, Germany) suprapure acids and Milli-Q water (18.2 MΩ cm) obtained by means of a Direct-Q 5 Ultrapure water system (Millipore Watertown, MA, USA) were used for the preparation of the samples and the standard solutions. A Stock Multi Element XVI standard solution (100 mg L^{-1} in 5% HNO_3) (Merck, Darmstadt, Germany) was used for the preparation of working standard solutions for ICP-MS determinations.

All of the water samples for the determination of inorganic parameters were, prior to the analyses, filtered through membrane filters with a pore size of 0.45 μm (syringe filter, Minisart, Sartorius Stedim Biotech GmgH, Goettingen Germany).