Removal of selected pesticides by nano zero-valent iron

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Abstract: This paper is focused on the possibility of using iron nanoparticles (nZVI — nano zero-valent iron) to remove selected specific synthetic substances, such as hexachlorobutadiene, pentachlorobenzene, hexachlorobenzene, lindane and heptachlor. Experimental measurements were performed in order to evaluate the effectiveness of the removal of substances and their specific removal rate. Evaluation of the results shows that nanoiron NANOFER 25 is a convenient reactant for the removal of heptachlor, lindane and hexachlorobenzene; while for pentachlorbenzene and hexachlorobutadiene removal, longer contact times are necessary to achieve significant removal efficiencies.

Keywords: nanoiron particles, nZVI, organochlorinated substances, persistent substances, priority substances, zero-valent iron

Introduction

Quality drinking water is one of the requisites for a healthy human population. However, growing industrialization and extensive use of chemicals have increased the amount of unwanted pollutants in sources of drinking water in countries all over the world. Priority substances were discharged to the aquatic system (groundwater and surface water) as waste products from industrial production or from substances known as insecticides, herbicides and fungicides which have been applied in forestry and agriculture for a long time. The amount of potentially hazardous substances entering the ecosystem is increasing every day. All priority substances monitored in this study are also known as organochlorinated pesticides (OCP) which are potentially carcinogenic, persistent and toxic. They can be absorbed by plants, animals and also people. Humans and animals are exposed to them mostly through their diet, occupationally or prenatally. Over 90 % of exposure comes from animal products due to bioaccumulation in fat tissues and through the food chain (Ritter et al., 2007). Contamination of soils and groundwater by chlorinated pesticides has been a worldwide environmental challenge and cost effective remediation technologies have been sought for decades.

Nanotechnology seems to be the answer to the search for an efficient, economic and ecologically friendly method to solve or reduce this problem. The use of nanotechnology and nanomaterials is very extensive. This technology applies particles with the dimensions of roughly 1—100 nm and has already found applications in many areas of daily life, e.g. in electronics, engineering, health, chemical industry as well as optical, automotive, cosmetics and military industries. Particles of nZVI can be used in on site reactors (e.g. pump-and-treat systems) or in situ applications (direct push injections, recirculation by injection/extraction wells, pneumatic fracturing (Grieger et al., 2010). Due to their nano-sized dimensions, nZVI particles have significantly larger available reactive surface areas (e.g. up to four orders of magnitude (Macé et al., 2006) compared to larger iron particles, which subsequently enhances contaminant degradation reactions (Chang and Kang, 2009; Lin et al., 2008). The core of iron nanoparticles (core—shell structure) consists of zero-valent iron (ca. 85 %) while the shell consists mostly of iron oxides and oxyhydroxides. Thus, iron nanoparticles exhibit characteristics of both a sorbent and a reducing agent (Černík et al., 2010).

The use of nZVI is a very promising method for removing not only organochlorinated pesticides but also many other types of micropollutants. The aim of this research was to study the potential of nZVI particles to improve the removal process of selected specific synthetic substances from water.

Materials and methods

NANOFER 25 nanoparticles used in this work had the average grain size of 50 nm. The particle size is one of the main and most important factors in this technology. Suspension of NANOFER 25 nZVI particles produced by NANOIRON s.r.o., Czech Republic, contains 14—18 wt. % of Fe, 2—6 % of Fe_3O_4, 0—1 % of carbon and 80 % of water. Specific surface area of these nanoparticles is larger than 25 m^2/g (www.nanoiron.cz). Experiments were

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performed with model wastewater containing chlorinated pesticides, i.e. hexachlorobenzene (HCHB), hexachlorobutadiene (HCHBD), pentachlorobenzene (PCHB), (1r,2R,3S,4r,5R,6S)-1,2,3,4,5,6-hexachlorocyclohexane (common name lindane, γ-HCH; abbreviation LIN) and 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene (common name heptachlor, abbreviation HCH); first three of these compounds are specified as priority hazardous substances (EU, 2000; 2008) while all pesticides except for HCHBD are listed in the Stockholm Convention of Persistent Organic Pollutants (Stockholm Convention, 2001; 2009). Experiments were carried out in a mechanically stirred reactor under laboratory conditions. The measurements were performed in a 2000 ml reactor containing 200 ml of NANOFER 25 and 1000 ml of model wastewater. A mechanically stirred reactor was used to homogenize the reaction mixture of water and nanoscale zero-valent iron (nZVI) and to perform the experiments. Nanofer suspension used in the experiments was added into the reactor at the beginning of the process.

Analytical methods

Quantification of organochlorinated pesticides in wastewater was achieved by a gas chromatographic method after liquid-liquid extraction. As the organic solvent for HPLC, n-hexane 96 % p.a. (Analytika, s.r.o.) was used. The extract was analyzed by gas chromatography employing a micro-electron capture detector (Agilent Technologies 7890A GC Systems). All parent organochlorinated compounds used for the preparation of synthetic wastewater and standard stock solutions were purchased from Supelco Co (Member of Sigma-Aldrich Group, USA) in high quality.

Results and discussion

Determination of the concentration of individual pesticides was performed after 4, 6, 8, 9 and 24 hours. The chosen initial concentration of pollutants was 107 ng/l for HCHBD, 49670 ng/l for PCHB ng/l, 5573 ng/l for HCHB, 5980 ng/l for LIN and 15613 ng/l for HCH. Fig. 1 shows the removal efficiency of pesticides during their reaction with zero-valent iron nanoparticles (nZVI). The highest treatment efficiencies were observed for LIN, HCHB and HCH, within about 4 h. After this time, the highest removal efficiency was achieved for lindane. The obtained data show that after 24 hours of the experiment, iron had reduced more than 97 % of all three substances. Final removal efficiencies of 99 % and 97 %, respectively, were observed for LIN and HCHB. Obviously, HCH was completely degraded / removed from model wastewater.

Removal of the remaining two studied pesticides by nZVI is presented in Fig. 2. Lower removal efficiency (about 25 %) was observed for HCHBD after 4 h of the process. At the same time, removal efficiency of PCHB reached only about 17 %. The removal efficiency of HCHBD reached the highest value (73 %) after 8 h of the process, and the maximum removal efficiency of PCHB was obtained after 24 h (85 %).

Time dependencies of volumetric removal rates for individual pollutants and processes are shown in Fig. 3. The highest removal rates of all pollutants except for HCHBD were observed after 4 h of the treatment. For HCHBD, the same removal rate was

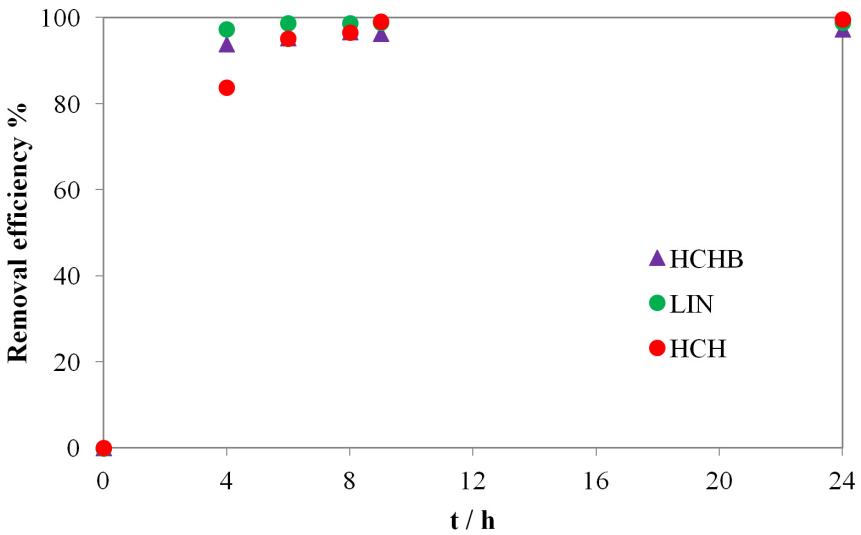

Fig. 1. Removal efficiency of organochlorinated compounds with nZVI.

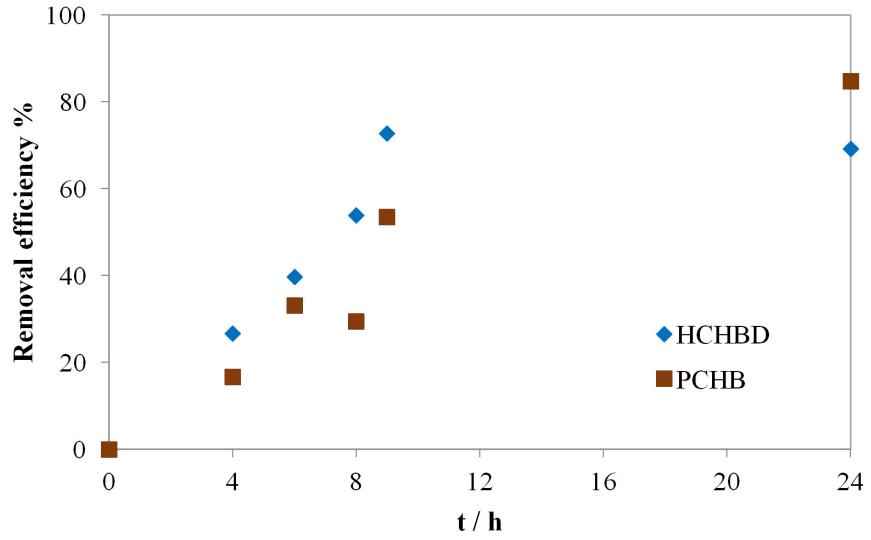

Fig. 2. Removal efficiency of organochlorinated compounds with nZVI.

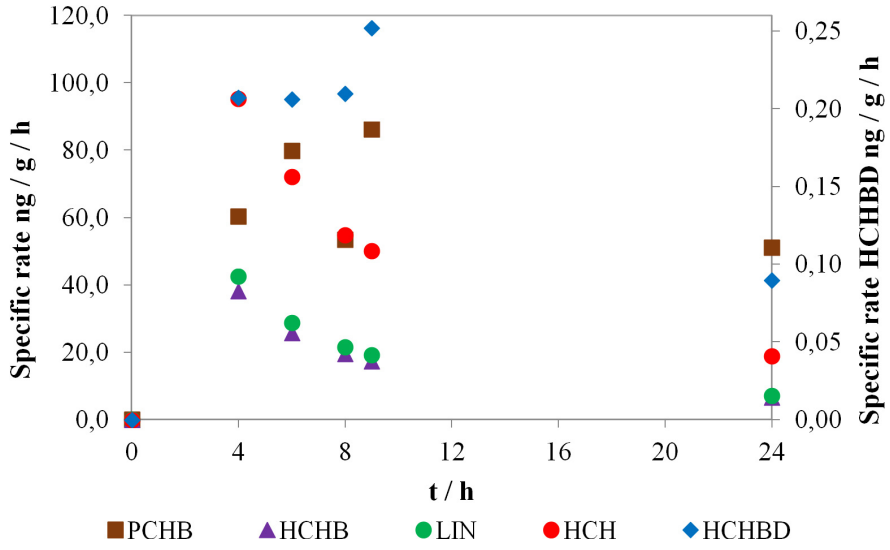

Fig. 3. Removal rates of organochlorine compounds with nZVI (HCHBD — right Y axis; other pollutants — left Y axis).

observed after 9 h of the process. As shown in Figs. 1—3, the highest specific removal rate corresponds to the maximum concentration decrease. Heptachlor HCH showed the highest affinity to nZVI of 95 $ng \cdot g^{-1} \cdot h^{-1}$. Also, higher affinity to nZVI was observed in case of PCHB (60 $ng \cdot g^{-1} \cdot h^{-1}$). HCHBD showed the lowest specific removal rate; lower by about three orders of magnitude compared to the pesticides studied.

Conclusion

The commercial suspension of Nanofer 25 nZVI particles was used in the removal of selected organochlorinated pesticides, showing very promising results in regard to removal efficiency of the majority of substances. The highest removal efficiencies were observed for HCH, LIN and HCHB, already within about 4 h (higher than 97 %). Maximum removal efficiency of 99.6 % was measured after 24 h for HCH. The second highest efficiency of 98.9 % was measured for LIN, followed by HCHB with a 97.3 % removal efficiency, PCHB with a 84.8 % removal efficiency and HCHBD with a 72.7 %. Lower affinity of the pesticides to nZVI is evident in case of HCHBD and PCHB even after 24 h of the treatment. The highest removal rate observed for PCHB suggests the possibility of process optimization and enhanced removal of this pollutant from model wastewater. This study has shown that the use of nZVI for the removal of synthetic organic substances is a promising option

due to its easy application, high reactivity and efficiency.

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