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Effect of coating on the environmental applications of zero valent iron nanoparticles: the lindane case

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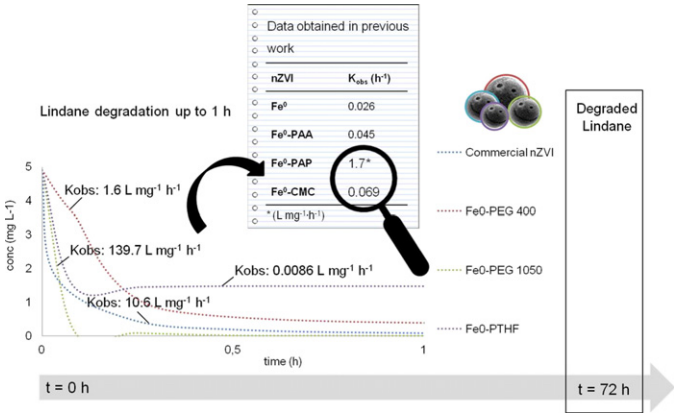
HIGHLIGHTS

- Iron nanoparticles modified with different polymers have been synthesized and evaluated.
- Polyelectrolyte coated zero-valent iron has been used to degrade lindane.
- Different polymeric coatings could be used according to desired degradation kinetics.
- Lindane by-products obtained by the treatment with modified zero-valent iron.

GRAPHICAL ABSTRACT



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ABSTRACT

Commercial stabilized slurry of zero-valent iron nanoparticles (nZVI) as well as laboratory-synthesized polymer–stabilized NZVI nanoparticles were used for lindane (γ-hexachlorocyclohexane) degradation studies in aqueous solution. In the present study, polymer-stabilized iron nanoparticles were stabilized using polyethylene glycol (PEG, Mn ~400 and ~950–1050) and polytetrahydrofuran (PTHF, Mn ~650). To study the effectiveness of the different nanoparticles, a quantitative monitorization of lindane degradation by using solid-phase extraction (SPE) and a qualitative measurement of generated volatile by-products by headspace-solid phase microextraction (HS–SPME) followed by GC/MS were carried out. The obtained data were compared and contrasted with the results obtained in previous work.

Results showed that the nanoparticles studied in this work possess superior dechlorination performance compared with previous observations. The freshly prepared Fe^0-PEG400, Fe^0-PEG1050 and Fe^0-PTHF exhibited high reactivity during the dechlorination process of lindane in a very short time. The results obtained with the synthesized nanoparticles were similar to those obtained with commercial nanoparticles. However, in all cases reactivity decreased at reaction's late stage. Degradation of lindane by the studied nanoparticles removed 99.9% of the lindane initial concentration after 72 h, except for Fe^0-PTHF nanoparticles, for which the reaction stopped after 5 min. In all cases, the reaction followed a second order kinetics. Finally, comparing the results from this study with our *previous work*, where different nature polymers were considered (Fe^0-CMC, Fe^0-PAA and Fe^0-PAP), more gradual degradation profile of lindane was observed for Fe^0-PAA and Fe^0-CMC. It should

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be noted that in the present case, the reaction of lindane was speeded up with commercial and Fe^0-PEG nanoparticles. Nevertheless, in the later case, the composition of by-products was affected by the presence of partially degraded intermediates. Taking into account the current technologies, the high removal rates obtained and the acceptable degradation times required, the proposed technology is suitable for its aimed purpose.

1. Introduction

One class of organic pollutants which has gained great attention in environmental studies is the organochlorine pesticides (OCPs) (Ahmed et al., 2015). Among them, lindane, the γ-isomer of hexachlorocyclohexane, is recognized internationally as toxic, bio-accumulative and persistent, representing a serious risk since its residues are still in the environment (Ghosh et al., 2009; Bijoy and Nimila, 2012). Contamination of soils and groundwater by chlorinated pesticides has been a worldwide environmental challenge, and cost effective remediation technologies have been a topic of importance for decades (Joo and Zhao, 2008; Saez et al., 2015).

Among the different innovative methods for remediation, treatments with nanoparticles such as zero-valent iron nanoparticles (nZVI), have received considerable attention in their use as a cost-effective and environmentally friendly agent for environmental remediation in the last years (Joo and Zhao, 2008; Singh et al., 2011; Khan et al., 2016). The primary attraction of using this kind of nanoparticles for remediation arises from its basic chemistry, specifically its ability to degrade contaminants to less harmful products through reduction. Many efforts have been devoted to the synthesis and application of nZVI, especially exploring new approaches in order to reduce their aggregation during the procedure of delivery and treatment (Xiao et al., 2009). Generally, due to the size effects, surface effects and high surface free energy, nanoparticles in the aqueous media tend to aggregate. In order to avoid it, coating nZVI with surface modifiers is one of the most promising strategies. Moreover, the surface modifications can also help to enhance mobility and provide increased efficiency in targeted adsorption for soil and groundwater remediation, (Zhou et al., 2016; CC Yang et al., 2007). The protection of the nanoparticles reactive centres through the surface modification, avoids the oxidation and prevents deposition (Li et al., 2006; Phenrat et al., 2009). Various nanoparticles stabilizing strategies have been reported (Schrick et al., 2004). Among them, the addition of polyelectrolytes is an established procedure that provides a significant decrease in the rate and degree of aggregation (Bolto and Gregory, 2007; Phenrat et al., 2008; Mackenzie, 2010). Polymeric or polyanionic coatings provide a negatively charged or uncharged surface in order to eliminate electrostatic attraction (Phenrat et al., 2007; Dalla Vecchia et al., 2009, Johnson et al., 2013; Laumann et al., 2014. The degree of stabilization depends on the adsorbed mass of polyelectrolyte and topography of the cover layer which are determined by properties of the polymers (e.g. molecular mass, composition, architecture) and type of charged groups, by the solution properties (e.g. pH, ionic strength, and the types of ions present) and finally by the particle characteristics (particularly, their surface charge density). Therefore, the resulting layer properties control the suspension generating new additional forces that may influence the interactions between particles (Szilagyi et al., 2014).

In a previous study, nZVI as well as polymer-stabilized nanoparticles were synthesized and used for lindane degradation in aqueous solution (San Román et al., 2013). The polymers considered were carboxymethyl cellulose (CMC), polyaspartate (PAP) and polyacrylic acid (PAA). In that work, sensitive and rapid methods were developed for lindane and its by-products detection and measurement based on solid-phase microextraction (SPE) and headspace-solid-phase microextraction (HS–SPME), respectively, which provided very valuable information for future applications of this type of decontamination tool for real environmental matrices. In addition, impacts of some nanoparticles stabilizers on the degradation process of lindane were evaluated and compared. For instance, the analysis of generated volatile by-products provided some understanding of the mechanism of the reaction under study. In this context, one of the conclusions that can be drawn from the previous work is that the key reaction during degradation of lindane is the removal of the halogen atoms via dichloroelimination and dehydrohalogenation processes. Removal of halogen atom(s), which is (are) usually responsible for the toxic character of the compound, reduces the risk of forming toxic intermediates during the degradation process (Camacho-Pérez et al., 2012).

Remediation using nanoparticles involves particular concerns that must be addressed with regard to the effectiveness and application of this new technology. These issues include remediation rate, kinetics and contaminant degradation by-products from remediation using nanoparticles, and whether nanoparticles maintain their reactivity during the time period of treatment (Singh et al., 2012). Taking this into consideration, in the present study, iron nanoparticles modified by polyethylene glycol (PEG, Mn ~400 and ~950–1050) and polytetrahydrofuran (PTHF, Mn ~650) were synthesized and evaluated to degrade lindane. In addition to these polymers, the effect of the use of commercial stabilized slurry of nZVI was also examined. The objectives of this study were to investigate the effect of the above listed nanoparticles on lindane degradation; as well as to analyze lindane degradation rate and lastly evaluate the effect of polymeric coating on lindane degradation, comparing the obtained results with those previously achieved.

2. Experimental

2.1. Chemical reagents, standards and materials

Methanol (HPLC gradient grade, 99.8%) was purchased from Prolabo (Leuven, Belgium), while ethanol (99.5%) and ethyl acetate (for GC calibration, 99.5%) were obtained from Panreac (Barcelona, Spain). Ultrapure reagent grade water purified by a Milli-Q gradient system (Millipore, Bedford, MA, USA) was used throughout this work. Lindane (97%) was purchased from Aldrich (St. Louis, MO, USA).

Standard stock solution of lindane in methanol at a concentration of 100 mg L^{-1} and stored at 4 °C was employed. Working solutions were prepared by appropriate dilution in ethyl acetate and stored at 4 °C. Water samples spiked with lindane were prepared in ethanol at a concentration of 5 mg L^{-1}. Sodium borohydride (98%) and iron chloride tetrahydrated (99%) purchased from Aldrich were used for the iron nanoparticle synthesis. For the iron nanoparticles stabilization polyethylene glycol (PEG, Mn ~400), polyethylene glycol (PEG, Mn ~950–1050) and polytetrahydrofuran (PTHF, Mn ~650, 0.05–0.07% BHT as stabilizer) obtained from Aldrich were utilized. In addition, commercial stabilized slurry of zero-valent iron nanoparticles (NANOFER 25S nZVI slurry, NANO IRON s.r.o., Rajhrad, Czech Republic) purchased from NANO IRON, s.r.o. was used.

SPME fibres coated with 50/30 μm of divinylbenzene–carboxen–polydimethylsiloxane (DVB–CAR–PDMS), obtained from Supelco (Bellafonte, PA, USA) were employed. Fibres were thermally conditioned in accordance with manufacturer's recommendations.

A SPME holder from Supelco was used to perform HS–SPME manually. A 12-port Visiprep SPE vacuum manifold purchased from Supelco, Millipore vacum pump (Milford, MA, USA) and Oasis HLB cartridges (10 mg, 1 mL) purchased from Waters (Milford, Massachusetts, USA), were employed in the SPE extraction procedure.

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