Removal of selected pesticides by ozone based processes

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Abstract Discharging various micropollutants into aquatic environment in general and in particular substances classified as priority, hazardous and persistent generate serious concerns due to their potential adverse effects on human health and the living organisms in the environment. Mostly these are synthetic and non-synthetic substances and their effective removal requires non-traditional processes, novel approach and technologies. Ozone based processes and nZVI (nano zero-valent iron) are considered the prospective ones. Five chlorinated pesticides, i.e. hexachlorobenzene (HCHB), hexachlorobutadiene (HCHBD), lindane (LIN), pentachlorobenzene (PCHB) and heptachlor (HCH) were selected as model pollutants. Higher volatility is characteristic for these substances. Research was focused on evaluation of efficiency and removal rates of selected organochlorine substances from model water by integrated ozonation and nZVI (O_3/nZVI) process. Effect of ozonation and nZVI treatments on the same components were also carried out and used as reference for comparison.

Keywords: nanoiron particles, nZVI, organochlorinated compounds, ozonation, zero - valent iron

1. Introduction

Micropollutants usually cause unfavorable effects in the aquatic environment where they may generate adverse effects on aquatic organisms and human health. 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). Mostly these are synthetic and non-synthetic substances and their effective removal requires non-traditional processes, novel approach and technologies.

Ozone (O_3) is a selective oxidant that is reactive towards double bonds, aromatic systems, non-protonated secondary, tertiary amines, and reduced sulfur species (Hollender *et al*., 2009). The main areas where ozone is used are disinfection, oxidation of inorganic compounds, oxidation of organic compounds including taste, color, odor and particle removal. Ozone is used to partly oxidize persistent substances with the goal of increasing their biodegrability in the subsequent biological treatment stage in waste water technology (Gottschalk *et al*., 2009). Ozone can react in two ways - direct reaction as molecular ozone or indirect reaction through the formation of secondary oxidants like free radical species, which increase the oxidation potential.

The use of nZVI to degrade a range of contaminants and micropollutants including chlorinated solvents has gained increasing amounts of attention in recent years, due to primarily of its larger range of application options and high degrees of reactivity (Li *et al*., 2006). NZVI has the ability to dehalogenate chlorinated compounds by reductive reaction mechanism. Due to the high specific surface area, nano - sized ZVI - particles are more reactive than granular materials. The interaction between nZVI and pollutants is nonspecific. In addition to the pollutant of interest, the electrons from iron oxidation are also consumed from the reduction of water (H_2O) or protons (H^+) to hydrogen (H_2) (Grieger *et al*, 2010). To increase the reactivity of ZVI particles, aggregation, precipitation, sedimentation and oxidation must be reduced. Therefore coatings are applied to increase the surface load in order to achieve electrostatic or electrosteric stabilization of the colloidal mixture.

2. Materials and methods

NANOFER 25 nanoparticles suspension 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 $m^2.g^{-1}$ (www.nanoiron.cz). Experiments were 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-hepta-chloro-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 reactor under laboratory conditions. The measurements were performed in 2000 ml reactor containing 5 ml of NANOFER 25 (equal to 1g Fe^0) and 1000 ml of model wastewater. Inert gas N_2 was used to homogenize the reaction mixture of water and nanoscale zero-valent iron (nZVI) in process without using ozone. NANOFER suspension used in the experiments was added into the reactor at the beginning of the process. Combined O_3/nZVI processes in model water was also investigated. A Life Tech ozone generator with the maximum ozone production of 5 $g.h^{-1}$ was used. Ozone was prepared from pure oxygen with the flowrate 60 $l.h^{-1}$.

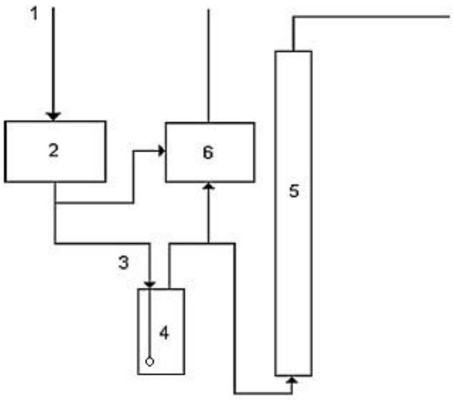

Fig. 1. Schematic diagram of the experimental apparatus, 1 – oxygen inlet, 2 – ozone generator, 3 – mixture of O_2 and O_3, 4 – ozonation reactor with frit, 5 – destruction of residual ozone, 6 – ozone content detector.

3. Analytical methods

Quantification of organochlorinated pesticides in wastewater was achieved by a gas chromatographic method after liquid-liquid extraction. n-Hexane, 96%, p.a., for HPLC (Analytika, s.r.o.) was used as an organic solvent. 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.

4. Results and discussion

The paper presents the result of a study aimed at the use nZVI suspension and combined O_3/nZVI processes. Removal of pesticides was also monitored through calculated DOC (dissolved organic carbon) as cumulative wastewater quality indicator. Determination of the concentration of individual pesticides in nZVI process was performed after 5, 15 and 30 min. Initial concentrations of pollutants were in the range of 107 $ng.l^{-1}$ for HCHBD up to 1592 $ng.l^{-1}$ for LIN. Fig. 2 shows the removal efficiency of pesticides during their reaction with zero-valent iron nanoparticles (nZVI). The highest treatment efficiencies 96% of all pollutants except LIN were observed during first 5 min. of the process. LIN reached this efficiency in 15. min of process. Degradation efficiency of DOC reached 90% already after 5 min. of process (Fig. 3).

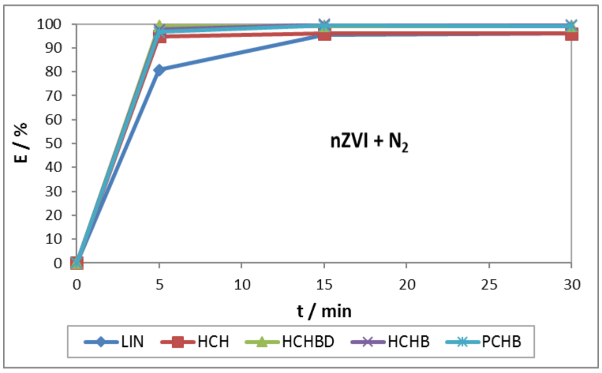

Fig. 2. Removal efficiency of organochlorinated compounds with nZVI

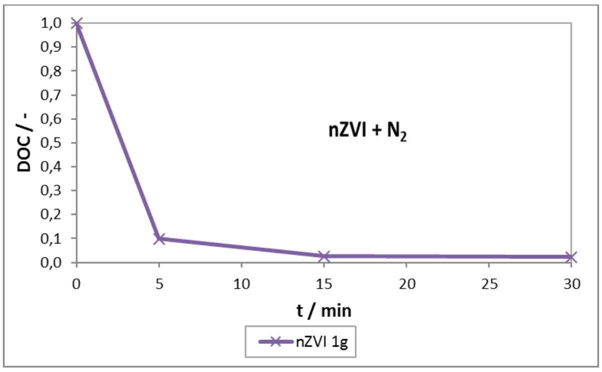

Fig. 3. Removal efficiency of DOC with nZVI

Removal efficiency of organochlorinated compounds using O_3 process is shown in Fig. 4. Longer reaction time as in the case of nZVI was necessary. The removal efficiency of HCHB and PCHB reached the highest value (97%) after 10 min. of the O_3 process. Lower removal efficiency (about 32 %) was observed for LIN after 20 min. of the process. Efficiency of DOC degradation doesn´t achieved such values as in case of nZVI process (Fig. 5).

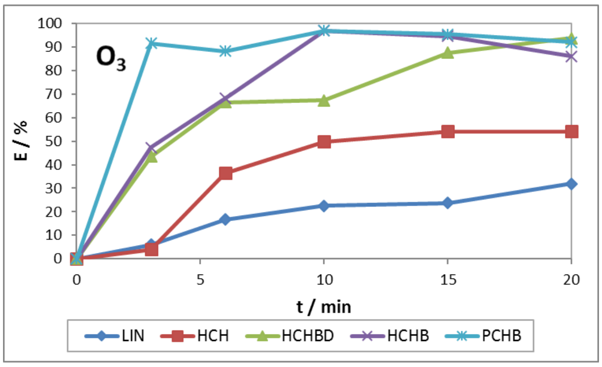

Fig. 4. Removal efficiency of organochlorinated compounds with O_3

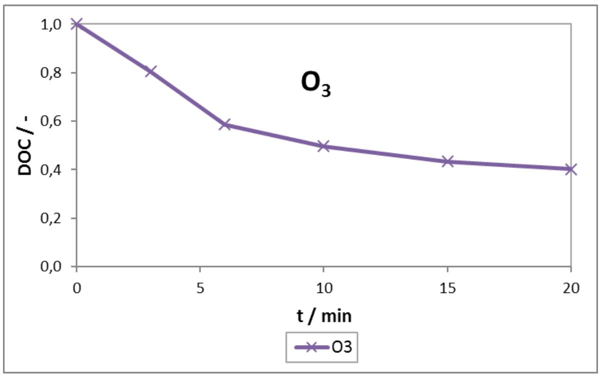

Fig. 5. Removal efficiency of DOC with O_3

In Fig. 6 is presented the removal efficiency of combined O_3/nZVI process. The highest removal rates for all pollutants were observed after 4 min. of the treatment. Already within about 4 min reached the degradation efficiency of HCH, HCHBD and HCHB the highest values. On the other hand, lower efficiency of this process is evident to LIN (41%). Time dependences of DOC values measured during process are shown in Fig. 7.

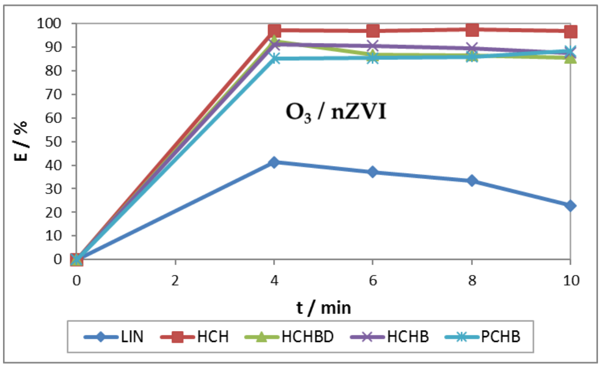

Fig. 6. Removal efficiency of organochlorinated compounds in O_3/nZVI process

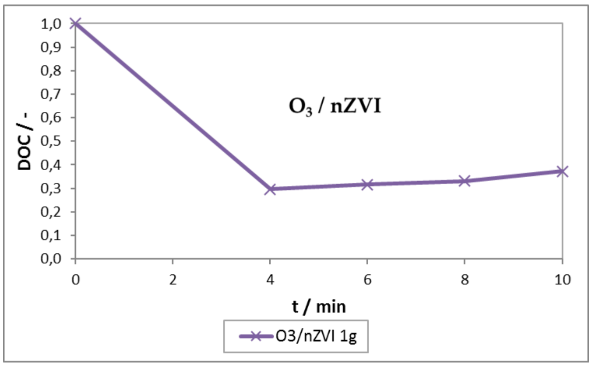

Fig. 7. Removal efficiency of DOC in O_3/nZVI process

5. Conclusions

The result shows that the effectiveness of 5 $ml.l^{-1}$ nano zero – valent iron suspension NANOFER 25 is capable of reducing chlorinated compounds. High removal efficiency observed for these pesticides (97% degradation in 5 min.) suggests the possibility of process optimization and enhanced removal of this pollutants from model wastewater. The same efficiency of LIN degradation by nZVI was reached in 15 min. In O_3 process was the efficiency of degradation lower, only 32% for LIN and 54% for HCH after 20 min. of process. By combined process O_3/nZVI was reached higher removal efficiency of organochlorinated compounds in comparison to single O_3 process. LIN was better degraded by nZVI process in the absence of ozone. This study has shown very promising potential of nZVI for the removal of synthetic organic substances is a promising option due to its easy application, high reactivity and efficiency.

References

EU, 2000. Directive 2000/60/EC of the European Parliament and of The Council of 23 October 2000 establishing a framework for community action in the field of water policy, Off. J. Eur. Communities, L 327/1.

EU, 2008. Directive 2008/105/EC of the European Parliament and of The Council of 16 December 2008 about environmental quality standards in the field of water policy, Off. J. Eur. Communities, L 348/84

Gottschalk C., Libra J. A., Saupe A. (2009), Ozonation of water and waste water: A practical guide to understanding ozone and its applications. WILEY-VCH Verlag GmbH &Co. KgaA, Weinheim, 2nd edition, 15-24; 21-22.

Grieger, K.D., Fjordboge, A., Hartmann, N.B., Eriksson, E., Bjerg, P.L., Baun, A. (2010), Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: risk mitigation or trade-off? J. Contam. Hydrology, **118** (3–4) (2010), pp. 165–183.

Hollender, J., Zimmermann, S.G., Koepke, S., Krauss, M., Mcardell, C.S., Ort, C., Singer, H., von Gunten, U., Siegrist, H., (2009), Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full scale post-ozonation followed by sand filtration. Environ. Sci. Technol **43**, 7862–9.

Li, X., Elliott, D.W., Zhang, W., (2006). Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. Crit. Rev. Solid State Mater. Sci. **31**, 11–22.

Nanoiron, Nanofer 25 slurry, Safety data sheet http://nanoiron.cz/en/nanofer-25, Retrieved: 15-03-2017

Ritter L., Solomon K.R., Forget J., Stemeroff M., O'Leary C., (1995). A review of selected persistent organic pollutants. The International Programme on Chemical Safety within the framework of the Inter-Organization Programme for the Sound Management of Chemicals http://www.who.int/ipcs/assessment/en/pcs_95_39_2004_05_13.pdf . Retrieved:15-03-2017.