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Removal of micropollutants by ozone based processes

Ján Derco [a,*], Jozef Dudáš [a], Mária Valičková [a], Katarína Šimovičová [b], Juraj Kecskés [a]

[a] Institut of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

[b] Water Research Institute, Nábrežie L. Svobodu 5, 812 49 Bratislava, Slovak Republic

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ABSTRACT

Discharging various micropollutants into aquatic environment, in particular substances classified as priority and hazardous ones, leads to serious concerns due to their potential adverse effects on human health and living organisms. Their effective removal requires novel processes. Ozone based processes are considered to be very promising. Results on ozonation, adsorptive ozonation and combined process of ozone with zero-valent iron nanoparticles are presented. Five selected organochlorine pesticides were used as organic contaminants in model water. High removal efficiencies of ozonation, except for lindane and hexachlorobutadiene, were observed. Even higher removal rates and efficiencies were measured using the O_3/UV process. However, the low removal efficiencies obtained for lindane and hexachlorbutadiene have not been explained. Adsorptive O_3/GAC and O_3/ZEO ozonation processes also provided high removal rates and efficiencies, but again, except for lindane. Significant reduction of the reaction time resulted from these processes. Very low removal efficiencies measured for hexachlorobenzene and hexachlorbutadiene with nZVI, were solved using the O_3/nZVI process. Moreover, the O_3/nZVI process is characterized by a significant reduction of the reaction time when compared with the ozonation processes. The results suggest that nZVI and O_3/nZVI processes have the highest potential to intensify the degradation and removal of organochlorine pollutants.

1. Introduction

Pollution of surface water and groundwater with pesticides represents a serious problem. Many pollutants are persistent in aquatic environment and have potential adverse health effects. Wastewater treatment plants are designed primarily to eliminate macronutrients. However, attention has been increasingly drawn to micropollutants since even low concentrations of these substances can have adverse effects on aquatic ecosystems and consequently on human health. The inability of biological wastewater treatment to effectively remove hazardous, toxic and biologically resistant pollutants shows that new treatment processes have to be developed [1,2].

Among various water and wastewater treatment processes, ozonation and ozone-based advanced oxidation processes are likely to become the key technologies for pesticides degradation and water and wastewater detoxification [3]. The use of nanotechnologies is also currently in the center of attention in many scientific fields as well as in practice, including environmental protection. Nanotechnology applies particles at dimensions of roughly 1–100 nm, with unique physical properties, e.g., high surface to volume ratio/specific surface area of about 25–40 $m^2 g^{-1}$, which enable novel applications. The core of iron nanoparticles (core–shell structure) consists of zero-valent iron while the shell consists mostly of iron oxides and oxyhydroxides. Thus, iron nanoparticles exhibit characteristics of both iron oxides (e.g., as a sorbent) and metallic iron (e.g., as a reductant) [4].

The main aim of this research was to study the potential of integrated O_3/nZVI processes to improve the removal of selected specific synthetic substances from water. Commercial suspension of Nanofer nZVI particles (NANOIRON, s.r.o., Czech Republic) was used. Five organochlorine pesticides, i.e., hexachlorobutadiene (HCHBD), pentachlorobenzene (PCHB), hexachlorobenzene (HCHB), (1*r*,2*R*,3*S*,4*r*,5*R*,6*S*)-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-1*H*-indene (common name heptachlor, abbreviation HCH) in water solution were investigated.

The first three of these compounds are classified as priority hazardous substances [5,6], and the last four are on the extended

* Corresponding author. Tel.: +42 1904171137; fax: +42 10259325792.
E-mail address: jan.derco@stuba.sk (J. Derco).

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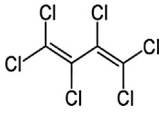
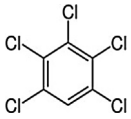
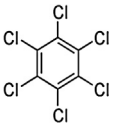
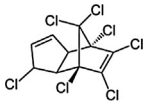
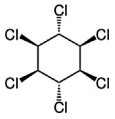
Table 1
Chemical formulas and CAS Registry numbers of the used pesticides.

Pollutant	HCHBD	PCHB	HCHB	HCH	LIN
Chemical structure					
CAS Registry no.	87-68-3	608-93-5	118-74-1	76-44-8	58-89-9

list of the Stockholm Convention on Organic Persistent Pollutants [7,8]. Chemical formulas and CAS Registry numbers of the used pesticides are given in Table 1.

As a result of bioacummulation, POPs can be found in people and animals living in regions such as the Arctic, thousands of kilometers away from any major POPs source. Specific effects of POPs can include cancer, allergies and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system.

Some POPs are also considered endocrine disruptors, which, by altering the hormonal system, can damage the reproductive and immune systems of exposed individuals as well as their offspring; they can also have developmental and carcinogenic effects. Brief specification of the studied substances can be found for example in [9].

Our research was focused on the evaluation of removal efficiency and removal rates for selected organochlorine substances from model water by integrated ozonation and nZVI (O_3/nZVI) processes. The effect of ozonation and nZVI treatment on the studied compounds was also investigated and used as reference for comparison.

2. Theoretical

Ozone reacts with organic compounds in two ways: by direct reaction as molecular ozone or by indirect reaction through the formation of secondary oxidants like free radical species [10,11]. In general, both mechanisms may occur depending on the chemical wastewater pollution. The rate of •OH formation depends on the water matrix, especially its pH, alkalinity, type and content of natural organics [12]. At low pH, the predominant reaction mechanism is the direct electrophilic attack by molecular ozone [13]. On the other hand, ozone decomposes in water to form •OH radicals which are stronger oxidizing agents than molecular ozone, thus inducing the so-called indirect ozonation. Indirect ozone oxidation is non-selective, faster and is favored under alkaline conditions [14]. Both reaction mechanisms lead either to mineralization or to transformation of organics by formation of products with higher oxygen content.

It is common knowledge that the work with ozone is also associated with potential risks. However it is a substance, identifiable already in very low concentrations. Practical applications in water treatment, wastewater treatment and in other industry, e.g., pulp and paper industry suggests that these risks are controllable, both in terms of health and protection of materials and equipment.

The major limitations of the ozonation process are the relatively high costs of ozone production combined with its very short half-life. Due to its short half-life, ozone must be generated always at the site. Other cost related problems of ozone utilization are the maximum concentrations of ozone in air or oxygen of approximately 4 to 8%, respectively, very low (5–10%) energy efficiency of the ozone production and the requirement of absolutely dry air or oxygen. Ozone utilization in waste water treatment is strongly related with gas liquid mass transfer in the reactor because of the low solubility of ozone in aqueous solutions [15,16], which has to be reflected in the reactor design. Thus, a novel process providing higher removal reaction rates and enhancing the efficiency of ozone utilization as well as the economy of ozone production should be developed.

Several processes of ozone utilization are used in combination with other techniques, e.g., with H_2O_2, UV, ultrasonic, etc., [16,17]. The improvement of organic pollutants removal efficiency was also observed when ozone was combined with adsorption processes, i.e., in adsorptive/catalytic ozonation [18–21].

Iron-based nanoparticles are referenced to be remarkably effective in the treatment of contaminated soil and groundwater. Conventional iron powder is used in water treatment. Because of their small size, iron nanoparticles are much more reactive and their slurry can be pumped directly to the contaminated site. The nanoscale zero-valent iron (nZVI) particles show significant potential for the removal of toxic and hazardous chemicals as a strong reductant with excellent contact with contaminants due to the large specific surface area. The use of nZVI particles for groundwater remediation is currently one of the most widely investigated environmental nanotechnological applications [22].

nZVI particles have a core–shell structure [23,24]; their core consists of ZVI (ca. 85%) and the outer layer consists of ferrioxihydroxide (FeOOH) and iron oxides [25], mainly Fe_3O_4 (NANOIRON, s.r.o., Czech Republic). Iron reacts with water and quickly forms an FeOOH layer on the particle surface. For instance, the results published by Wang et al. [26] revealed that nZVI is converted to Fe_2O_3 and Fe_3O_4 in bromate reduction.

Both iron oxides of the original iron nanoparticles and those formed on the surface as the result of the dehalogenation process are products of zero-valent iron oxidation and they decrease its dehalogenation potential. Iron oxides can adsorb pollutants and potentially also catalyze ozone decomposition (adsorptive/catalytic ozonation). Ling et al. [27] and Qiang et al. [28] applied Fe(III) loaded activated carbon as the catalyst to improve the degradation of typical organophosphorus pesticide ometoate by ozone. Wang et al. [29] applied Fe_2O_3 as the catalyst of ozone oxidation of monochlorobenzene. Wang et al. [30] achieved higher conversion of chlorobenzene and improved the stability of the Fe_2O_3 catalyst compared with the MnO_2 catalyst during ozonation. Results published by Zhang and Ma [31] showed that catalytic ozonation with FeOOH can substantially enhance nitrobenzene (NB) degradation compared with ozonation alone due to the active sites on the FeOOH surface.

Thomas et al. [32] developed an integrated reductive/oxidative process for the treatment of water contaminated with nitroaromatic compounds (NACs). The process combines zero-valent iron and ozonation; the results showed that iron reduces 2,4-DNT