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Remediation of hexachlorocyclohexanes by cobalt-mediated activation of peroxymonosulfate

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ABSTRACT

Hexachlorocyclohexane isomers (HCHs) are one of the most ubiquitous and most easily detected organochlorine pesticides in environmental samples. This global distribution is enabled by HCH persistence. Moreover, HCH tends to bioaccumulate in human and animal adipose tissue. Since certain HCHs cause central nervous system, reproductive, and other endocrine damages, there is a necessity of a suitable remediation method to remove HCH from contaminated groundwater and soil. This study was conducted to evaluate the potential of peroxymonosulfate (Oxone) induced by cobalt salt ($Co(NO_3)_2$; Co(II)) to degrade HCHs. Cobalt(II) nitrate has been chosen instead of cobalt(II) chloride (which presents better activation properties for Oxone) in order to avoid an excess of chloride interference and more additional chlorination by-products. The optimal conditions (oxidant dose as well as cobalt dose) were determined for spiked water with HCH (0.85 μM of summed HCH isomers). Optimal oxidant dose was established by running a test with three different Oxone concentrations (molar ratio of Oxone:$Co(NO_3)_2$—1:0.1): 0.06, 0.6, and 6 mM. Degradation curves of summed HCH isomers were fitted into the pseudo-first-order kinetic model, and reaction rates are shown to be 0.03, 0.31, and 0.55 min^{-1} for doses 0.06, 0.6, and 6 mM, respectively. Further experiments were carried out to determine the optimal Oxone:$Co(NO_3)_2$ molar ratio. Effectiveness of HCHs decontamination by Oxone:$Co(NO_3)_2$ in various molar ratios was in the order 1:0.1 > 1:1 > 1:0.01 > 1:0.001. It was observed that surplus of $Co(NO_3)_2$ can slow down the degradation rate constants. A reaction between sulfate radicals and $Co(NO_3)_2$ could be responsible for this phenomenon, which can lead to the formation of sulfate ions without HCHs oxidation. In addition, tests with higher HCH dose (close to the solubility limit) were carried out to determine by-products of decontamination. In these tests 2,4,6-trichlorophenol (2,4,6-TCP) was found to be the major intermediate of HCH isomers degradation. Trace levels of the trichlorobenzene (TCB), tetrachlorophenol (TeCP), and pentachlorophenol (PCP) were detected as well. The study revealed that Oxone induced by Co(II) shows a high degradation rate with HCH isomers, which can make it an attractive method for HCHs decontamination in the future.

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1. Introduction

Hexachlorocyclohexanes (HCHs) represent one of the dominant and extensively researched kinds of chlorinated pesticides that have recently been included in the list of persistent organic pollutants (POPs) [1]. Hence, it is crucial to establish cost-effective remedial technologies to treat water, soil and waste contaminated by HCH isomers.

Degradation of HCH can be achieved by various remedial techniques using both biological and chemical methods. Phillips et al. provided an overview of early studies of lindane-contaminated soil treatment in which they suggest that degradation of HCH isomers is faster under anoxic conditions and that microbial degradation is the primary route of HCH removal from soil. In addition, biodegradation of HCH isomers in an aerobic/anaerobic environment is enabled by the fungal metabolism of *Sphingomonas paucimobilis* [2]. Boyle et al. reported the dehalogenation of lindane under sulfate-reducing conditions by anaerobic bacteria from marine sediments, *Desulfovibrio africanus* and *Desulfococcus multivorans*, yielding benzene and monochlorobenzene [3]. Elliott et al. studied the degradation of lindane by zero-valent iron nanoparticles (nZVI). They identified *γ*-3,4,5,6-tetrachlorocyclohexene as a key reaction intermediate of lindane dechlorination. Trace levels of additional products including benzene and biphenyl were detected but only in experiments with high lindane concentrations conducted in 50% ethanol. Following nZVI treatment, up to 80% of the chlorine from the lindane molecules ended as chloride in water in comparison with only 38% of the expected chloride concentration was observed from the microscale iron experiment [4]. Singh et al. performed the degradation of lindane-spiked soil using stabilized Pd/Fe^0 bimetallic nanoparticles. Pentachlorocyclohexene, tri- and dichlorobenzene were identified as intermediate products while benzene was formed as the most stable end product. In addition, carboxymethyl cellulose (CMC) stabilized bimetallic Pd/Fe^0 nanoparticles displayed up to 7-fold greater efficiency for lindane degradation in comparison with plain nZVI [5]. Zinovyev et al. conducted dehalogenation of lindane in a multiphase catalytic reduction system with Pd/C, Pt/C, and Raney-Ni, in which at the temperature of 50˚C and atmospheric pressure full conversion of lindane to 1,2,4-tricholorobenzene (1,2,4-TCB) was achieved in 5–10 min via base assisted dehydrochlorination, followed by metal-catalyzed hydrodechlorination with hydrogen to benzene [6].

Although reductive dehalogenation of HCHs was reported many times, there have been relatively few investigations on the use of chemical oxidation to degrade HCHs in the literature.

One of the oxidizing reagents which could be beneficially applicable for this purpose is peroxymonosulfate (Oxone) (Fig. 1).

Oxone is a source of a powerful oxidant peroxymonosulfate (HSO_5^-) which can be further induced to form sulfate radicals (Eq. (1)).

It is this formation of sulfate radicals that makes Oxone applicable in many industries and can be introduced for removing contaminants and environmental remediation. Sulfate radical-advanced oxidation process (SR-AOPs) can be used for simultaneous removal of refractory organic contaminants [7,8] and has a high efficiency removal of halogenated pollutants [9]. Compared to $OH^{\bullet}$, $SO_4^{-\bullet}$ has higher reduction potential at neutral pH and is more selective for direct electron transfer [10]. Anipsitakis and Dionysiou reported that Co-catalyzed activation (Co(II)) of Oxone served as a highly efficient route for achieving complete oxidation of organic pollutants. Anipsitakis et al. [8] reported that HSO_5^- has a high oxidation potential and the production of $SO_4^{-\bullet}$ and the mineralization of organic compounds can be expressed as follows (Eqs. (1) and (2)):

$$CoOH^+ + HSO_5^- \rightarrow CoO^+ + SO_4^{-\bullet} + H_2O \quad (1)$$

$$SO_4^{-\bullet} + \text{organics} \rightarrow \langle \text{manysteps} \rangle \rightarrow CO_2 + H_2O \quad (2)$$

The main aim of this article was to describe the effects of cobalt-mediated activation of peroxymonosulfate

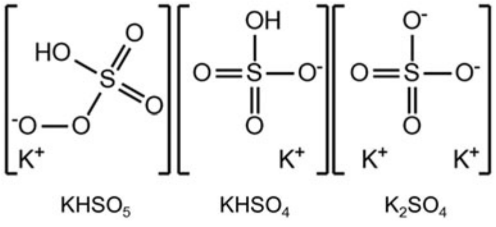

Fig. 1. Model of Oxone compounds.

(an active Oxone compound) on HCH isomers degradation. According to our knowledge, there is no report describing the degradation of HCH isomers using Oxone.

2. Materials and methods

2.1. Reagents and solutions

All of the chemicals used in the experiments were of analytical reagent grade. Oxone (OXONE, 99.0%) and cobalt(II) nitrate hexahydrate (99.999%) were purchased from Sigma-Aldrich; sodium thiosulfate pentahydrate (used for quenching reactions) (99.0%) was purchased from Lach-Ner. A saturated stock solution of HCH was prepared by dissolving standard HCH (isomer mixture α:β:γ:δ = 1:1:1:1; 99.3%; Sigma-Aldrich Co.; 8.5 μM) in deionised water. Deionised water (18.2 MΩ cm^{-1}) was prepared by an ELGA purelab flex system (ELGA, Veolia Water, Marlow, UK).

2.2. Analytical

HCH isomers were quantified by a gas chromatography (Thermo Trace 1310 combined with an MS detector TSQ 8000 triple quadrupole). Headspace solid-phase microextraction (HS-SPME) was utilized for sample preparation and injection (PDMS SPME fibers, Supelco). A TR-Pesticide chromatographic column, 30 m in length, 0.25 mm in diameter, was used for gas chromatography. For detection of the polar chlorophenols, as by-products of the oxidation reactions, sample aliquots were derivatized with acetic anhydride [11]. For calibration, standard mixtures of HCH (Neochema, Pesticides Mix 5) were employed along with deuterated γ-HCH (Ehrenstorfer GmBH) as an internal standard.

A ultraviolet-visible spectrophotometer (HACH LANGE s.r.o., Czech Republic) with matched 1-cm quartz cells was used for the determination of peroxymonosulfate (an active part of Oxone) concentration according to the method developed by Wacławek et al. [12]. At selected time points, 0.2 cm^3 samples were taken from the reactors, mixed with a 5 cm^3 potassium iodide solution, and the resulting mixtures were then measured using the spectrophotometer (characteristic wavelength of 395 nm).

2.3. Experiment setup and calculations

Experiments were performed at room temperature in 200-ml glass bottle containing 200 ml solution. Solution was stirred magnetically at the constant rate of 350 rpm.

Tests were performed with three different Oxone concentrations (6, 0.6, and 0.06 mM). In addition, after establishing the optimal Oxone concentration for HCHs decontamination, experiments with various molar ratios between Oxone (6 mM) and cobalt(II) nitrate (6, 0.6, 0.06, and 0.006 mM) were done.

Experiments were performed at least twice using freshly prepared samples. The mean of the data was calculated from these tests.

Pseudo-first-order kinetic model (Eq. (3)) was applied for the evaluation of the kinetics of HCHs degradation:

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{3}$$

where C and C_0 are the summed HCH isomers concentrations at time (t) and $t = 0$, respectively, and k is the reaction rate constant.

3. Results and discussion

3.1. Effect of various Oxone doses on HCH degradation

In the presence of $Co(NO_3)_2$ alone, no significant HCH removal was observed during the 30 min of the experiment. As increasing Oxone concentrations were added into the solution, the degradation of summed HCH isomers appeared. The variation in Oxone dosage and increased efficiency of HCH decontamination are presented in Fig. 2.

Degradation curves of summed HCH isomers can be fitted well with the pseudo-first-order kinetic

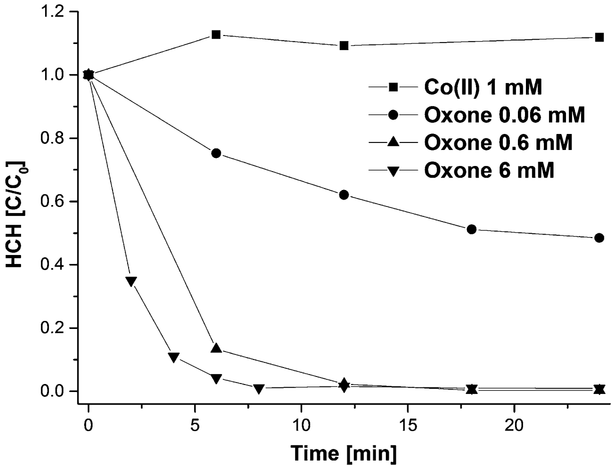

Fig. 2. Kinetics of summed HCH isomers degradation by various Oxone doses (C_{HCHs} = 0.85 μM, molar $ratio_{Oxone:Co(II)}$ = 1:0.1).

Table 1
Oxone dose dependence on HCHs removal

Sample name	Oxone concentration (mM)	Oxone/Co(II) molar ratio	Pseudo-first-order rate constant (min^{-1})	R^2
Oxone 0.06 mM	0.06	1:0.1	0.03	0.990
Oxone 0.6 mM	0.60	1:0.1	0.31	0.999
Oxone 6 mM	6.00	1:0.1	0.55	0.997

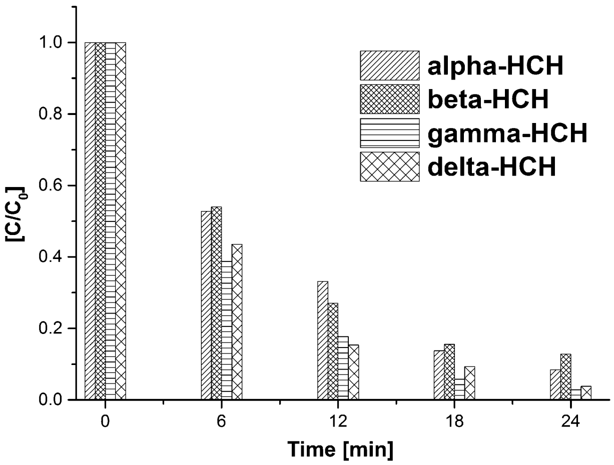

Fig. 3. Kinetics of HCH isomer degradation by Oxone activated by Co(II) ($C_{\text{HCHs}} = 0.85\ \mu\text{M}$, $C_{\text{Oxone}} = 6\ \text{mM}$, molar ratio$_{\text{Oxone:Co(II)}} = 1:0.01$).

model and the calculated rate constants can be found in Table 1.

Fig. 3 shows the kinetics of the degradation of individual isomers by Oxone induced by Co(II). Although differences between the degradation rate constants of the individual isomers were not significant, α-HCH and β-HCH show the lowest degradation rate, smaller in comparison with γ-HCH and δ-HCH. After 12 min, γ-HCH and δ-HCH concentrations were approximately a half of the concentrations of α-HCH and β-HCH. These results are in agreement with our previous study concerning HCH oxidation with electro-activated persulfate, which revealed α- and β-isomers as the most persistent ones from all HCH isomers [13].

3.2. Effect of various Co(II) doses on HCH degradation

In Fig. 4, the effect of various Oxone/Co(NO_3)$_2$ molar ratios with a fixed Oxone dose (6 mM) on HCHs degradation can be seen.

In the absence of Co(II) or Oxone, the HCHs degradation is negligible. But after mixing this compounds in certain concentrations, HCHs are continuously degraded to the point when Oxone and Co(II) were coupled in the molar ratio of 1:1. Degradation efficiency caused by Oxone induced by Co(II) in molar ratio of 1:0.1 is higher than in 1:1.

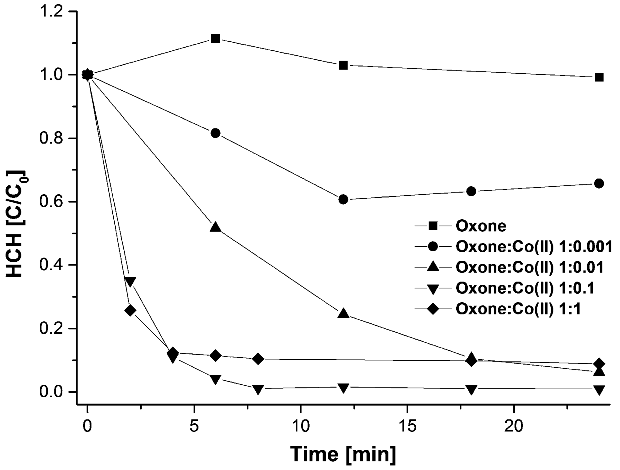

Fig. 4. Kinetics of summed HCH isomers degradation by various Oxone/Co(II) molar ratios ($C_{\text{HCHs}} = 0.85\ \mu\text{M}$, $C_{\text{Oxone}} = 6\ \text{mM}$).

The kinetics of peroxymonosulfate decomposition induced by Co(II) were studied to explain this change

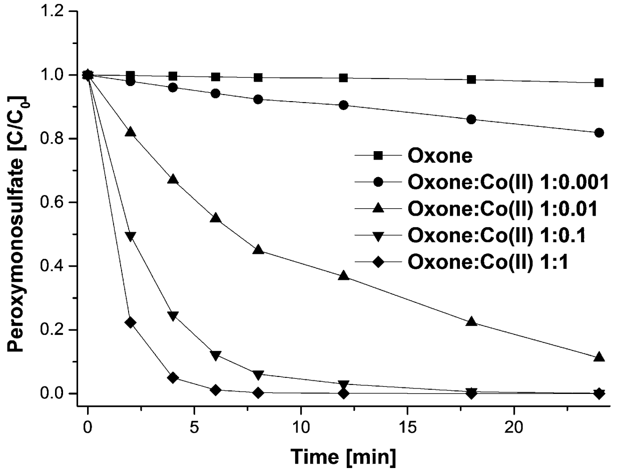

Fig. 5. PMS decomposition during the experiment with various cobalt concentrations ($C_{\text{HCHs}} = 0.85\ \mu\text{M}$, $C_{\text{Oxone}} = 6\ \text{mM}$).

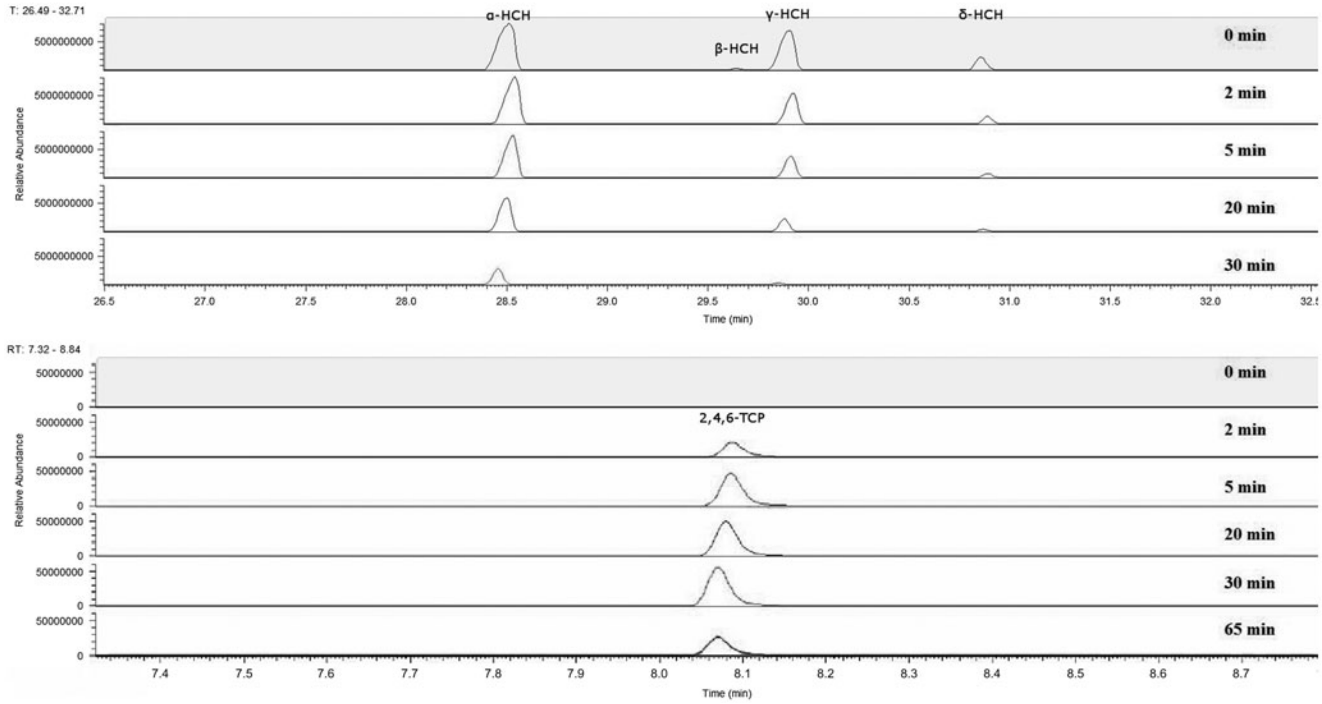

Fig. 6. Production of 2,4,6-TCP during oxidation of HCHs (C_{HCHs} ~ 40 μM, C_{Oxone} = 6 mM, molar ratio$_{\text{Oxone:Co(II)}}$ = 1:0.1).

in the rate of HCH degradation (Fig. 5). Similarly to HCH removal, the rate of peroxymonosulfate decomposition is not significant without cobalt salt dose but is enabled as the Co(II) dose increases. The trend is consistent with HCH degradation up to molar ratio of Oxone:Co(II)—1:0.1. The maximal peroxymonosulfate decomposition for a Oxone:Co(II) molar ratio of 1:1 and the simultaneous decrease in HCH degradation (Fig. 4) indicate that the excess of Co(II) can also act as a sulfate radical scavenger at high concentrations as expressed by Eq. (4) [14]:

$$\text{Co(II)} + \text{SO}_4^{-\bullet} \rightarrow \text{Co(II)} + \text{SO}_4^{2-} \quad (4)$$

3.3. Intermediates

GC/MS full scan analysis after derivatization and SPME injection revealed the formation of 2,4,6–trichlorophenol (2,4,6-TCP) during cobalt-mediated Oxone treatment of HCHs (Fig. 6).

Based on the results presented above, it can be concluded that chlorine and hydrogen atoms were abstracted from the Cl–C–H groups (constituting HCHs), which could be the cause of penta- and tetrachlorocyclohexene formation. These by-products after further oxidation could be transformed to trichloro-cyclohexadiene-ol and ultimately 2,4,6-TCP.

Experiments on rats have shown that 2,4,6-TCP have moderate acute toxicity [15].

Degradation of 2,4,6-TCP by sulfate radicals was well described in a recent study [16]. It was determined therein, that after ring cleavage, there is formation of ring-opening products (e.g. 2,4-dichloro-5-oxo-2-hexenedioic acid and 1,1,3,3-tetrachloro-2-propanone) which are further oxidized to low-molecular weight organic compounds and finally transformed to CO_2 and H_2O.

In our study, trace levels of the trichlorobenzene (TCB), tetrachlorophenol (TeCP), and pentachlorophenol (PCP) were detected as well. TeCP and PCP could be formed in the chlorination process of 2,4,6-TCP. This phenomenon was described by Anipsitakis and Dionysiou [9]. Future research has to be done to quantify these intermediates and to determine the exact degradation pathway of HCHs oxidized by $\text{SO}_4^{-\bullet}$.

4. Conclusions

Applied study unveiled that cobalt-mediated Oxone activation is a suitable method to degrade HCH isomers. It is worthy to note that summed HCH isomers (0.85 μM) can be almost entirely degraded under the optimal conditions of Co(II) dose (0.6 mM) and Oxone concentration (6 mM). Furthermore, it was observed that surplus of $\text{Co(NO}_3)_2$ negatively influences the degradation of HCHs. Responsible for this phenomenon could be a reaction between sulfate radicals and excess of Co(II). Experiments in very concentrated HCH solution had shown 2,4,6-TCP as a major intermediate. Performed research revealed that Oxone coupled with Co(II) has a high reaction rate with HCH isomers, and future study has to be performed in order to establish exact degradation pathways for HCHs and to confirm effectiveness of proposed method in the field.

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