

## REMEDICATION 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 tend to bioaccumulate in human and animal adipose tissue. Since certain HCHs cause central nervous system, reproductive, and other endocrine damage there is necessity of a suitable remediation method to remove HCH from contaminated groundwater and soil. The present study was conducted to evaluate the potential of peroxymonosulfate (Oxone) induced by cobalt salt ( $\text{Co}(\text{NO}_3)_2$ ;  $\text{Co}(\text{II})$ ) to degrade HCHs.

Cobalt (II) nitrate has been chosen instead of Cobalt (II) chloride (which presents better activation properties for Oxone (Anipsitakis and Dionysiou, 2003)) in order to avoid an excess 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  $\mu\text{M}$  of summed HCH isomers).

Optimal oxidant dose was established by running a test with three different Oxone concentrations (molar ratio of Oxone: $\text{Co}(\text{NO}_3)_2$  - 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 shown to be: 0.03, 0.31 and 0.55  $\text{min}^{-1}$  for doses: 0.06, 0.6 and 6 mM respectively.

Further experiments were carried out to find out optimal Oxone: $\text{Co}(\text{NO}_3)_2$  molar ratio. Effectiveness of HCHs decontamination by Oxone: $\text{Co}(\text{NO}_3)_2$  in various molar ratios was in order: 1:0.1>1:1>1:0.01>1:0.001. It was observed that surplus of  $\text{Co}(\text{NO}_3)_2$  can slow down degradation kinetics. A reaction between sulfate radicals and  $\text{Co}(\text{NO}_3)_2$  could be responsible for this phenomenon, that can lead to 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 test 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.

Presented study revealed that Oxone induced by  $\text{Co}(\text{II})$  shows a high degradation rate with HCH isomers, which can make it an attractive method for HCHs decontamination in the future.

**Keywords:** Hexachlorocyclohexanes, HCH, chlorobenzenes, lindane, peroxymonosulfate, monopersulfate, AOP, Oxone.

### 1. Introduction

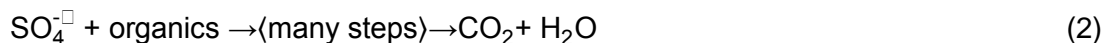
Hexachlorocyclohexanes (HCHs) represent one of the dominant and extensively researched kinds of chlorinated pesticides not to mention that they joined lately the list of persistent organic pollutants

(POPs) (Memon *et al.*, 2014). Hence it is crucial to establish cost-effective remedial technologies to treat water, soil and waste contaminated by HCH isomers.

One of the chemical reagents which could be beneficially applicable for this purpose is peroxymonosulfate (Oxone). Oxone is a source of a powerful oxidant peroxymonosulfate ( $\text{HSO}_5^-$ ) which can be further induced to form sulfate radicals (Eq. 1).

Formation of sulfate radicals allows to use Oxone 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 (Duan *et al.*, 2015; Anipsitakis *et al.*, 2006) and has a high efficiency removal of halogenated pollutants (Anipsitakis and Dionysiou, 2003). Compared to  $\text{OH}^\cdot$ ,  $\text{SO}_4^{\cdot-}$  have higher reduction potential at neutral pH and are more selective for organic pollutants oxidation (Neta *et al.*, 1988).

Anipsitakis and Dionysiou (2003) 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.* (2006) reported that  $\text{HSO}_5^-$  has a high oxidation potential and the production of  $\text{SO}_4^{\cdot-}$  and the mineralization of organic compounds can be expressed as follows (Eq. 1 and 2):



The main aim of this article was to describe the effects of cobalt-mediated activation of Oxone 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. Analytical

HCH isomers were quantified using gas chromatographic separation (TR-Pesticide column, 30 m in length, 0.25 mm in diameter) and triple quadrupole-MS detection. Samples were measured with SPME technique (Derouiche *et al.*, 2007).

### 2.2. Reagents and solutions

All of the chemicals used in the experiments were 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 the reaction) (99.0%) was purchased from Lach-Ner. A saturated stock solution of HCH was prepared by dissolving standard HCH (isomer mixture  $\alpha:\beta:\gamma:\delta = 1:1:1:1$ ; 99.3%; Sigma-Aldrich Co.; 8.5  $\mu\text{M}$ ) in deionised water. Deionised water ( $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ ) was prepared by an ELGA purelab flex system (ELGA, Veolia Water, Marlow, UK).

### 2.3. Experiment setup and calculations

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

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 evaluation of the kinetics of HCHs degradation.

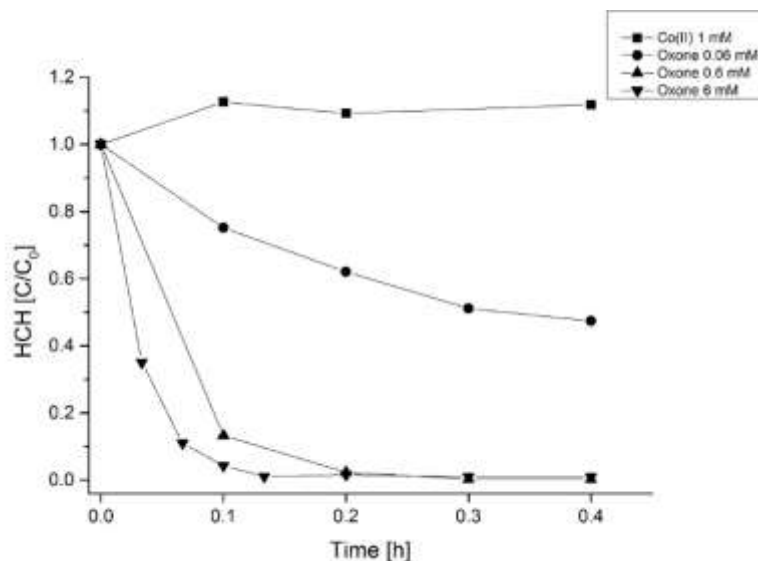
$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (3)$$

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

#### 3.1. Effect of various Oxone doses on HCH degradation

In the presence of  $\text{Co}(\text{NO}_3)_2$  alone, no significant HCH removal was observed during the 30 minutes of the experiment. As increasing Oxone concentrations were added into the solution, the degradation of summed HCH isomers appeared. The variation of Oxone dosage and increased efficiency of HCH decontamination is presented in Figure 1.



**Figure 1:** Kinetics of summed HCH isomers degradation by various Oxone doses ( $C_{\text{HCHs}} = 0.85 \mu\text{M}$ , molar ratio $_{\text{Oxone:Co(II)}} = 1:0.1$ ).

Degradation curves of summed HCH isomers can be fitted well with The pseudo first-order kinetic model and the calculated rates can be found in Table 1.

**Table 1:** Oxone dose dependence on HCHs removal.

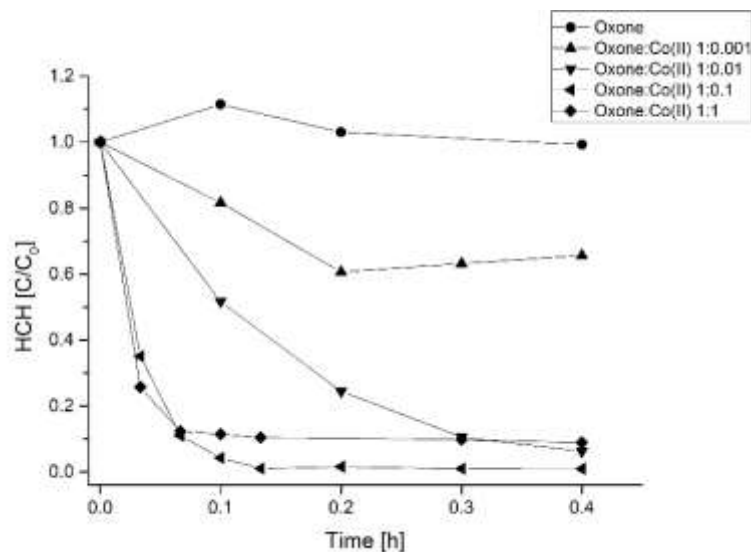
Sample name	Oxone concentration [mM]	Oxone/Co(II) molar ratio	First-order rate constant [ $\text{min}^{-1}$ ]	$R^2$
Oxone 0.06 mM	0.06	1:0.1	0.03	0.990
Oxone 0.6 mM	0.60	1:0.1	0.31	0.999
Oxone 6 mM	6.00	1:0.1	0.55	0.997

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

Figure 2 shows the effect of various Oxone/Co(II) molar ratios with a fixed Oxone dose (6 mM) on HCHs degradation. 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 1:1. Degradation efficiency caused by Oxone coupled with Co(II) in molar ratio 1:0.1 is higher than 1:1.

This indicates that Co(II) may act as a scavenger for the  $\text{SO}_4^{\cdot -}$  in accordance with Eq. 4, limiting the oxidation of HCHs in the presence of excess Co(II).

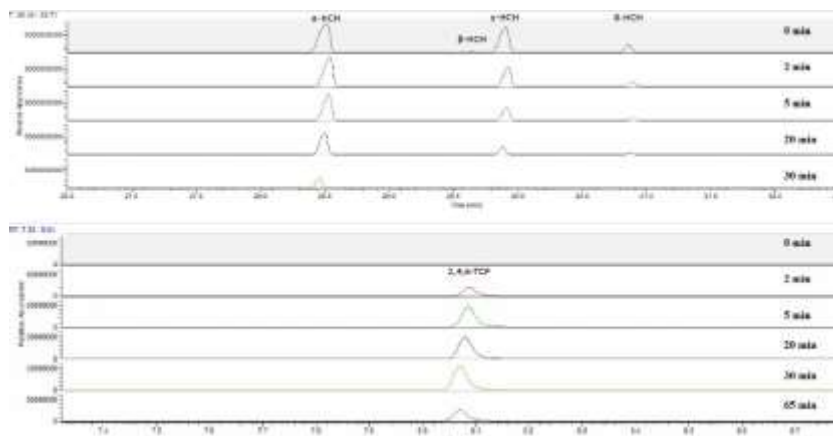




**Figure 2:** Kinetics of summed HCH isomers degradation by various Oxone/Co(II) molar ratio ( $C_{\text{HCHs}} = 0.85 \mu\text{M}$ ,  $C_{\text{Oxone}} = 6 \text{ mM}$ ).

### 3.3. Intermediates

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



**Figure 3:** Production of 2,4,6-TCP during oxidation of HCHs ( $C_{\text{HCHs}} \sim 40 \mu\text{M}$ ,  $C_{\text{Oxone}} = 6 \text{ mM}$ ,  $C_{\text{Co(II)}} = 0.6 \text{ mM}$ ).

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 (U.S. Department of Health and Human Services, 1993).

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 (2003). Future research have to be

done to quantify these intermediates and determine exact degradation pathway of HCHs oxidized by  $\text{SO}_4^{\cdot-}$ .

#### 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  $\mu\text{M}$ ) can be almost entirely degraded under the optimal conditions of Co(II) dose (0.6 mM) and Oxone concentration (6 mM). 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 have to be made in order to establish degradation pathways for HCHs as well as to confirm effectiveness of proposed method in the field.

#### ACKNOWLEDGEMENTS

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