



***Basic Research in Chemistry and
Biotechnology for Elimination of Halogenated
Hydrocarbon Pollutants of Aquifers and Ground
Water***

OXIDATION WORKING GROUP

IAB kick-off meeting

Debrecen, 10/10/2009





Oxidative dehalogenation

Destructive oxidation of chlorinated solvents to carbon dioxide, water, and chloride ion (mineralization) seems to be a promising method for removing this type of pollutants from industrial waste, contaminated ground water, and soil.

Oxidations with almost all of the known and practically important oxidizing agents (such as oxygen, ozone, hydrogen peroxide, chlorine dioxide, peroxy monosulfate, peroxy disulfate, permanganate) are favored thermodynamically. However, some of the reactions of this type are kinetically very sluggish because of the large kinetic barrier. Speeding up the oxidation reactions seems to be an important key task for practical application.

On the other hand, one should consider a process for this purpose that would only produce final products that can be considered harmless in the environment.



Oxidizing agents we plan to use

Elementary **oxygen** would be an ideal reagent for our purposes (cheap, harmless, etc.), but it is difficult to activate it especially under the conditions of the target application. So we do not consider seriously its application in the present research.

Ozone,
Hydrogen peroxide,
Peroxo monosulfate,
Peroxo disulfate,
Chlorine dioxide,
Potassium permanganate

The reagents listed above give environmental friendly byproducts, they do not have very long lifetime in the environment, cost is not unbearable much.



Ozone

One of the strongest oxidizing agents, capable of mineralizing halogenated organics dissolved in water

The oxidation is expected to be fast

Commonly used for the treatment of water in municipal and industrial applications

Environmentally friendly, no undesirable byproduct

Large body of literature is available

Should be prepared on site which is an energy consuming operation with an expensive apparatus

Low solubility in water



Hydrogen peroxide and catalysts

H_2O_2 gives water as byproduct

Any excess of this reagent has no long lifetime in the environment

The reaction with chlorinated organics usually rather slow at ambient temperature. Catalysts are needed to speed up the reaction.

The catalyst used in the process, in addition to being efficient in activating the stoichiometric oxidant, should be environmentally friendly and/or should decompose to give benign final products

Confirmation of the efficiency of iron complexes as catalysts

Fe(III)TPPS (TPPS sulfonated tetraphenyl porphine)

Fe(III)phthalocyanines

Fe(III)TAML (this compound is an effective hydrogen peroxide activator, available commercially)



Peroxomonosulfate ion

Peroxo disulfate ion

Both reagents commercially available in large quantities

Small kinetics barrier, expected rather fast reactions with chlorinated organics.

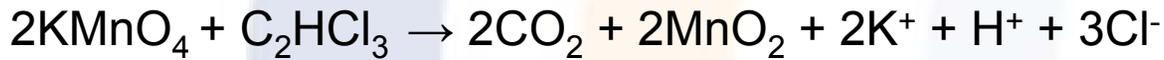
They form sulfate ion as byproduct, which causes no environmental problem



Permanganate ion

KMnO_4 can completely mineralize chlorinated hydrocarbons in a diluted aqueous solution

Reaction with trichloroethylene



Similar stoichiometric reaction takes place with other chlorinated hydrocarbons.

Many papers are published about the possible use of this reaction for the in situ chemical oxidation to remediate chlorinated-hydrocarbon contaminated aquifer. The reaction takes place rather fast. At ambient temperature halftime ranges between 10 min and 10 h depending on the reagent concentrations and their ratios.

MnO_2 precipitates causing clogging problem. The clogging can be prevented by using excess phosphate buffer. Phosphate keeps Mn(IV) in water soluble complex.



Strategic lines of the planned research

Review the corresponding literature

Preliminary experiments in order to choose appropriate oxidizing agent

Find appropriate catalyst

Confirmation of the efficiency of the selected catalyst

Studies of the stoichiometry, kinetics, and mechanism of the selected reactions

Findig possibilities for delivering the oxidizing agent to the contamination site

Publication if allowed

Please advise



Controlled release KMnO_4

The ability to release a compound at a controlled rate from a reservoir to the target host is important in variety of different applications

In situ construction of stable reaction zones underground is possible in such a way

An extruded form of KMnO_4 is commercially available for removing grease and hydrogen sulfide odor in surface water. This product uses the porous matrix comprising silica and clays as a means of delaying the otherwise instant dissolution of KMnO_4

Polymer or paraffin matrix is better

Polyester resin – potassium permanganat combination is much better. It can serve as a controlled release source for many years or even a decade (*Eung Seok Lee, Franklin W. Schwartz, Chemosphere 66, 2058-2066, 2007*).