Advanced Oxidation An Effective Process for the Removal of 1,4-Dioxane and TCE in Contaminated Groundwater

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Abstract

The treatment of groundwater and other water or wastewater streams contaminated with hard to degrade micro pollutants is one of the most challenging applications for state of the art water treatment systems. Increasing regulatory requirements for the reduction or elimination of these contaminants requires alternate treatment processes. The thresholds given by the authorities for these micro pollutants are often in the range of their detection limits. Especially in California (USA) these regulations have brought conventional treatment processes to reach their limitation.

The combination of different treatment processes like an ozone treatment, and UV-radiation, combined with the dosing of hydrogen peroxide results in a more powerful process, called AOP (Advanced – Oxidation – Process). These processes are able to reduce these micro pollutants efficiently and in many cases results in contaminant levels which are below regulatory requirements.

Pilot trials were carried out on an industrial site contaminated with1,4-dioxane and chlorinated compounds like tetrachlorethene (PCE) and trichlorethene (TCE) to find out which combination delivers the best results concerning economical aspects. In this case the combination of ozone and hydrogen peroxide delivered the best results.

Key words: Advanced oxidation; AOP; micropollutants; TCE; 1,4-Dioxane; groundwater

Introduction

Many industrial sites used chlorinated solvents in degreasing operations, 1,4-dioxane was commonly used as a solvent stabilizer. Historical handling, storage and disposal practices resulted in the release of these solvents and stabilizers to ground water. At an industrial site in Southern California, ground water is contaminated with tetrachlorethene (PCE), trichlorethene (TCE) and 1,4-dioxane. Water is drawn from onsite wells, which is then sent through the treatment process prior to discharge. Initially, regulatory requirements only required the treatment of chlorinated compounds. For the removal of the chlorinated compounds, the water was passed through a pre-filter and then through two 4000 pound GAC vessels which performed well regarding the CHC reduction. However the 1,4-dioxane passes the GAC with no significant reduction. Increasingly tight regulations with lower limits and the need to treat for 1,4-dioxane prompted the investigation of advance oxidation.

Pilot trials were carried out to test different treatment options. For this purpose a pilot AOP system was built up, which has the ability to treat the well-water by four different methods:

1) ozone
2) ozone / hydrogen peroxide
3) ozone / UV
4) hydrogen peroxide / UV

During the test period the pilot system treated well water, which had passed through two serial 25 micron filters. The active carbon adsorbers (GAC) were not used.

Analytical Methods

The analysis of the samples for VOC, TOC, dioxane, pH, hardness, iron, manganese and conductance were made by using the following EPA methods:

VOC → EPA 8260 B
TOC → SM 5310 D
1,4-Dioxane → SRL 524M-TCP
pH → SM 4500 H+B
Hardness → SM 2340 C
Conductance → SM 2510 B

The analysis for ozone in the gas-phase, dissolved ozone and hydrogen peroxide were conducted by using the following methods:

Ozone in gas-phase: WEDECO ozone analyser HC 500
Ozone dissolved: → Orbisphere dissolved ozone analyser (*Hach-Ultra*)
Hydrogen peroxide: → DIN-Method 38 409 H15

Characteristics of the treated groundwater

The well water from the storage tank passed trough two serial 25 micron filter bags and was therefore free of suspended solids. The water showed a slight yellow color and a low organic background (TOC <3.0 mg/L). Storing the well water in a black tank resulted in the water temperature during the trials increasing up to 26°C. The initial temperature of the well water was not recorded. This increase in temperature has an impact on the ozone demand of the water, resulting in a faster decomposition of the dissolved ozone.

<u>Analysis</u>

TOC:	2.3 - 2.8	[mg/L]
pH:	6.8 - 7	
Conductivity:	4800	[µS/cm]
Iron:	0.19 - 0.57	[mg/L]
Manganese:	0.07	[mg/L]
Transmission$_{254\ nm}$:	87	[%]

Description of the pilot plant

The AOP pilot unit was installed in a 20'-container. The following flow chart shows the basic design of this unit.

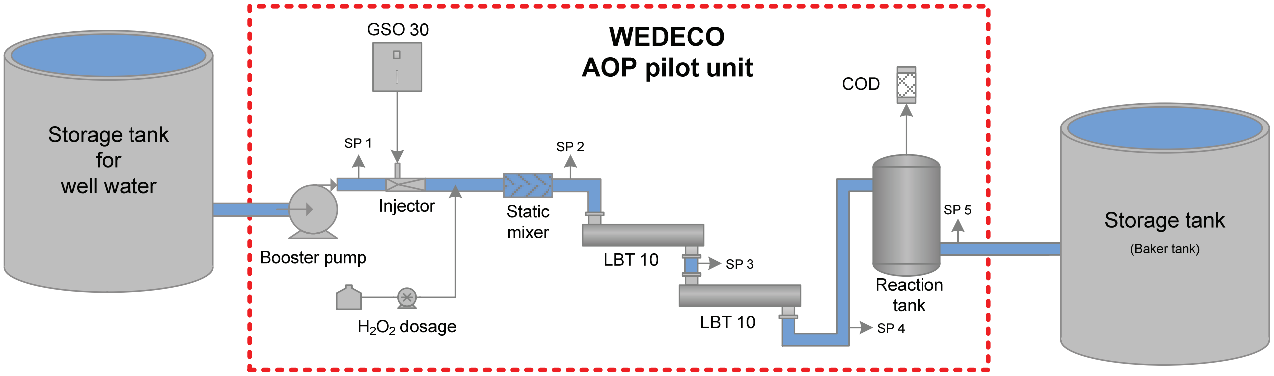

Figure 1: Flow chart of the AOP pilot unit.

The design of the AOP pilot unit allows testing of different combined processes. Three different single processes were installed in this unit:

1. ozone
2. hydrogen peroxide
3. UV

The flexible design allows for any combination of the above treatment processes to be combined to determine the optimal treatment process for a given requirement.

Components

Ozone generator:	WEDECO GSO 30 (Ozone capacity: 100 g/h)
UV-Device:	2 x WEDECO LBT 10 with an output of 130 W UVC (Low-pressure)
Hydrogen peroxide:	Peristaltic pump with a flow of 0.6 L/h

Test procedure

The contaminated well-water was filtered through a 25 micron filter and than pumped into a storage tank. A variable feed pump was used to fix the water flow into the pilot unit. The water flow for the trials was fixed at 2.2 m³/h.

Three different AOP's were tested under various conditions:

- Hydrogen peroxide/UV
- Hydrogen peroxide/Ozone
- Ozone/UV

Goal of these tests was the reduction of 1,4-dioxane and TCE to under their detection limits. For evaluating the hydrogen peroxide/UV process two different dosages of hydrogen peroxide were tested. The amount of UVC – radiation was fixed for both settings at 115 W UVC/m³.

The hydrogen peroxide/Ozone process was conducted with different ozone and hydrogen peroxide ratios. Important in this process is the consumption of ozone by the water. The optimal ratio depends on the dissolved ozone concentration, not on the applied amount. During the trials it was observed, that a long retention time delivers better results than a short one.

The Ozone/UV process was also conducted with various settings. The applied ozone amount and the UVC radiation were varied, to find the best treatment procedure regarding the degradation of 1,4-dioxane and TCE.

Results

Table 1. Results.

	H_2O_2 / UV	**H_2O_2 / Ozone**	**Ozone / UV**
H_2O_2 - Dosage	20 g / m³	5 g / m³	-
Ozone - Dosage	-	10 g / m³	13 g / m³
UVC – Power	115 W / m³	-	57.5 W / m³
Rated Power	360 W / m³*	180 W / m³**	414 W / m³
1,4-Dioxane influent	34 µg/l	25 µg/l	32 µg/l
1,4-Dioxane effluent	18 µg/l	<2 µg/l	9 µg/l
1,4-Dioxane % Reduction	47.1%	>92%	71.8%
TCE influent	32 µg/l	28 µg/l	33 µg/l
TCE effluent	18 µg/l	< 1 µg/l	7 µg/l
TCE % Reduction	43.7%	>96.4%	78.7%

* Based on two lamps with 360 W power consumption
** Based on a power – consumption of 18 kW for 1 kg ozone (including PSA oxygen production)

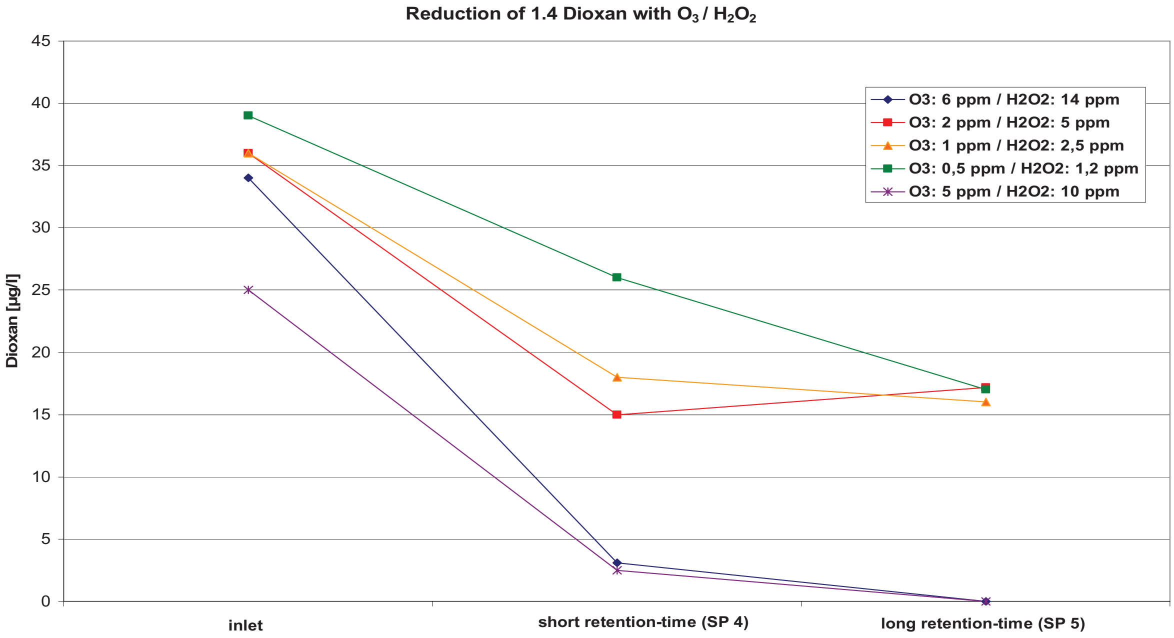

Figure 2: Degradation of 1,4-dioxane with ozone/H_2O_2.

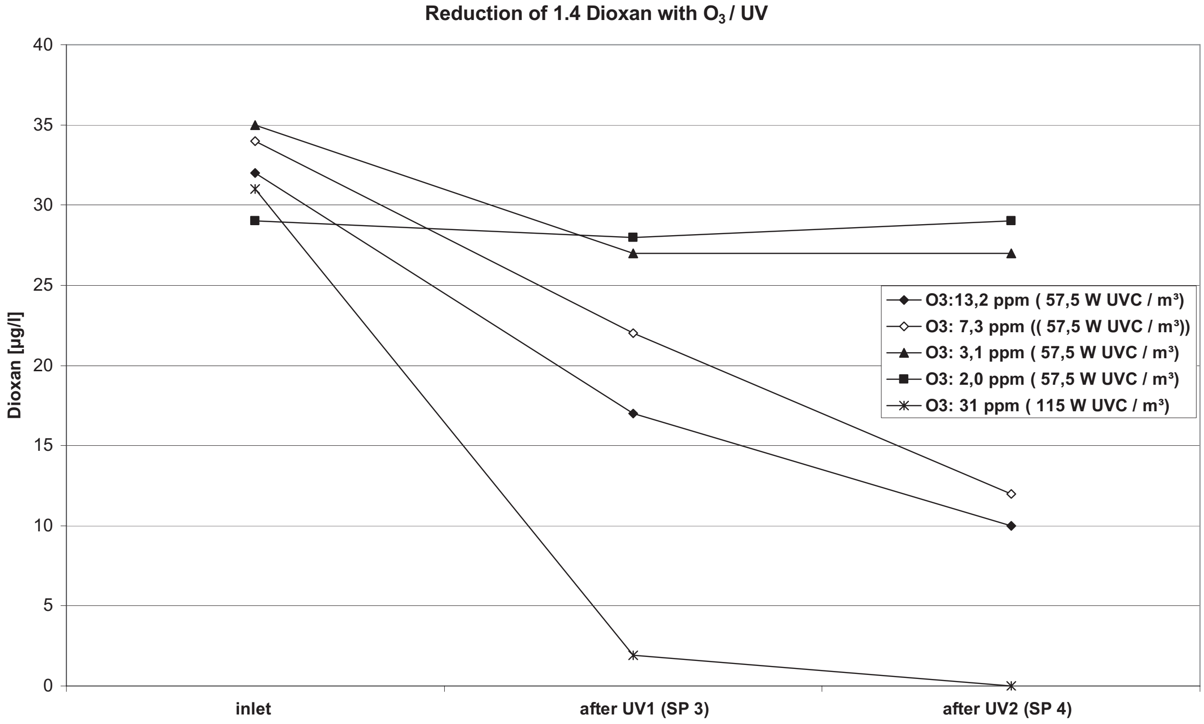

Figure 3: Degradation of 1,4-dioxane with ozone/UV.

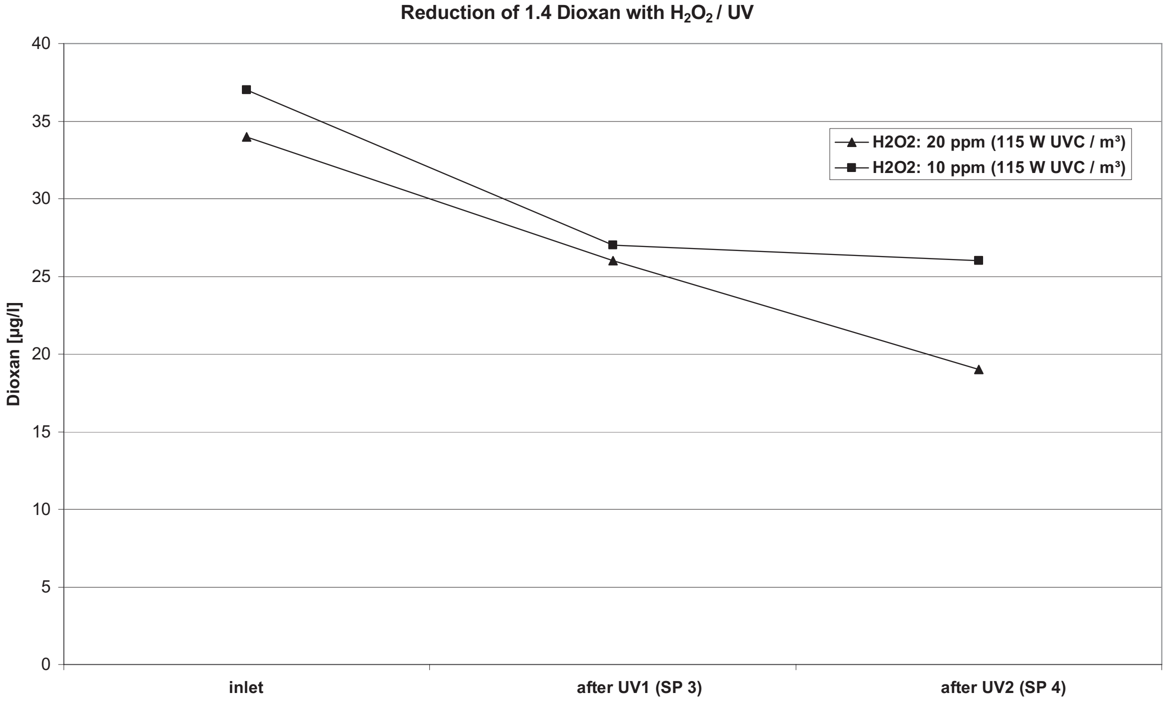

Figure 4: Degradation of 1,4-dioxane with H_2O_2/UV.

Byproducts

The formation of by- products of the chlorinated compounds were checked regarding the EPA 8260 B procedure. According to these results, no byproducts were formed. Most of the checked compounds were even degraded by the application of the different AOP's.

Table 2. Behavior of byproducts during H_2O_2 / O_3 process.

Compound	Inlet [µ/l]	Outlet [µg/l]
Trichlorethene	28	<1
Tetrachlorethene	25	3,9
1,1 Dichlorethane	2,1	1,6
1,1 Dichlorethene	15	<1
c- 1,2 Dichlorethene	6,3	<1
Vinylchloride	<0,5	<0,5

Conclusions

The treatment of hard to degrade micropollutants in a groundwater matrix is a field of application, where AOP's can be used successfully. The selection of the right AOP must be evaluated for each case considering the water matrix, the treatment goal and special regulations.

In this case, the ozone hydrogen peroxide process was the most economical and successful one. Based on the test results ozone hydrogen peroxide was able to reduce the target compounds to near or below the detection limits. Of the three processes evaluated, ozone hydrogen peroxide also had the lowest operating cost based on input power consumption. Pilot testing is essential in determining the most effective process for a given water chemistry and in determining the proper dosages for successful treatment.