- POSTERS -

USING OF PHOTOCHEMICAL H_2O_2/UVC DECONTAMINATION CELL FOR HEAVILY POLLUTED WATERS

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Abstract

The presented contribution focuses on the complex study of the pilot-scale photochemical H_2O_2/UVC system arranged as the *ex-situ* decontamination cell for heavily polluted waters (contamination with organic substances. The method principle comprises the rational decomposition of hydrogen peroxide induced by UV-C (254 nm). The produced OH radicals are very efficient oxidation species enabling the direct destruction of wide spectrum of organic compounds (polyaromatic hydrocarbons, chlorinated hydrocarbons, aniline, nitrobenzene etc.). Concentrations mentioned compounds in groundwater were very effectively reduced by photochemical oxidation H_2O_2/UVC (efficiency up 95%). This contribution also brings details on the feasibility of the designed processes in comparison with traditional approaches.

Keywords: Photochemical oxidation, H_2O_2, UVC radiation, remediation, contaminated water, decontamination cell, pilot scale

1. Introduction

Enormous effort is devoted to the development and optimization methods using in-situ chemical oxidation (ISCO), in which different oxidizing agents, e.g. $KMnO_4$, H_2O_2, H_2O_2/Fe^{2+} (Fenton's reagent), $Na_2S_2O_8$, etc. are injected into the rock environment for decomposition of pollutants [1, 2]. The biggest advantage of this technology is the decomposition of pollutants within the contamination cloud without requirements for further handling of contaminated media (groundwater, soil, etc.) [1]. On the contrary, extraneous oxidizers are introduced into the rock environment and the process monitoring of oxidation efficiency is very difficult. A series of competing reactions with focal matrix (e.g. decomposition of humic substances or oxidation of inorganic nitrogen) often occur and that significantly increase the consumption of oxidizing agents. The largest problem represents oxidation of chromium ions towards toxic chromate or dichromate (VI) [3].

This work introduces a new on-site technology based on photochemical oxidation of organic pollutants by hydroxyl radicals which is one of the most effective oxidation agents. Hydroxyl radicals are generated by UV decomposition of H_2O_2 at 254 nm. That allows oxidation of persistent organic pollutants in waters including polyaromatic hydrocarbons. The technology represents, in connection with hydraulic barrier, a specific set up of reactive chemical barrier. In this study, remediation set-up uses a pulsing pumping with decontamination outside saturated zone. That enables an easy monitoring of oxidation process in which H_2O_2 is carefully dosed in order to eliminate the remaining unreacted H_2O_2.

2. Principle of photochemical oxidation and pilot scale unit description

The principle of photochemical oxidation is a decomposition of H_2O_2 by ultraviolet irradiation towards hydroxyl radicals that react with organic pollutants. The simplified mechanism is given by following equations [4]:

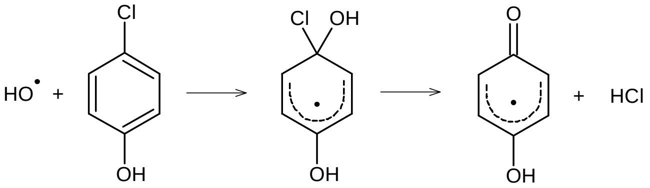
$$H_2O_2 + h\nu \rightarrow 2\ OH\bullet \quad (1)$$

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \quad (2)$$

$$HO_2\bullet + H_2O_2 \rightarrow OH\bullet + H_2O + O_2 \quad (3)$$

$$2\ HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (4)$$

The equation 1 shows the direct decomposition of H_2O_2 molecule, equations 2 and 3 display additional reactions yielding superoxide and hydroxide radicals. The equation 4 illustrates the radical recombination yielding H_2O_2 which can occur at specific conditions and also has to be taken into account [5]. Hydroxyl radicals then react with dissolved organic compounds in a series of chain reactions towards harmless inorganic products, e.g. CO_2 and H_2O. In case of substituted hydrocarbons also relevant mineral acids. The reaction mechanism of H_2O_2 and organic compound is dependent on the type of organic compound [2]. The example of common model pollutant attack, such as 4-CP, is given by equation 5 [6]:



(5)

Equation 5 represents only the first step of reaction and is usually followed by a series of chain reactions towards CO_2 a H_2O. Reaction tests were carried out in a photoreactor, which consists of a cylindrical quartz tube (1200 x 153 mm, glass thickness 5 mm). The quartz tube is surrounded by 20 low-pressure germicidal UV lamps (Narva, LT 36W/UV-C). Manufacturer declares that UV lamps don't contribute to ozone formation due to the glass filter. The inlet part of photoreactor consists of redistributor and series of plastic sieves that ensure the uniform flow through irradiated zone in reactor. Outer jacket of the reactor is made of highly polished aluminum sheet that ensures minimal loses of irradiation and also consists of lengthwise sheets to conduct the heat away.

All 20 lamps were kept active and the flow rate of 50 $l \cdot min^{-1}$ was set up for all described experiments within this paper. The residence time in reaction zone was 16.5 s. It is obvious that the unit is constructed as a recirculation unit (Fig. 1 left). Contaminated water is propelled from the storage tank (1) with centrifugal pump (2) to the low part of photoreactor (6), it is irradiated and then brought back to the storage tank. The whole process is repeated as many times as it is needed [7]. Hydrogen peroxide batcher (8) is used for continuous dosing of H_2O_2 to the contaminated water through the mixing valve (9) before entering the centrifugal pump (2). Both parts together serve as a reaction mixture homogenizer.

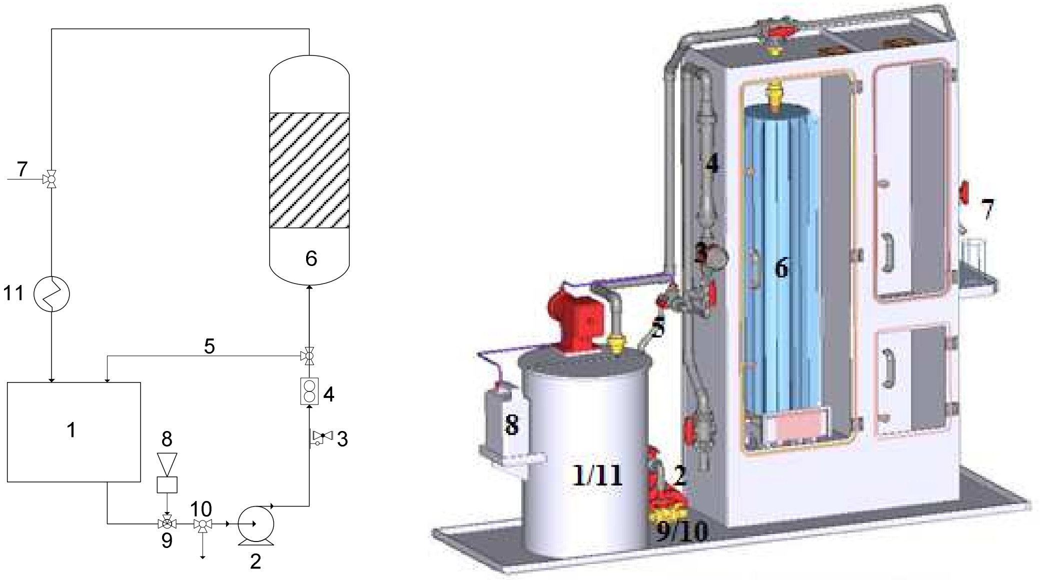


Fig. 1: Left – scheme of the photochemical unit, 1) storage tank, 2) centrifugal pump, 3) membrane valve, 4) flowmeter, 5) by-pass, 6) photoreactor, 7) sampling place, 8) hydrogen peroxide batcher, 9) mixing valve, 10) outlet valve, 11) cooler (inside storage tank); Right – the real appearance of the unit

3. Pilot tests of H_2O_2/UVC decontamination unit

Pilot scale H_2O_2/UVC unit was placed in laboratories of Biodegradace ltd. company on industrial site DEZA Ostrava. The company was processing the black coal tar but the production was already moved to another site. As already mentioned in previous chapter, pilot scale unit processes the contaminated water discontinuously. The volume of treated water is usually 100 l.

Three different areas with various types and origins of contamination were chosen for such purposes. The first area was former industrial site where company for black coal tar processing operated (DEZA Ostrava). There is a broad spectrum of organic substances, mainly aromatic hydrocarbons (BTEX fraction, cresols etc.), non-polar crude oil based hydrocarbons and polyaromatic hydrocarbons (naphthalene, anthracene, phenatrene, fluoranthene, chrysene etc.). Concentration of contaminants varies between units and tens of mg/l and often exceeds their solubility in water so they create a separate free phase. The entire area is currently remediated by a series of 14 bore holes that create a system of hydraulic barrier. This barrier prevents spreading of contamination cloud towards the source of drinking water for the city of Ostrava.

The figure 3 shows the rate of removal of chosen contaminants in groundwater from DEZA Ostrava industrial site. The H_2O_2 dosing rate was set to 2 ml.L^{-1}.hod^{-1}.

It is noticeable that the fastest decrease of chosen contaminants can be found within the first 30 min of the experiment. The concentration decrease of PAHs (the main y axis) correlates well with the decrease of TOC (the adjacent y axis) [8].

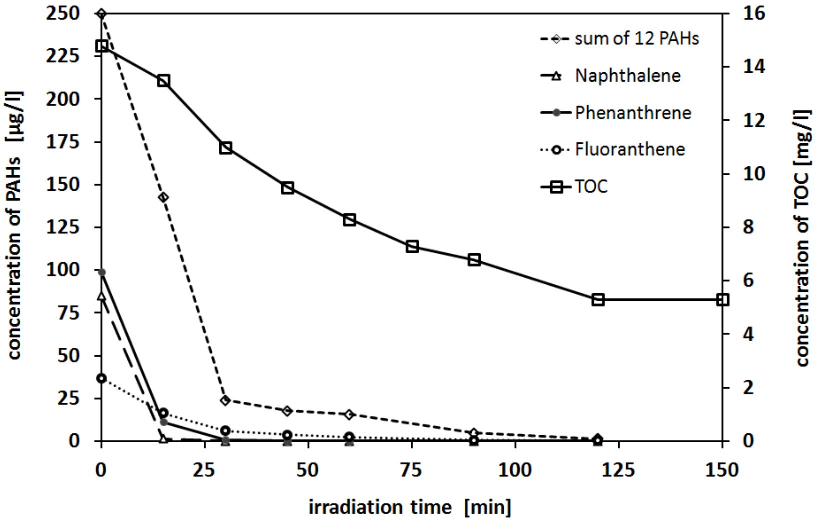


Figure 2: Kinetics of chosen contaminants degradation in DEZA Ostrava groundwater; The rate of H_2O_2 continuous dosing was 2 ml.L^{-1}.h^{-1}.

It is very interesting that the decrease of TOC stopped on the value of 5 mg/l and didn't decrease with prolonged reaction time. There can be several reasons for such observation. The groundwater can also contain natural background of humic acids that are resistant to oxidation or creation of specific very stable reaction intermediates which could be complicatedly treated should be taken into account as well. Also analyses and sampling of such complex matrix with these types of contaminants are very problematic and can bring uncertainty.

The second locality was area of former chemical cleaning plant and gasworks in the city of Ústí nad Labem. The contamination was caused by using perchloroethylene as a cleaning and degreasing preparation. The main contaminants are then chlorinated aliphatic hydrocarbons, namely perchloroethylene and products of its microbial decomposition, trichloroethylene, dichloroethylenes and vinylchloride. The area is equipped with a network of monitoring boreholes with sufficient capacity.

The figure 4 shows the rate of removal of chlorinated hydrocarbons in groundwater from Ústí nad Labem industrial site. The H_2O_2 dosing rate was set to 1 ml.L^{-1}.hod^{-1}. The H_2O_2 dosing rate was lower than in previous case because groundwater from Ústí nad Labem contains less complicated pollutants than groundwater from DEZA Ostrava.

The very fast degradation of chlorinated hydrocarbons is noticeable on the figure 4. All the contaminants were removed within 30 min of the experiment (the main y axis). The adjacent y axis shows corresponding increase in chloride anions content. We can observe very good correlation between chloride anions increase and chlorinated hydrocarbons decrease [9]. It is important to note that the concentration of hydrocarbons was also measured in the headspace of storage tank in order to determine the influence of stripping. Hydrocarbons weren't detected in the headspace of storage tank so the influence of their stripping is insignificant.

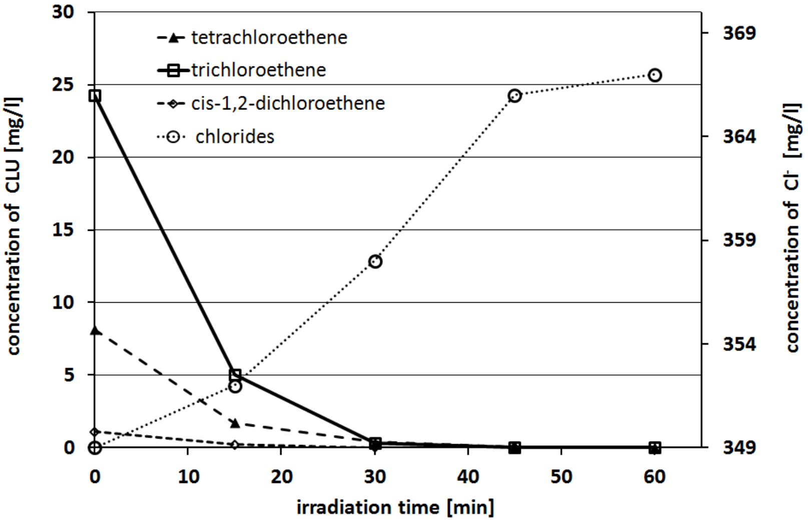


Figure 3: Kinetics of chlorinated hydrocarbons degradation in Ústí nad Labem groundwater; The rate of H_2O_2 continuous dosing was 1 ml.L^{-1}.h^{-1}.

The third locality was area of chemical plant in Ostrava where the main groundwater contaminants are benzene, nitrobenzene and aniline. The concentration of these pollutants often exceeds 100 mg/l and the origin of this contamination is long-term (over 50 years) manufacturing of aniline. The main advantage of this groundwater is that there are only 3 pollutants and the can be easily analyzed by HPLC.

The figure 5 shows the rate of removal of nitrobenzene and aniline in groundwater from Ostrava chemical plant site. Benzene wasn't monitored because its content was less than 1 mg/l. The H_2O_2 was dosed continuously at 2 ml.L^{-1}.hod^{-1}.

We can observe that nitrobenzene and aniline are oxidized with significantly slower rate than previous contaminants showed on figures 3 and 4. High initial concentrations of nitrobenzene and aniline are caused by their good solubility in water. We can observe that aniline was completely removed after 3,5 hours and nitrobenzene was removed after 8 hours of oxidation. Difficult removal of nitrobenzene is caused by nitro- group. In references [10, 11] are shown details of photochemical oxidation of aniline and nitrobenzene. Nitrobenzene deactivates aromatic ring in terms of electrophilic addition.

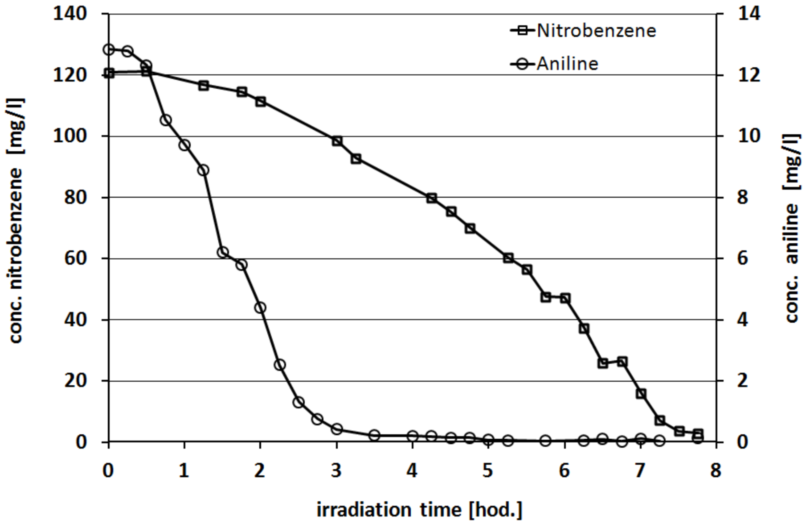


Figure 4: Kinetics of nitrobenzene and aniline in Ostrava chemical plant groundwater; The rate of H_2O_2 continuous dosing was 2 ml.L^{-1}.h^{-1}.

The effectiveness of the process is further verified by mineralization of organic nitrogen towards inorganic anions NO_2^- a NO_3^- (see table 1). We can notice that toxic NO_2^- content reached its maximum after 3 hours and then it is decreasing until complete removal because it is oxidized to NO_3^-. Its concentration progressively increases during the whole experiment and cleaned water without NO_2^- would easily meet limits for release to terminal recipient.

Table 1: Changes in contents of various types of nitrogen during photochemical oxidations of aniline and nitrobenzene (mg/l).

mg/l	0 hr.	1 hr.	3 hr.	5 hr.	6 hr.
aniline	32.3	7.5	0.5	< 0.5	< 0.5
nitrobenzene	36.2	32.7	2.3	< 0.5	< 0.5
NO_3^-	2.2	11.1	17.0	25.7	30.2
NO_2^-	0.02	1.91	10.60	5.33	0.80
$N_{org.}$	10.8	8.3	5.2	3.3	2.4

4. Operational possibilities of H_2O_2/UVC unit

The results from a series of pilot tests performed show a very good applicability of the technology for degradation of a broad spectrum of organic pollutants from ground- or wastewaters. Experimentally was proved that photochemical H_2O_2/UVC unit can serve as an active part of reactive chemical barrier. The whole arrangement is described by figure 6. Reactive chemical barrier will be formed by suitable sealing wall that will be anchored to the impermeable bedrock with boreholes for pumping groundwater. It is also possible to consider a series of boreholes creating a hydraulic barrier instead of sealing wall.

Each borehole will be equipped with mobile H_2O_2/UVC unit (placed in container or skid module) together with a pretreatment step. There will be necessary to introduce also a supplementary tank for equalizing the pulsing flow of water and homogenization of contaminants. Additionally it is necessary to apply a technology for reduction of non-dissolved and dissolved metallic ions (Fe, Mg etc.), whose compounds would pollute the inner surface of a quartz tubes. Sedimentation with aeration, sand filter and electrocoagulation were tested during pilot experiments. Electrocoagulation seems to be the most suitable because it is able to remove up to 90 % of dissolved metallic ions and it is also able to reduce the content of organic pollutants up to 40 %. That would reduce the residence time in the oxidation unit and decrease the operation cost. Cleaned water is then injected back to ground behind the sealing wall or hydraulic barrier.

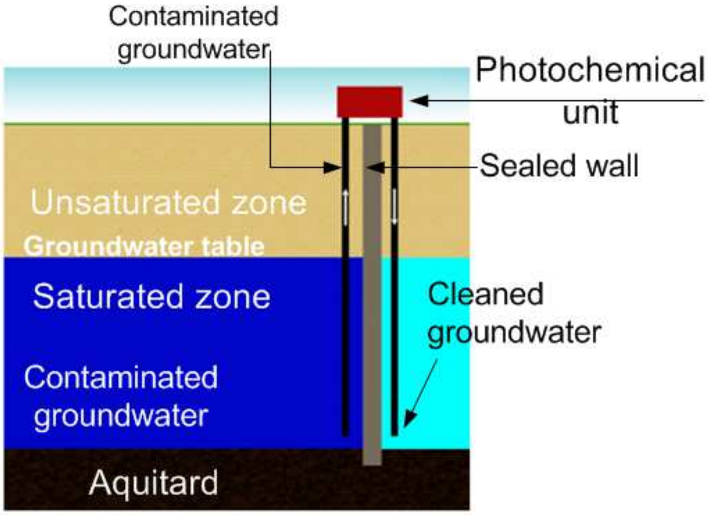


Figure 5: H_2O_2/UVC on-site arrangement of reactive chemical barrier for remediation of groundwaters.

The operational cost of the technology for groundwater treatment was evaluated. It was found that 75 % of total cost comprises electricity consumption for germicidal lamps and recirculation pump operation. Hydrogen peroxide cost and maintenance expenses are minor. The large excess of hydrogen peroxide didn’t lead to reduce the expenses significantly because hydroxide radicals interact by side reactions and residence time wasn’t considerably shortened. The price of 1 m^3 treatment with hardly decomposable pollutants was evaluated to 2 EUR. The authors also considered broadening of technology by arrangement of battery of photochemical reaction units.

5. Conclusion

The paper was focused on testing of H_2O_2/UVC oxidation for treatment of heavily contaminated groundwaters as an alternative to conventional in-situ treatment techniques of chemical oxidation ISCO. It was determined that hydroxyl radicals formed by UVC decomposition of H_2O_2 are very effective for oxidation of organic compounds. All the tested contaminations were completely removed bellow the detection limit. The advantage of tested technology is the on-site placement and possibility of own regulation (H_2O_2 dosing, flow rate, residence time etc.). The considerable disadvantage is the necessity of contaminated water pumping from/to the soil and careful adjustment of the entire oxidation process. Particular reactors are able to be completed to larger modules or skid units and it is easy to scale up their capacity even for large flow rates. The largest disadvantage is very high energy consumptions and consequently the operational cost that prevent the larger practical expansion of this technology in comparison with other ISCO technologies. This technology can be contributive in combination with other technologies especially in sensitive areas and areas with strict remediation limits.

5. References

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