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# ASPECTS REGARDING THE DEGRADATION OF BTEX COMPOUNDS FROM AQUEOUS SOLUTION BY ADVANCED OXIDATION PROCESSES (AOPS)

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**Abstract.** Over the past two decades, environmental regulatory have became more stringent because of increased awareness of human health and ecological risks associated with environmental contaminants. In many cases, conventional treatment technologies have low removal rates for many environmental contaminants, including benzene, toluene, ethylbenzene and xylene (BTEX). These compounds can affect the natural receiving water quality, even low concentration alternative treatment technology like advanced processes (AOP) was necessary. The UV photooxidation is one of the advanced oxidation processes successfully applied. The pre-treatment of waste water through AOPs leads to the less toxic and more degradable intermediaries, thus ensuring the efficiency of the biological treatment steps. It was studied the degradation of benzene from synthetic solution (0.5 mmol $dm^{-1}$) by direct UV photolysis with/without adding of hydrogen peroxide. The experimental results show that the efficiency of degradation and the improving of the biodegradation characteristics of treated water (BOD/COD ratio) are affected by: pH, the dose of the oxidising agent, the contact time.

*Keywords*: benzene, advanced oxidation process, UV-photooxidation, hydrogen peroxide.

## AIMS AND BACKGROUND

Treatment of aqueous solution containing recalcitrant organics is of widespread concern in industry. Enormous quantities of groundwater are contaminated with volatile organic compounds as benzene, toluene, xylene, etc. Additionally, many manufactaring facilities produced water containing these compound, which, if not properly treated, contaminated surface water, air and/or soil.

In order to remove these types of compounds it was necessary to develop some strong treatment methods, which allow either their mineralisation or at least their conversion into biodegradable structures. One of the possible ways is the application of the advanced oxidation processes[1].

The AOPs technologies are based on the *in situ* producing (generating) of free radicals with high oxidative power like hydroxyl radicals. They strong react with the most organic pollutants from water either by drawing out a hydrogen atom, or by addition. Under the action of the hydroxyl radicals a set of oxidative

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reactions is initiated, leading to less toxic intermediaries which can be treated by biological methods in optimal conditions of development.

One of the frequently advanced oxidation processes applied is the UV photolysis. This process is accelerated by the addition of oxidants (hydrogen peroxide, ozone and others)[2-4].

In this work it was studied the degradation of the benzene from synthetic solutions, with the establishing of the working parameters influence (pH, oxidant dose, contact time) on the conversion efficiency of this pollutant into biodegradable intermediaries.

## EXPERIMENTAL

In order to carry out the study, a set of experiments of direct photolysis (UV system) and by adding the oxidant ($UV/H_2O_2$ system) was performed.

The laboratory installation used consists of one glass reactor with cooling system into its coat, equipped with a mercury lamp connected to a UV type TQ 150 generator (Heraeus Hanau) which is electrically fed at 220 V, 50 Hz frequency and a power of 180 W. The mercury lamp emits UV light radiations ($\lambda$ = 240-320 nm) at a flow of 1-1.8 W.

Samples of benzene synthetic solution were subjected to photolysis (51 mg/l).

The experiments were conducted at the following conditions: pH = 5-10; doses of oxidant corresponding to the molar ratios $H_2O_2$:Bz between 5:1 and 17.5:1; contact times = 15-60 min.

The analytical control was carried out by evaluation of the following indicators: pH, COD-Cr, BOD and benzene.

## RESULTS AND DISCUSSION

The experiments of photolysis were conducted by using a synthetic solution in different working conditions. There was emphasised the possibility of benzene turnover into biodegradable intermediaries, by photooxidation.

In the following presentation are showed the obtained results.

*The influence of pH.* The study of the pH influence on the photochemical degradation of benzene was made on the base of the experimental results in direct photolysis carried out at pH values of 5, 7 and 10. The results presented in Table 1 revealed the following aspects:

– The decreasing of benzene concentration with efficiencies over 70% are obtained in the slight acid-neutral pH field; at the same time increasing of BOD/COD ratio from 0.2 to 0.26 are registered;

– The pigmentation in yellow of treated samples is probably determinated by the benzene convertion into coloured quinonic intermediaries;

– The increasing of COD-Cr values for treated samples is determinated by generation of photodegradation intermediaries with less volatility comparatively with benzene;

– In the working conditions the degradation by direct photolysis of benzene to more biodegradable intermediaries is slow and, subsequentely, it was necessary to accelerate the process by adding oxidant.

**Table 1**. The influence of pH on the photochemical degradation of benzene

| No | $pH_i$ | Treated samples characteristics | | | | | | η benzene removal (%) |
|---|---|---|---|---|---|---|---|---|
| | | colour | pH | COD-Cr ($mgO_2/l$) | BOD ($mgO_2/l$) | BOD/ COD-Cr | benzene (mg/l) | |
| 1 | 5 | yellow | 3.6 | 112 | 22.4 | 0.20 | 15.08 | 70.5 |
| 2 | 7 | yellow | 5.2 | 123.7 | 32.16 | 0.26 | 11.57 | 77.3 |
| 3 | 10 | light yellow | 9.2 | 90 | 17.1 | 0.19 | 20.25 | 60.3 |

Work conditions: contact time = 60 min, samples volume = 800 ml; Initial sample characteristics: COD-Cr = 70 $mgO_2/l$, BOD = 16.1 $mgO_2/l$, BOD/COD-Cr = 0.23, benzene = 51.07 mg/l.

*The influence of oxidant dose.* In order to assess the influence of oxidant dose on the degradation efficiency there were carried out experiments of photolysis in UV/$H_2O_2$ system. There were tested different oxidant doses corresponding to $H_2O_2$: Bz ratios of 5:1 to 17.5:1, at pH=7 and the contact time of 60 min. In Table 2 there are presented the obtained results revealing the following conclusions:

– The increasing of the oxidant dose has a positive effect on the degradation process of benzene; so that, when the molar ratio $H_2O_2$:Bz varying from 5:1 to 17.5:1, is observed the improvement of BOD/COD ratio from 0.19 to 0.33;

– The efficiency of benzene removal has an ascendant evolution with the oxidant dose; the values obtained are between 91-99.9%;

– The advanced oxidation of organic intermediaries (quinonic compounds) is emphasised by discolouring of the treated samples.

**Table 2.** Influence of oxidant dose on the photochemical degradation of benzene

| No | Molar ratio $H_2O_2$:Bz | Treated samples characteristics | | | | | | η benzene removal (%) |
|---|---|---|---|---|---|---|---|---|
| | | colour | pH | COD-Cr ($mgO_2/l$) | BOD ($mgO_2/l$) | BOD/ COD-Cr | benzene (mg/l) | |
| 1 | 5 : 1 | yellow | 3.7 | 80.02 | 15.2 | 0.19 | 4.54 | 91.1 |
| 2 | 7.5 : 1 | dark yellow | 3.55 | 105.4 | 22.13 | 0.21 | 1.05 | 98 |
| 3 | 10 : 1 | dark yellow | 3.4 | 122 | 30.5 | 0.25 | 0.46 | 99.1 |
| 4 | 15 : 1 | light yellow | 3.25 | 158.4 | 52.27 | 0.33 | 0.24 | 99.5 |
| 5 | 17.5 : 1 | light yellow | 3.07 | 165 | 54.5 | 0.33 | < 0.001 | 99.99 |

Work conditions: molar ratio of $H_2O_2$:Bz = 5:1 – 17.5:1. pH = 7, contact time = 60 min, samples volume = 800 ml; Initial sample characteristics: COD-Cr = 70 $mgO_2/l$, BOD = 16.1 $mgO_2/l$, BOD/COD-Cr = 0.23, benzene = 51.07 mg/l.

*The influence of the contact time.* In order to establish the optimal conversion parameters of the pollutants into non-toxic intermediaries, there was also studied the influence of contact time on the process efficiency.

The experiments were carried out at the oxidant dose corresponding to molar ratio $H_2O_2$:Bz=15:1 and different values of contact times. The results presented in Table 3 emphasise the following aspects.

**Table 3.** Influence of contact time on the photochemical degradation of benzene

| No | Contact time (min) | Treated samples characteristics | | | | | | η benzene removal (%) |
|---|---|---|---|---|---|---|---|---|
| | | colour | pH | COD-Cr ($mgO_2$/l) | BOD ($mgO_2$/l) | BOD/ COD-Cr | benzene (mg/l) | |
| 1 | 15 | yellow | 4.02 | 103.2 | 206 | 0.2 | 4.03 | 92.1 |
| 2 | 30 | light yellow | 3.6 | 145 | 43.5 | 0.3 | 1.25 | 97.6 |
| 3 | 60 | light yellow | 3.25 | 158.4 | 52.27 | 0.33 | 0.24 | 99.5 |

Work conditions: molar ratio of $H_2O_2$:Bz = 15:1, pH = 7, samples volume = 800 ml; Initial sample characteristics: COD-Cr = 70 $mgO_2$/l, BOD = 16.1 $mgO_2$/l, BOD/COD-Cr = 0.23, benzene = 51.07 mg/l.

The improvement of the degradative process efficiency with the period of UV exposure:

- Increasing of contact time from 15 to 60 min assures the mitigation of the remanent benzene concentration at ≤ 4 mg/l;
- At similar values of exposure time the increasing of BOD/COD-Cr ratio values at 0.3-0.33 are registered.

## CONCLUSIONS

By applying the photolysis at proper conditions in UV/$H_2O_2$ system is assured the conversion of aromatic compounds, refractory polutants present in waste water into biodegradable intermediaries.

The case study made on benzene synthetic solution revealed that the efficient degradation of the pollutant into intermediaries sensible to bacterial oxidation is made in the following conditions: pH = 7, dose of oxidant corresponding to molar ratio $H_2O_2$:Bz = 15:1, contact time of 30 min.

## REFERENCES


1. J. E. OLDENCRANTS, D. TOBOCMAN, S. DUGAN: Chemical Oxidation Technologies for the Nineties, **5**, 159 (1997).
2. K. V. TOPUDURTI, M. M. LEWIS, S. K. HIRSH: Environmental Progress, **12** (1), 54 (1993).
3. US Environmental Protection Agency (U.S.EPA): Applications Analysis Report, EPA/540/AR-93/520 (1994).
4. H. SPRENGEL, K. V. TOPUDURTI: Environmental Engineer. TetraTech EM, 1998.



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