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ADVANCED TERTIARY TREATMENT OF MUNICIPAL EFFLUENTS IN ORDER TO REUSE THEM AS WATER FOR IRRIGATION

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Abstract. Our research is an attempt to treat the municipal treatment plants influents in a three-step (anoxic, anaerobic and aerobic) pilot installation and photoinduced oxidation processes for xenobiotics removal. The advanced treated effluents could be reused as irrigation water (STAS 9450/88). Degradation of chlorobenzenes using various photoinduced oxidation processes such as UV/H_2O_2, UV/O_3 and UV/H_2O_2/O_3 was investigated. Comparative analyses of removal efficiencies for trichlorobenzene (TCB) and hexachlorobenzene (HCB) taking into account tested operating parameters were performed. The operating parameters with significant influence upon the removal efficiencies of chlorobenzenes in homogeneous advanced oxidation processes (AOPs) are as following: micropollutants concentrations, reaction/irradiation time and oxidants doses (H_2O_2, O_3). The selected variant, based on laboratory experiments could be used as tertiary treatment step for the municipal wastewater treatment plant, after verification of microbiological indicators, and the final effluent could be used in agricultural purposes – irrigations.

Keywords: xenobiotics, AOPs, photolysis, ozonation, water reuse.

AIMS AND BACKGROUND

In the context of the EU environmental legislation GD No 351/2005 contains the Program for step-by-step elimination of discharges, emissions and losses of prior dangerous substances.

Trichlorobenzene (TCB) and hexachlorobenzene (HCB) are considered to be prior dangerous substances and were detected in some municipal effluents. Thus, they are included into the reducing/elimination program for discharges. The admitted discharging limits into inside and transitorily waters, for TCB and HCB, are very low (0.4 μg TCB/l, 0.02 μg HCB/l) according to the European legislation[1].

In this context, the adding of tertiary step to classical treatment flow from municipal wastewater treatment plant, based on advanced oxidation processes

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(AOPs), could be a viable solution for removal/reducing of dangerous/prior dangerous substances.

There were tested the most used advanced oxidation processes in order to assure a high removal efficiency of residual specific (TCB, HCB) and global (COD) organic load from the final effluent of municipal wastewater treatment plant (with no tertiary treatment endowment)[2,3].

EXPERIMENTAL

The treatment experiments were conducted in pilot installation provided with aeration, anoxic and anaerobic vessels.

Pilot installation works with 2 re-circulation systems: re-circulation of biological sludge from bottom of secondary settler to denitrification anoxic vessel and re-circulation of sludge from aeration vessel to denitrification anoxic vessel.

The pilot installation performs biooxidation of organic substances and ammonium, decreasing of nitrates (by denitrification) and elimination of phosphorous by anaerobic–aerobic biological process.

The analytical control was performed for pH, COD, BOD, TCB and HCB (Table 1).

Photoinduced oxidation processes were used because xenobiotics (TCB and HCB) are recalcitrant to biological processes. There were tested the followings advanced oxidation systems in order to remove chlorobenzenes (CBs): UV/H_2O_2; UV/O_3 and $UV/H_2O_2/ O_3$.

The photodegradation experiments were carried out in a laboratory UV-reactor system (Haereus) with a medium-pressure mercury lamp which emits mainly in the range of 200–280 nm (UVC). It is equipped with a quartz cooling jacket and immersed in the center of the reactor containing CBs solution. The ozone source was a TRAILIGAZ Labo 5 LO generator – France. The CBs content of initial biological effluent was below 1 μg/l and, in order to study the photodegradation for higher levels of concentrations, there were added TCB and HCB.

The composition of tertiary treated water was as follows: pH: 7–8; TDS: 1144–1272 mg/l; chlorides: 412–681 mg/l; sulphates: 52–65 mg/l; iron: 0.3–3.6 mg/l; average COD ≈ 75 mg O_2/l; TCB: 0.4–32.2 μg/l; HCB: 0.088–7 μg/l.

The analytical control was performed for: pH, COD (reflux method), TCB, HCB (GC), ozone. Also, microbiological characteristics of some treated effluents were evaluated. The operating parameters for 3 tested oxidation systems were as follows:

- UV/H_2O_2: reaction/irradiation time = 30–120 min; H_2O_2 (O^*) doses = 21.25 (10) ÷ 85 (40) mg/l;

Table 1. Monitoring data of pilot treatment installation

No crt.	Indicator	U.M.	IS	ES_1	ES_2	ES_3	ES_4	ES_5	ES_6	ES_7	IS	ES_8	ES_9	ES_{10}	ES_{11}
1	pH	–	6.92	7.69	8.84	7.95	7.59	7.77	7.85	7.61	7.13	7.65	7.62	7.73	7.80
2	COD	mgO_2/l	286	26.4	39.6	83.6	44	35.2	26.4	36.8	114.4	44	52.8	35.2	44
3	BOD	mgO_2/l	95.8	6.57	10.7	17.9	9.5	6.81	5.3	8.97	17.6	11.18	15.01	7.00	9.99
4	TCB	µg/l	0.0533	–	0.0332	–	–	–	0.0451	–	–	–	0.0223	–	–
5	HCB	µg/l	0.0152	–	0.0142	–	–	–	0.0136	–	–	–	0.0142	–	–

• UV/O_3: reaction/irradiation time = 20–90 min; active oxygen dose (corresponding to ozone dose) = 10–38 mg O^*/l; O_3 (O^*) doses = 31 (10) – 113 (38) mg/l;

• $UV/H_2O_2/O_3$: reaction/irradiation time = 10–60 min; total oxidants doses (O^*/H_2O_2 + O^*/O_3) = 13 (10+3) ÷ 30 (10+20) mg/l.

RESULTS AND DISCUSSION

The pilot treatment installation has carried on with high removal efficiencies of organic load, treated effluents being in the frame of stipulated indicators values for natural receiver discharges – HG 352/2005 NTPA 001.

The results of advanced oxidation tests in order to remove TCB and HCB are emphasised in the frame of Tables 2–6 as characterisation data of the final treated effluents (pH, residual micropollutants concentrations), removal efficiencies of global organic load (COD) and specific organic load (TCB, HCB) according to operating parameters (reaction time, oxidant doses, initial pollutants concentrations).

Table 2. Influence of H_2O_2 doses on chlorobenzenes (< 1 μg/l) degradation efficiency (τ_{irr} 30 min)

No	Sample	H_2O_2 (O*) dose (mg/l)	TCB residual (μg/l)	η TCB (%)	HCB residual (μg/l)	η HCB (%)	COD residual (mg O_2/l)	η COD (%)
1	H1	21.25 (10)	0.356	27.3	0.030	65.9	54.3	12.8
2	H2	31.8 (15)	0.320	34.5	0.026	70.5	53.5	14.2
3	H3	42.5 (20)	0.300	38.8	0.020	77.3	51.9	16.7

Initial characteristics of biological effluent: pH = 7.88; TCB = 0.49 μg/l; HCB = 0.888 μg/l; COD = 62.3 mg O_2/l.

Table 3. Influence of H_2O_2 doses on chlorobenzenes (tens μg/l) degradation efficiency (τ_{irr} 60 min)

No	Sample	H_2O_2 (O*) dose (mg/l)	TCB residual (μg/l)	η TCB (%)	HCB residual (μg/l)	η HCB (%)	COD residual (mg O_2/l)	η COD (%)
1	H4	21.25 (10)	2.64	91.8	0.20	97.0	66.9	10.6
2	H5	42.50 (20)	0.81	97.5	0.09	98.7	59.5	20.5
3	H6	53.12 (30)	0.43	98.7	0.03	99.6	43.4	42.0
4	H7	85.00 (40)	0.15	99.5	0.01	99.9	35.2	53.0

Initial characteristics of biological effluent: pH = 7.9; TCB = 32.2 μg/l; HCB = 7 μg/l; COD = 74.8 mg O_2/l.

Table 4. Influence of irradiation time at high levels of chlorobenzenes concentrations (tens μg/l)

No	Sample	H_2O_2 (O*) dose (mg/l)	TCB residual (μg/l)	η TCB (%)	HCB residual (μg/l)	η HCB (%)	COD residual (mg O_2/l)	η COD (%)
1	H1	30	8.70	73.0	0.20	97.0	67.5	9.8
2	H2	60	2.64	91.8	0.18	97.4	66.9	10.6
3	H3	120	2.50	92.2	0.09	98.7	65.5	12.4

Initial characteristics of biological effluent: pH = 7.9; TCB = 32.2 μg/l; HCB = 7 μg/l; COD = 74.8 mg O_2/l.

Table 5. Influence of O_3 doses on chlorobenzenes (tens μg/l) degradation efficiency

No	Sample	H_2O_2 (O*) dose (mg/l)	Irriga-tion time (min)	TCB residual (μg/l)	η TCB (%)	HCB residual (μg/l)	η HCB (%)	COD residual (mg O_2/l)	η COD (%)
1	O1	31 (10)	20	2.73	91.5	0.364	94.8	62.8	16
2	O2	38 (12.5)	30	1.77	94.5	0.05	99.3	56.7	24.2
3	O3	75 (25)	60	0.54	98.3	0.017	99.7	78.6	35
4	O4	90 (30)	75	0.42	98.7	0.026	99.6	28.83	61
5	O5	113 (38)	90	0.31	99.0	0.015	99.8	20.3	73

Initial characteristics of biological effluent: pH = 7.9; TCB = 32.2 μg/l; HCB = 7 μg/l; COD = 74.8 mg O_2/l.

Table 6. Influence of oxidants doses on chlorobenzenes(tens μg/l) degradation efficiency

No	Sam-ple	H_2O_2 (O*) dose (mg/l)	Irriga-tion time (min)	TCB residual (μg/l)	η TCB (%)	HCB residual (μg/l)	η HCB (%)	COD residual (mg O_2/l)	η COD (%)
1	OH1	13	10	5.22	83.8	0.28	96	57.42	23.2
2	OH2	17	20	1.92	94.0	0.048	99.3	57.06	23.7
3	OH3	25	50	0.32	99.0	0.09	98.7	49.32	34
4	OH4	30	60	0.20	99.4	0.018	99.7	45.4	39.3

Initial characteristics of biological effluent: pH = 7.9; TCB = 32.2 μg/l; HCB = 7 μg/l; COD = 74.8 mg O_2/l.

The comparative evaluation of main microbiological indicators for the treated samples (UV/H_2O_2 system) is presented in Table 7.

Table 7. Microbiological characteristics of biological effluent before and after photooxidative treatment

No	Microbiological indicators	Maximum admitted values (STAS 9450–88) (no./dm³)	Samples			
			initial	H5	H6	H7
1	aerobic hetero-trophic bacteria	–	4.3×10^6	1.7×10^5	10^4	1.5×10^3
2	total coliforms	10 (M1 category) – 10^7	1.4×10^5	95	–	–
3	fecal coliforms	0 – 10^6	2.1×10^4	–	–	–

Influence of oxidant dose. Degradation yields of TCB and HCB are depending on the amount of •OH radicals generated by UV decomposition of H_2O_2, having an ascendant evolution along the applied H_2O_2 doses, at constant irradiation/reaction time (τ_{irr} 30 min – low CBs concentrations, below 1 μg/l; τ_{irr} 60 min – high CBs concentrations, tens μg/l);

– oxidative degradation of chlorobenzene was quite effective and well over 90% only for initial concentrations of tens μg/l (TCB ≤ 32 μg/l, HCB ≤ 7 μg/l):

• molar ratios H_2O_2/CBs are very high (229 ÷ 458/1) in the case of low CBs initial concentrations (TCB = 0.49 μg/l, HCB = 0.088 μg/l), residual values below the admitted limits being registered for the H_2O_2/CBs ratio = 458/1 (Table 2 – TCB res. = 0.3 μg/l, HCB res. = 0.02 μg/l);

• low molar ratios H_2O_2/CBs, about 3 ÷ 13/1 are applied for the biological effluent containing higher CBs initial concentrations (TCB ≤ 32 μg/l, HCB ≤ 7 μg/l) ; the best degradation efficiencies and the compliance of the treated effluent with the enforced regulations are realised for the H_2O_2/CBs ratios 12–13/1 (Table 3 – TCB res. ≤ 0.15 μg/l, HCB ≤ 0.01 μg/l);

– the maximum yield of COD removal is about 50% for the highest oxidant doses tested, corresponding to the H_2O_2/CBs ratios = 12–13/1.

Influence of irradiation/reaction time. At constant and low molar ratio of H_2O_2/CBs = 3.1/1 (Table 4), the removal efficiencies of specific organic micropollutants (TCB, HCB) emphasise an increasing evolution with irradiation/reaction time ($\tau_{irr.}$ = 30 ÷ 120 min);

• Although, the removal yields are situated over 92%, the residual concentrations of TCB (2.5 μg/l) and HCB (0.09 μg/l) are not in compliance with the imposed limits, the increasing of H_2O_2 doses being compulsory, as was presented above. Among the identified intermediates presented in various studies[4–7] which have been carried out to investigate the degradation pathways of haloaromatic compounds by UV/H_2O_2 system, must be mentioned: chlorophenols, biphenyl, chlorobiphenyl isomers, benzaldehyde. At longer enough irradiation time (h), the subsequent degradation of these compounds might lead up to mineralisation. Regarding the admitted limits for some of the above-mentioned intermediates products, included in GD No 351/2005, these are more large than those corresponding to chlorobenzenes (chlorophenols – 10 μg/l for each isomer, biphenyl = 1 μg/l). Besides the chlorobenzenes and other micropollutants degradation, UV/H_2O_2 treatment assures also the disinfection of biological effluents (Table 7). As tertiary treatment, UV radiation as an environmental technology is selected for disinfection of municipal WWTPs effluents before discharging into natural receivers.

UV/O_3 SYSTEM

Influence of ozone dose

• The photoxidation process in the presence of ozone was carried out in order to verify the influence of various O_3 doses on the degradation efficiency of chlorobenzenes (tens μg/l) from biological effluents;

• Ozone photolysis in aqueous solution generates hydrogen peroxide that in secondary reactions leads to hydroxyl radicals (•OH), which are considered the main oxidant agent of the system;

• The variation of ozone doses between 31–113 mg O_3/l was accomplished by the variation of ozone generating time and inevitably of irradiation time;

• The increase of applied ozone dose leads to the improving of degradation efficiencies of TCB (η = 91.5–99%) and HCB (95–99.8%), according to the data presented in Table 5;

• Ozone doses over 90 mg O_3/l are able to assure residual CBs concentrations under the imposed limits for discharge (O5 sample: TCB res. = 0.31 μg/l, HCB res. = 0.015 μg/l and O9 sample: TCB res. = 0.38 μg/l, HCB res. = 0.012 μg/l);

• The evolution of COD removal yields has an ascendant behaviour with the applied O_3 dose, but the maximum value are situated below 73%;

• Regarding pH evolution, must be mentioned the increase of it (pH = 8.3–8.8) during the photoxidation process, some of them being over the admitted value.

UV/H_2O_2/O_3 SYSTEM

• In order to verify the possibility to improve the oxidant consumption for advanced photodegradation of CBs (tens μg/l), were tested the both agents (O_3 and H_2O_2) in the following experimental conditions:

– fixed H_2O_2 dose (~ 21 mg/l);

– variable O_3 doses (9–60 mg/l) with simultaneous variation of reaction/irradiation time, between 10–60 min;

• The degradation efficiencies of TCB (32.2 μg/l) and HCB (7 μg/l) are increasing with the increase of •OH production (i.e. – total oxidants dose), the variation domain being: 84–99% for TCB and 96–99.7% for HCB;

• The highest efficiencies (η>99%) are obtained for OH4 sample (initial oxidant dose = 30 mg O^*/l), with residual concentrations for the specific xenobiotics placed under the admitted limits in the treated effluent;

• The COD removal yields in the above-mentioned conditions are varying between 23 and 39%, and the pH of the treated effluent presented a similar evolution as those registered for UV/O_3 system (slight alkalisation).

CONCLUSIONS

The obtained results of advanced oxidation tests (UV/H_2O_2, UV/O_3 and $UV/H_2O_2/O_3$), which were performed to remove xenobiotics as trichlorobenzene and hexachlorobenzene below the admitted concentrations levels for agricultural purposes emphasised the followings aspects:

- AOP offers the most effective way of oxidising organic contaminants to less harmful compounds, and at the same time the possibility of advanced disinfection of biological effluent by UV radiation;
- However, for economical reasons and from the feasibility point of view, the UV/H_2O_2 system is proposed as tertiary treatment step for the effluents of municipal WWTPs;
- The effluent can be used for agricultural purposes taking into account the salinity indicators and other parameters stipulated in the Romanian standard referring to irrigation water.

REFERENCES

1. Directive 76/464/EECN.
2. B. LANGLAIS, D. A. RECKHOW, D. R. BRINK: Ozone in Water Treatment. Applications and Engineering. Lewis Publishers, USA, 1991.
3. M. I. STEFAN: Advanced Oxidation Processes for Water and Wastewater Treatment. Fundamentals of UV Photolysis (Ed. S. A. Porson). IWA Publishing, 2004, 8–33.
4. M. DIMEGHANI, O. K. ZAHIR: Kinetics and Mechanism of Chlorobenzene Degradation in Aqueous Samples Using Advanced Oxidation Processes. J. Environ. Qual., **30**, 2063 (2001).
5. R. ANDREOZZI, A. INSOLA: Reactivity toward Ozone of 2-hydroxypyridine in Aqueous Solution. Ozone Eng. Sci., **14**, 177 (1992).
6. R. ANDREOZZI, A. INSOLA: Quinoline Ozonation in Aqueous Solution. Water Res., **26**, 639 (1992).
7. J. R. BOLTON, E. LIPCZYNSKA-KOCHANY: Flash Photolysis/HPLC application. Environ. Sci. Technol., **26**, 259 (1992).

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