APPLYING OF PHOTOLYTIC PROCESSES IN ADVANCED DEGRADATION OF SOME XENOBIOTICS FROM MUNICIPAL WASTEWATER

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Abstract
This paper presents the systematic researches for removal of xenobiotics (trichlorobenzene-TCB, hexachlorobenzene-HCB) from the effluent of classical municipal wastewater treatment plant in order to reuse it for agricultural purposes.
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 TCB and HCB taking into account tested operating parameters were performed.
The operating parameters with significant influence upon the removal efficiencies of chlorobenzenes in homogeneous 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.

KEY WORDS: trichlorobenzene, hexachlorobenzene, AOPs, photolysis, ozonation

INTRODUCTION

In the context of EU environmental legislation the 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 so, 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 with 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 (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

There were tested the followings advanced oxidation systems in order to remove chlorobenzenes (CBs):

- UV/H_2O_2;
- UV/O_3;
- $UV/H_2O_2/ O_3$.

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). This one 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 was added TCB and HCB.

The composition of filtered biological effluent 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;
- COD: 61-88 mg O_2/l;
- TCB: 0.4-32.2 μg/l;
- HCB: 0.088-7 μg/l;
- presence of microbiological load (fecal coliforms, aerobic heterotrophic bacteria).

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;
- **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 DISCUSSIONS

The results of advanced oxidation tests in order to remove TCB and HCB are emphasized in the frame of tables no. 1÷3, 5, 6 as characterization 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).
The comparative evaluation of main microbiological indicators for the treated samples (UV/H_2O_2 system) is presented in the table no. 4.

UV/H_2O_2 system

- ***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 1 - 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 realized for the H_2O_2/CBs ratios 12 - 13/1 (table 2 - TCB res. ≤ 0.15 μg/l, HCB ≤ 0.01 μg/l)
  - the maximal yield of COD removal is about 50% for the highes 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 H_2O_2/CBs = 3.1/1 (table 3), the removal efficiencies of specific organic micropollutants (TCB, HCB) emphasizes an increasing evolution with irradiation/reaction time (τ 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 (hours), the subsequent degradation of these compounds might lead up to

mineralization. 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 4). As tertiary treatment, UV radiation as an environmentaly technology is selected for disinfection of municipal WWTPs effluents before its discharging into natural receivers.

UV/O_3 system

- ***Influence of ozone dose***
  - The photooxidation 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 tables 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 ascendent 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 photooxidation 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), it was 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 concentartions 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 alkalization).

CONCLUSIONS

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

- AOP offers the most effective way of oxidizing organic contaminants to less harmfull compounds, and in 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 tretment 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 Romanian standard referring to irrigation water.

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