Cavitation Based Advanced Oxidation Processes for Wastewater Treatment – Comparison of Hydrodynamic and Sonocavitation Systems

Boczkaj G.*, Gągol M., Fedorov K., Cako E.

Gdansk University of Technology, Faculty of Chemistry, Department of Process Engineering and Chemical Technology, G. Narutowicza 11/12 Str. 80-233 Gdansk, POLAND.

*corresponding author: e-mail: grzegorz.boczkaj@pg.edu.pl

Abstract

Cavitation based advanced oxidation processes (Cav-AOPs), are a promising alternative to currently used wastewater treatment technologies. Amplified interest in this "hot" topic results in increased number of research on several aspects relating to formation of cavitation phenomena and its utilization for wastewater treatment as well as hybrid processes based of application of external oxidants effectively converted to radical species in cavitation conditions. The paper discusses a state of the art of cavitation based AOPs, as well as presents recent developments in this field of our research group. The principles of cavitation combined with AOPs will be presented followed by evaluation of their effectiveness in oxidation of organic contaminants and comparison of hydrodynamic and acoustic cavitation processes used for same type of pollutants. An examples of degraded particular pollutants will include chlorinated and nitro derivatives as well as other emerging environmental pollutants. Applications for disinfection of water will be also addressed. The paper will present also results of studies on degradation of pharmaceuticals as well as pre-treatment of real post-oxidative effluents formed during bitumen production as an examples of possible implementation of cavitation based processes in real industrial scenario.

Keywords: AOP; wastewater treatment; hydrodynamic cavitation; sonocavitation; acoustic cavitation.

1. Introduction

Cavitation based Advanced Oxidation Processes (Cav-AOPs) are currently a one of "hot" topics in chemical engineering and environmental sciences [1-2]. A recognized as a destructive and strongly undesirable phenomena in the industry, due to its destructive activity to the fittings of the process installations, revealed to be possible to be used in positive manner as a source of energy for chemical reactions. During the implosion of cavitation bubbles, a focused energy and resulting high temperature allows to effectively degrade many chemical compounds present in the cavitated liquid phase [3-8]. The main reactions taking place in the cavitation zone are reactions of thermal decomposition of chemical moieties as well as oxidation reactions with dissolved oxygen and hydroxyl radicals produced in this conditions.

This paper presents recent developments in the field of Cav-AOPs. Studies were performed for model effluents as well as real industrial effluents for evaluation of treatment effectiveness regarding several groups of organic compounds (aromatic hydrocarbons, sulfur, nitrogen and oxygen containing organic compounds) as well as sulfide ions. A by-products formation issue was evaluated in respect to process parameters of cavitation, addition of external oxidants as well as composition of the aqueous matrix.

2. Materials and Methods

All chemicals were of min. 99% purity. The hydrodynamic cavitation as well as sonocavitation large laboratory scale treatment systems were described in our previous papers [3-5].

Model effluents were prepared by mixing of calculated dose of each pollutant with aqueous matrix (deionized water + *depending on the studies* pH correction by acid or base addition + *depending on the studies* inorganic salts). Real effluents were obtained from local refinery – a post-oxidative effluents from bitumen production with high load (and wide variety) of organic pollutants were used in these studies.

During the treatment process a samples were collected for process analysis. Details of analytical procedures regarding control of typical WWT parameters (pH, COD, BOD, sulfide ions) were described in [3-5]. A dedicated papers refer to procedures based mainly on gas chromatography and mass spectrometry (GC-MS) for detailed analytics regarding oxygen [9], sulfur [10], nitrogen [11] containing compounds, carboxylic acids [12] and aromatics [13].

3. Results and Conclusions

Application of hydrodynamic cavitation or acoustic cavitation as standalone treatment process is effective for degradation of several groups of organic compounds. Optimization studies revealed a quite

uniform optimal conditions for degradation of organic pollutants under cavitation phenomena – characterized by cavitation number of σ_{cav}=0,14. The effectiveness in relation to BTEX and volatile organosulfur (VSCs) compounds exceeded 90% after 180 min of the treatment. Comparison of these two alternative methods of cavitation effect generating reveals that hydrodynamic cavitation (H-Cav) is about 5-10% more effective comparing with acoustic cavitation (S-Cav) for the individual model compounds - it follows from the higher intensity of cavitation in the throat of a Venturi tube than in the operating zone of ultrasonic transducers (for 40kHz frequency – commonly used for sonocavitation). These results were obtained at strongly basic pH (approx.10.5), which indicates that Cav-AOPs have applicational value for treatment of many types of industrial effluents which are formed under these conditions. Some types of effluents contain high concentration of sulfide ions, which inhibits the possibility of their pH change to acid where several types AOPs are very effective. Cav-AOPs seems to be a good solution for such issues. Same time, addition of external oxidants allows to speed up the treatment process. A combined process of cavitation with peroxone (simultaneous injection of O_3 and H_2O_2) allows to obtain total degradation of BTEX and VSCs in 60 minutes of treatment. Comparison of sole cavitation processes in terms of by-products formation reveals that for both conditions several nitro-derivatives are formed – which can be degraded if the treatment process is aided by external oxidants.

Studies of same processes for application to real industrial effluents proved their performance, however, due to high load of organic pollutants (COD approx. 10 000 mg of O_2/dm^3) the needed treatment time is doubled. Same time, total pollution load – expressed by COD changes – is lowered by 10% for individual cavitation processes. Highest effectiveness (40% of COD reduction) was obtained for combined process of hydrodynamic cavitation and ozonation. Also for treatment of real effluents it was confirmed, that H-Cav and S-Cav provide comparable effectiveness – with a slight better performance of H-Cav along with much lower costs of the treatment in terms of energy consumption as well as investment costs.

In terms of sulfide ions, the studies revealed highly effective degradation obtained for processes based on sole use of cavitation phenomena. Studies performed for H-Cav and S-Cav confirmed total removal of sulfide ions in 180 minutes. A combined process with peroxone allows to obtain >99% degradation in time of 15 minutes and total abatement up to 30 minutes.

Cav-AOPs revealed to be synergistic with classic AOPs. The synergy relates to higher rate constants for combined processes and higher yield of radical species formed from external oxidants. This approach allows to extend the applicability pH range of hydrogen peroxide to basic pH conditions – an effective formation of hydroxyl radicals takes place under cavitation conditions instead of H_2O_2 decomposition by hydroxyl ions. Regarding ozonation and peroxone technology – cavitation allows to increase the mass transfer of ozone into the aqueous phase resulting in higher utilization of the dose of ozone. Performed studies confirmed also a synergistic effects in relation to persulfates. Cavitation phenomena effectively activate the persulfate yielding in formation of sulfate radicals. In overall a synergism values obtained during the studies are between 1.2-2.0.

An interesting behavior was observed in relation to treatment effectiveness as well as by-products formation of cavitation processes performed in presence of different inorganic acids. Our studies confirmed significant increase of degradation effectiveness of Cav-AOPs performed in presence of sulfuric acid. It follows form the in situ formation of sulfate radicals in the collapse zone of cavitation bubbles.

In overall, several new achievements were obtained in terms of industrial and environmental practice for water and wastewater treatment, which proved usefulness of Cav-AOPs and their potential for routine applications.

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