



Vancouver, Canada

May 31 – June 3, 2017/ Mai 31 – Juin 3, 2017

TOXICITY AND BIODEGRADABILITY STUDY ON ENHANCED PHOTOCATALYTIC OXIDATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN OFFSHORE PRODUCED WATER

Liu, Bo^{1,2}, Chen, Bing¹, Zhang, Baiyu¹, Zheng, Jisi¹ and Liang, Jing¹

¹ Northern Region Persistent Organic Pollution Control (NRPOP) Laboratory, Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada

² bo.liu@mun.ca

Extended Abstract:

Photocatalysis has showed excellent performance in oxidizing and mineralizing polycyclic aromatic hydrocarbons (PAHs). However, the efficacy of the sole technology could be significantly diminished in offshore produced water (OPW) due to its complicated composition. The prolonged retention time might not meet the requirements in the field because of the daily heavy discharge of OPW. It may further lead to the incomplete degradation of organics and the generation of intermediates with higher toxicity and persistence. Photocatalysis coupling with ozonation was proved to be a better solution in treating vary types of wastewater. Therefore, the integrated approach was applied in the treatment of PAHs in OPW. Glass slides coated with immobilized TiO₂ was used as catalysts in the process. The Microtox® toxicity and biodegradability of untreated, ozone treated and integrated process treated OPW effluents were evaluated.

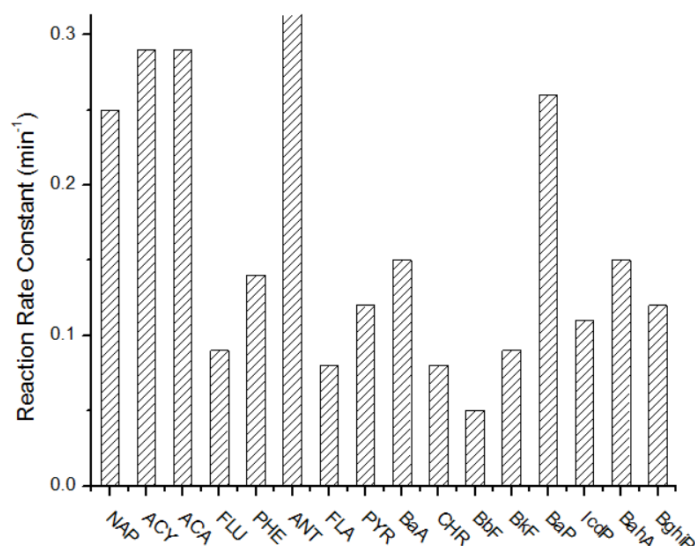


Figure 1: First order degradation rate constants of 16 PAHs in the integrated ozonation and photocatalysis process

The degradation of PAHs in the integrated ozonation and photocatalysis system was illustrated in Figure 1. NAP, ANY, ANA, PHE, ANT, BaA and BaP were completely removed within 15 minutes. 90% of 16 PAHs

were degraded within 1 hour. Only BbF was more resistant but the concentration was reduced to a negligible level. The system showed a promising performance in degrading PAHs in produced water.

PAHs removal of integrated ozonation and photocatalysis was simulated with the apparent-first-order kinetics. In general, almost all the correlation coefficients (R^2) between the simulated model and experimental data in the integrated system were higher than 0.9, indicating a good fitness of the model. In comparison with ozonation, the reaction rate constants of almost all the PAHs were enhanced in the integrated system. Especially for the highly persistent and toxic compounds such as BaA, BaP and BghiP, their reaction rate constants were increased from 3 to 20 times. It was indicated that the significant enhancement by integrating photocatalysis and great potential of the developed method for produced water treatment.

The compounds with aromatic structure can be quickly degraded by the presence of ozone, UV light and TiO_2 , as more than 90% of total phenols and PAHs were removed within 15-minute treatment time. However, aliphatic hydrocarbons, especially for those with higher molecular weight were relatively resistant to the system. The removal rate of aliphatic hydrocarbons was 23.8%.

Most of PAHs have the toxicity values lower than 1 mg/L. In addition, the concentration of phenols is much higher than their EC_{50} values (15.1 mg/L), the toxicity of OPW is strongly related to their PAHs and phenols' concentrations. The depletion of PAHs during the treatment strongly increased the EC_{50} values of treated OPW. The ozonated by products were proved as a key factor contributed to the toxicity of the effluent, especially the oxidative products of bromide (e.g. bromoform and bromate) was linearly correlated with the acute toxicity. In ozonation process, tribromomethane ($CHBr_3$) and bromodiodomethane ($CHBrI_2$) was dramatically produced and persisted as high as 1000 ppb. The integration with photocatalysis reduced the concentration of these DBPs to a much lower level, as the $CHBr_3$ was declined to 8.3% of its peak concentration, which significantly reduced the toxicity of OPW effluent.

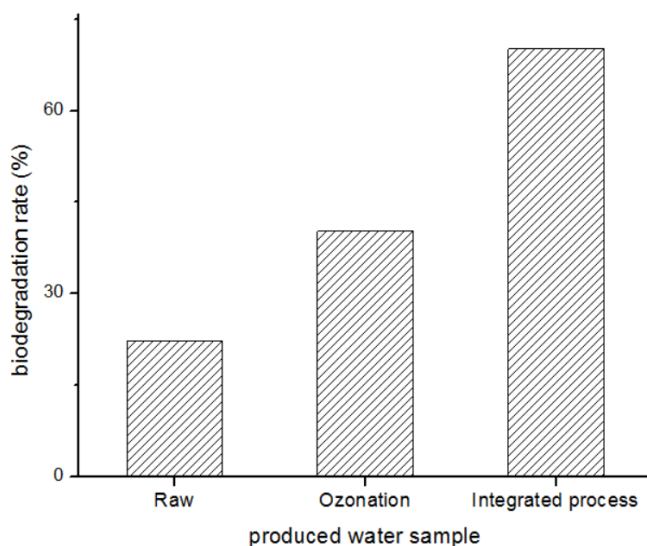


Figure 2: comparison of the biodegradation rates of untreated, ozonated, and integrated treated OPW samples

The advance of the integrated system was further proved by the enhanced biodegradability of OPW effluent (Figure 2). Compared with the degradation rates of untreated and ozonated samples, the effluent treated by the integrated system has the largest reduction rate of total organic carbon. The lower concentration of toxic compounds and the higher concentration of more biodegradable compounds produced by the integrated system thus led to the highest biodegradability of the treated OPW effluent. In this study, the integrated process showed a great potential in the effective treatment of OPW, the reduction of toxicity and the enhancement of biodegradability.