Next-generation electrochemical technology for the treatment of hospital wastewater: electrogenerated sulfate radicals for complete destruction of persistent pollutants (ELECTRO-HOSPITAL)

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Hospitals produce large quantities of chemically and microbiologically loaded effluents with high cytotoxic and genotoxic potential. Given the numerous activities practiced in hospitals, hospital wastewater effluents contain a plethora of different chemicals: drug residues, heavy metals, radioisotopes, organohalogens, resulting in particular from the use of disinfectants, as well as pathogenic microorganisms, some of which are multi-resistant to antibiotics. Several studies have reported increased toxicity of hospital wastewater compared to domestic sewage. Hospital wastewater effluents have been identified as the primary sources of DNA-damaging compounds, and are considered as the major source of antibiotic resistance genes in the environment. In some occasions, hospital effluents were found to exhibit significantly higher pollution, up to 3.5 g L^{-1} of chemical oxygen demand compared to municipal sewage (i.e., 100-500 mg L^{-1}). In industrialized countries hospital wastewater is rarely treated prior to the discharge into public sewer system, although chlorine disinfection may be practiced for pathogen control purpose. This makes hospitals potential hotspots for many persistent and/or toxic pollutants that undergo very little degradation in sewage treatment plants. Given the large volume of toxic products consumed in hospitals, implementation of efficient, on-site wastewater treatment is necessary in order to reduce the impact of hazardous pollutants on the environment. There is no established technology for the treatment of hospital wastewater. Biological treatment is inefficient in removing more persistent and/or toxic organic contaminants such as antibiotics, antiepileptic drugs, X-ray agents, and chlorinated organics formed in the reaction of disinfectants used in hospitals (e.g., NaOCl) with the organic matter. Ozonation can remove some antibiotics at high rates but is inefficient for X-ray agents and requires very high O3 dosages. Advanced oxidation processes are considered as more efficient than ozonation, yet they are still not capable of degrading organohalogens.

The project ELECTRO-HOSPITAL investigates the performance of electrochemical oxidation for the treatment of hospital wastewater, based on electrochemical generation of sulfate and hydroxyl radicals. Electro-oxidation at boron-doped diamond (BDD) anodes is known to efficiently electrogenerate strong oxidant species, hydroxyl radicals ($^{\bullet}OH$, standard reduction potential, E^0=1.89-2.72 V) from the electrolysis of water at the anode, without any addition of chemicals. However, hydroxyl radicals are very non-selective and easily scavenged by the background matrix. In recent years, an innovative oxidation technology based on the generation of another strong oxidant species, sulfate radical ($SO_4^{\bullet-}$, E^0=2.50-3.10 V), has obtained great scientific and technological interest for wastewater treatment and in situ chemical oxidation. Sulfate radicals are known for their high selectivity for the oxidation of organic contaminants. The main limitation of oxidation processes based on sulfate radicals is that they are produced from activation of persulfate or peroxymonosulfate via heat, UV, alkali or transition metal catalysis, which are all very impractical activation methods.

In this project, we have discovered that besides forming hydroxyl radicals, BDD anodes are also capable of generating sulfate radicals in the presence of sulfate ions. We have observed around 10 times faster

oxidation rates of several persistent contaminants typical for hospital wastewater (e.g., X-ray agents, antibiotics, antiepileptic drugs) in the presence of sulfate concentrations as low as 150 mg/L. Sulfate is widely distributed in nature and may be present in natural waters at concentrations ranging from a few to several hundred mg/L. Hospital wastewater typically contains up to 100 mg/L of sulfate. However, the content of sulfate can be significantly higher, up to 1,000 mg/L, when hospital waste incineration is applied, due to the contributions of the wash tower effluent from the incinerator.

One of the major outcomes of the project is the elucidation of the mechanism of sulfate ions oxidation at the BDD anode (Figure 1). We have discovered that, besides sulfate radicals, sulfate ions are also oxidized to persulfate which is further activated at the anode surface, and may contribute to the oxidation and mineralization of the organics. The formation ofsulfate-based oxidants was confirmed through elucidation of the mechanism of oxidation of X-ray agents typical for hospital wastewater, iopromide and diatrizoate (Radjenovic & Petrovic, Water Research, 2016). Furthermore, we have seen that the presence of sulfate ions in the system decreases the detrimental effect of chloride and formation of toxic organochlorine byproducts (Radjenovic & Petrovic, Water Research, submitted). These findings are highly relevant for real life application of electrochemical treatment, as formation of chlorinated byproducts is one of its main limitations. The project findings suggest that this can be significantly decreased by increasing the amount of sulfate. The added sulfate could be separated after the anodic oxidation using electrodialysis, to avoid issues with increased sulfate concentration in wastewater.

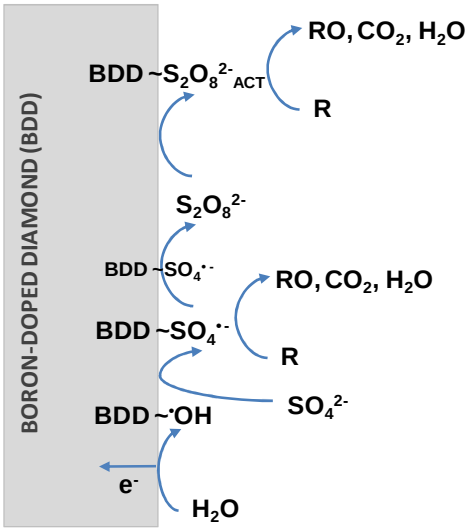

Figure 1 *Mechanism of sulfate ion oxidation at BDD anode (Farhat, Tait, Keller & Radjenovic, Envviron Sci Technol, 2015).*

Although the focus of the project was on the contaminants characteristic for hospital wastewater, activation of sulfate at BDD electrodes may have significant implications in the treatment of sulfate-containing waters (e.g., wastewater from fermentation industry and other types of industrial wastewater). Moreover, it may be a feasible alternative to persulfate injection and activation applied in *in situ* chemical oxidation (ISCO) treatment of contaminated groundwater. By placing an electrochemical reactive barrier, one can activate the sulfate present in contaminated groundwater plume to degrade persistent organic contaminants.

Project website: http://www.icra.cat/projects/next-generation-electrochemical-technology-treatment/78

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