Degradation of Emerging Groundwater Pollutants via Advanced Oxidation Processes

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Fenton's Reagent

The Fenton method is often the first AOP studied when working with a new organic pollutant due to the simplicity of the experiments. This method is based on the catalytic decomposition of hydrogen peroxide by ferrous ions to produce hydroxyl radicals, as shown in the figure. A large downfall of the Fenton method is the production of iron sludge from the ferric oxide produced.

$$Fe'' + H_2O_2 = Fe''' + OH' + OH$$
$$OH + H_2O_2 = H_2O + HO_2$$
$$HO_2 + H_2O_2 = O_2 + H_2O + OH$$
$$OH + Fe'' = Fe''' + OH',$$

Figure 1: Mechanism for Hydroxyl Radical Formation Using Fenton's Reagent

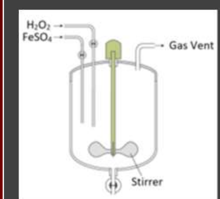

Figure 2: Example Reactor for Oxidation of Pollutants Using Fenton's Reagent

To reduce this sludge, the reaction can be run under acidic conditions, which increases the solubility of the ferrous ion. UV light applied to the system has also been proven to be efficient in reducing the iron sludge due to the increase of hydroxyl radicals in the presence of light.

UV + Hydrogen Peroxide

Combining hydrogen peroxide and UV light has been proven efficient to remove toxic organic pollutants. This process forms the hydroxyl radical by photolysis of hydrogen peroxide, as shown in the reaction in Figure 3.

$$H_2O_2 \xrightarrow{h\nu} 2\,OH^{\circ}$$

Figure 3: Mechanism for Hydroxyl Radical Formation by Photolysis of Hydrogen Peroxide

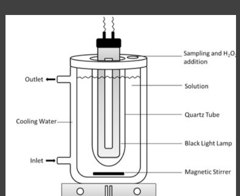

Figure 4: Example Reactor Set-Up for Oxidation of Pollutants Using UV Light + Hydrogen Peroxide

While effective at removing pollutants, this AOP also offers the potential of being implemented easily as UV is already widely accepted and implemented as a disinfectant. The combination of hydrogen peroxide and UV light could also be integrated with downstream biological processes as the intermediates formed in this oxidation process are biodegradable.

Background

In recent years, many commonly used compounds have been found to be persistent in the environment with many of them suspected to be carcinogens, such as 1,4-Dioxane and Perfluorooctanoic Acid (PFOA). While various methods are currently used to remove these contaminants from groundwater, Advanced Oxidation Processes (AOPs) have proven to be a viable, economical alternative. The four AOPs outlined in this poster focus on creating and using hydroxyl radicals to oxidize organic compounds into stable inorganic compounds.

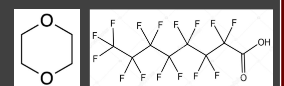

Figure 5: Pollutants of Interest, (a) 1,4-Dioxane and (b) Perfluorooctanoic Acid (PFOA)

Analytical Methods

Solid Phase Microextraction (SPME) uses a fiber to adsorb the analyte which is then inserted into an oven and heated to remove the analyte from the fiber. From there the analyte moves in the gas phase into the mass spectrometer for analysis.

High-Performance Liquid Chromatography (HPLC) is an analytical method that uses a mobile and a stationary phase to separate components based on the components' affinity for each phase. It is typically used for non-volatile compounds that cannot be analyzed with gas chromatography.

Mass Spectrometry is used in tandem with the analytical methods above to identify compounds based on their mass and their relative abundance via peak height.

References

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Haber, F., & Weiss, J. (1934). The Catalytic Decomposition of Hydrogen Peroxide by Iron Salts. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, *147*(861), 332–351.

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Peroxone

The peroxone process involves the reaction of ozone with hydrogen peroxide which results in highly reactive hydroxyl radicals. The commonly accepted mechanism for the formation of the hydroxyl radicals is shown in Figure 6.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
$$HO_2^- + {}^{\bullet}OH \rightarrow {}^{\bullet}O_2H + O_2 + {}^{\bullet}OH^-$$
$$HO_2^- + O_3 \rightarrow {}^{\bullet}OH + {}^{\bullet}O_2 + O_2$$
$$O_3 + OH^- + e^- \rightarrow HO_2^- + O_2$$
$$O_3 + H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}O_2^- + O_2 + H^+$$

Figure 6: Commonly Accepted Peroxone Process Mechanism

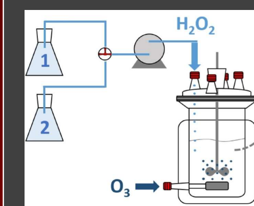

Figure 7: Example Schematic for Peroxone Reactor with Continuously Fed Hydrogen Peroxide

The peroxone process is carried out by sparging ozone through a reactor containing the pollutant and hydrogen peroxide that is either constantly fed or added in a single dose. This process has been proven in industrial conditions as an effective way to degrade pollutants.

UV + Ozone

The process combining UV radiation and ozone is very similar to that of UV and hydrogen peroxide. As shown in the reaction in Figure 8, hydrogen peroxide is formed from the reaction of ozone and water when exposed to radiation.

$$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 + O_2$$

Figure 8: Mechanism for Hydroxyl Radical Formation by Photolysis of Hydrogen Peroxide

The system then follows the same process as the combination of UV and hydrogen peroxide.

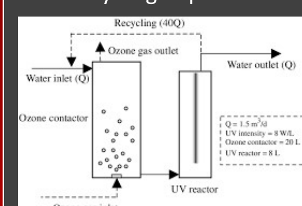

Figure 9: Example Reactor Set-Up for Oxidation of Pollutants Using UV Light + Ozone

As both ozone and UV light are already used for disinfecting processes, the AOP can be easily implemented. Conversion of the preexisting systems only require a change to a dual-wavelength UV lamp as well as providing a way for the ozone to enter and leave the UV reactor.