

Chemical Oxidation

Chemical oxidation technologies have been used for many years to degrade a wide range of pollutants in wastewater and drinking water.

Advanced chemical oxidation typically involves the use of chemical oxidants (e.g. ozone or hydrogen peroxide) to generate **hydroxyl** radicals (i.e. $\bullet\text{OH}$), one of the strongest oxidants known.

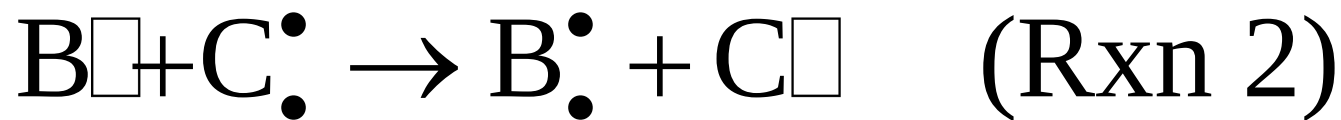
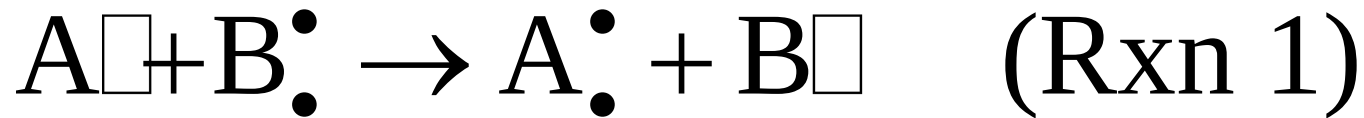
Hydroxyl radicals are reactive and non-selective, capable of rapidly degrading a number of organic compounds.

A brief description of the chemistry of radicals with specific reference to the hydroxyl radical follows.

Note: $\cdot\text{OH}$ is the same as $\text{OH}\cdot$

A free radical is a molecule that has an unpaired electron (represented by a dot next to the chemical structure, e. g., $A\cdot$)

A radical needs to pair its unpaired electron with another electron and will react with another molecule in order to obtain this missing electron. If a radical achieves this by "stealing" an electron from another molecule that other molecule itself becomes a radical (Reaction 1), and a self-propagating chain reaction is begun (Reaction 2).



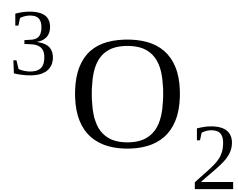
If a radical pairs its unpaired electron by reacting with a second radical, then the chain reaction is terminated, and both radicals "neutralize" each other (Reaction 3).



Triplet Oxygen:

Ordinary oxygen, O₂, is actually a pair of free radicals because each O has an unpaired electron. However, the electron spins of these electrons are parallel which make the O₂ molecule in the triplet state.

In the triplet state the molecule is not very reactive. This molecule can be symbolized as:

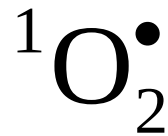




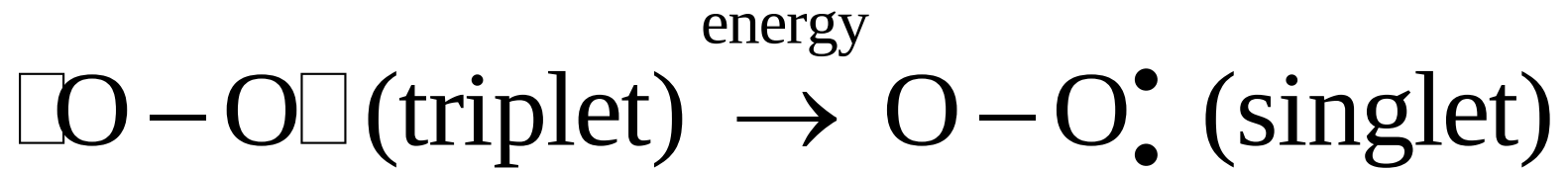
Triplet oxygen is the ground state of the oxygen molecule. The electron configuration of the molecule has two unpaired electrons occupying two degenerate molecular orbitals.

Unpaired electrons in degenerate orbitals can have the same spin, so the total spin S of the molecule is 1. This is known as a triplet configuration because the spin has three possible alignments in an external magnetic field.

Triplet oxygen can be activated by the addition of energy and transformed into reactive oxygen species. If triplet oxygen absorbs sufficient energy to reverse the spin of one of its unpaired electrons, it forms the singlet state. Singlet oxygen, abbreviated ,



has a pair of electrons with opposite spins; though not a free radical it is highly reactive.

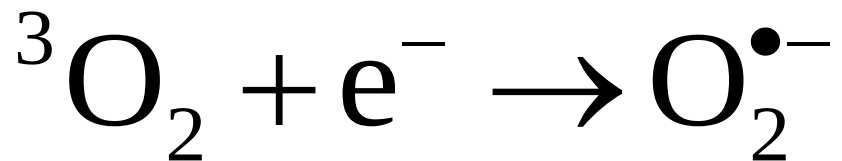


According to rules of physical chemistry the "relaxation" (excess energy loss) of singlet oxygen back to the triplet state is "spin forbidden" and thus singlet oxygen has a long lifetime for an energetically excited molecule. It must transfer its excess energy to another molecule in order to relax to the triplet state.

Superoxide:

Triplet oxygen can also be transformed into a reactive state if it accepts a single electron. The result of monovalent reduction of triplet oxygen is called superoxide, abbreviated $\text{O}_2^{\bullet-}$. Superoxide is a radical.

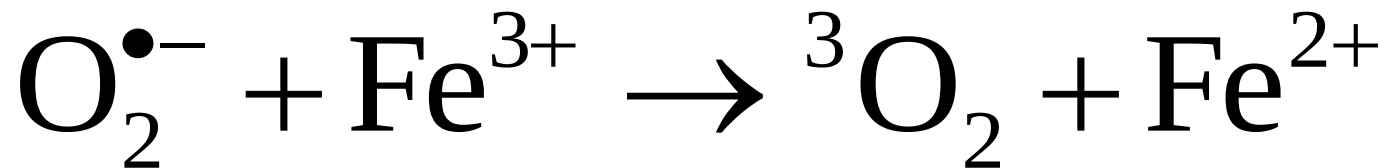
This reaction can be written as:



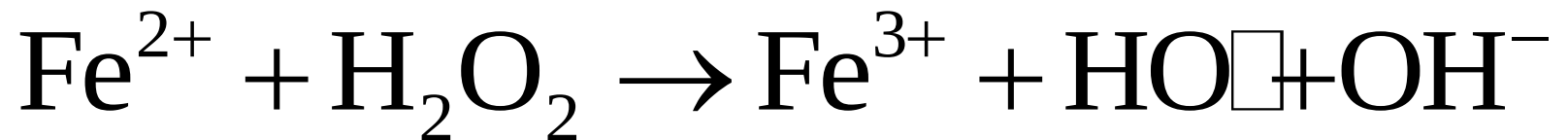
Superoxide is also important in the production of the highly reactive hydroxyl radical $\text{OH}^\bullet$

There are a number of ways that this radical can be produced. In most cases the superoxide acts as a reducing agent (donates electrons).

For example in the Fenton reagent reaction superoxide donates an electron to reduce Fe^{3+} .

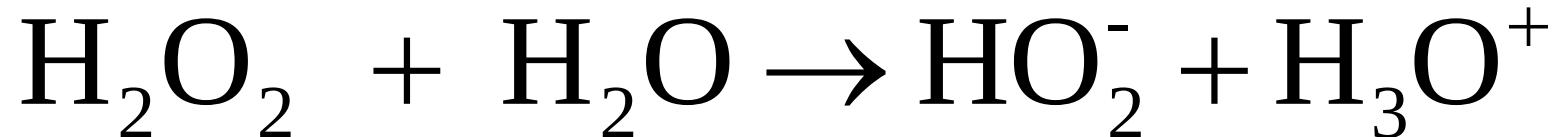


Fe^{2+} then catalyzes the breaking of the oxygen-oxygen bond of hydrogen peroxide to produce a hydroxyl radical ($\text{OH}\cdot$) and a hydroxide ion (OH^-):

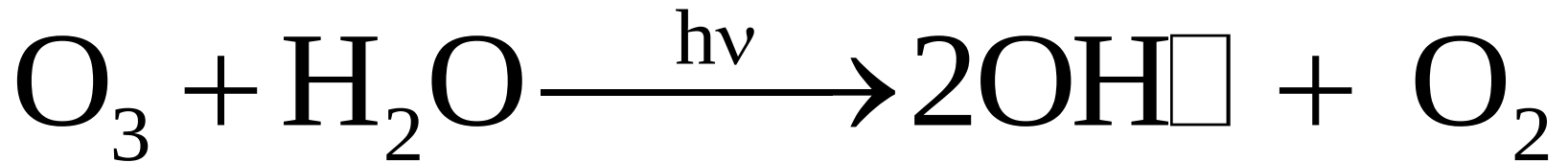


Advanced Oxidation Processes (AOP)

- Ozone/Peroxide:

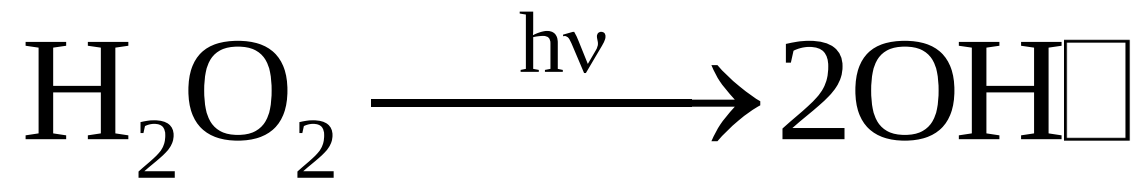


•UV/Ozone:



Considered less economical than $\text{O}_3/\text{H}_2\text{O}_2$ or $\text{H}_2\text{O}_2/\text{UV}$

- UV/Peroxide:



The UV oxidation process is generally done with low pressure lamps operating at 65 watts of electricity for ozone systems and lamps operating at 15kW to 60kW for hydrogen peroxide systems.

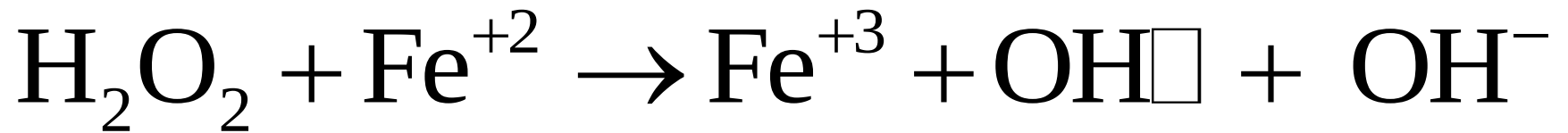
Limitations of UV/oxidation (O_3 or H_2O_2) include:

- The aqueous stream being treated must provide for good transmission of UV light (high turbidity causes interference).
- Free radical scavengers can inhibit contaminant destruction efficiency. Excessive dosages of chemical oxidizers may act as a scavenger.

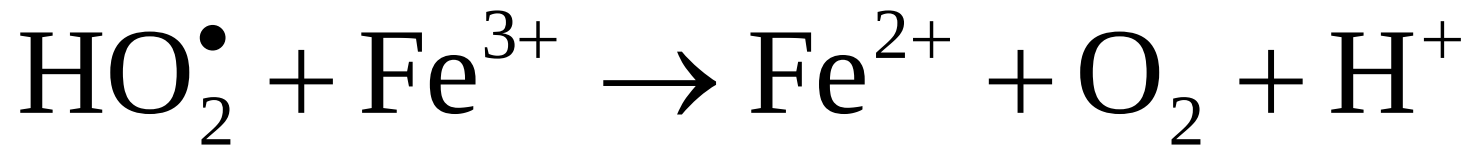
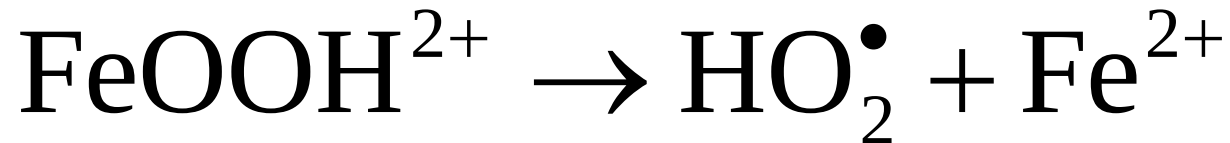
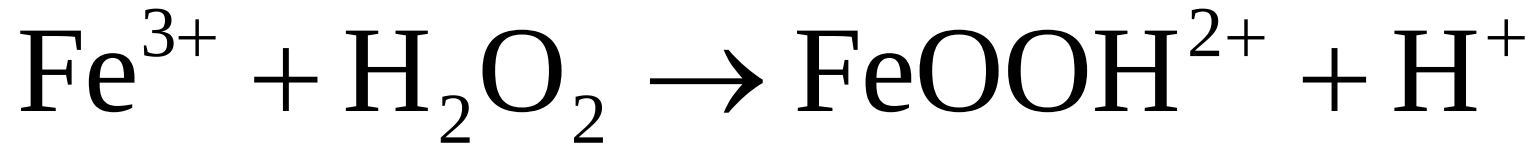
- The aqueous stream to be treated by UV/oxidation should be relatively free of heavy metal ions (less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling of the quartz sleeves.
- Costs may be higher than competing technologies because of energy requirements.

- Pretreatment of the aqueous stream may be required to minimize ongoing cleaning and maintenance of UV reactor and quartz sleeves.
- Handling and storage of oxidizers require special safety precautions

- Fenton's Reagent:



There are a complex series of chain reactions proceeding simultaneously which can regenerate Fe^{+2}



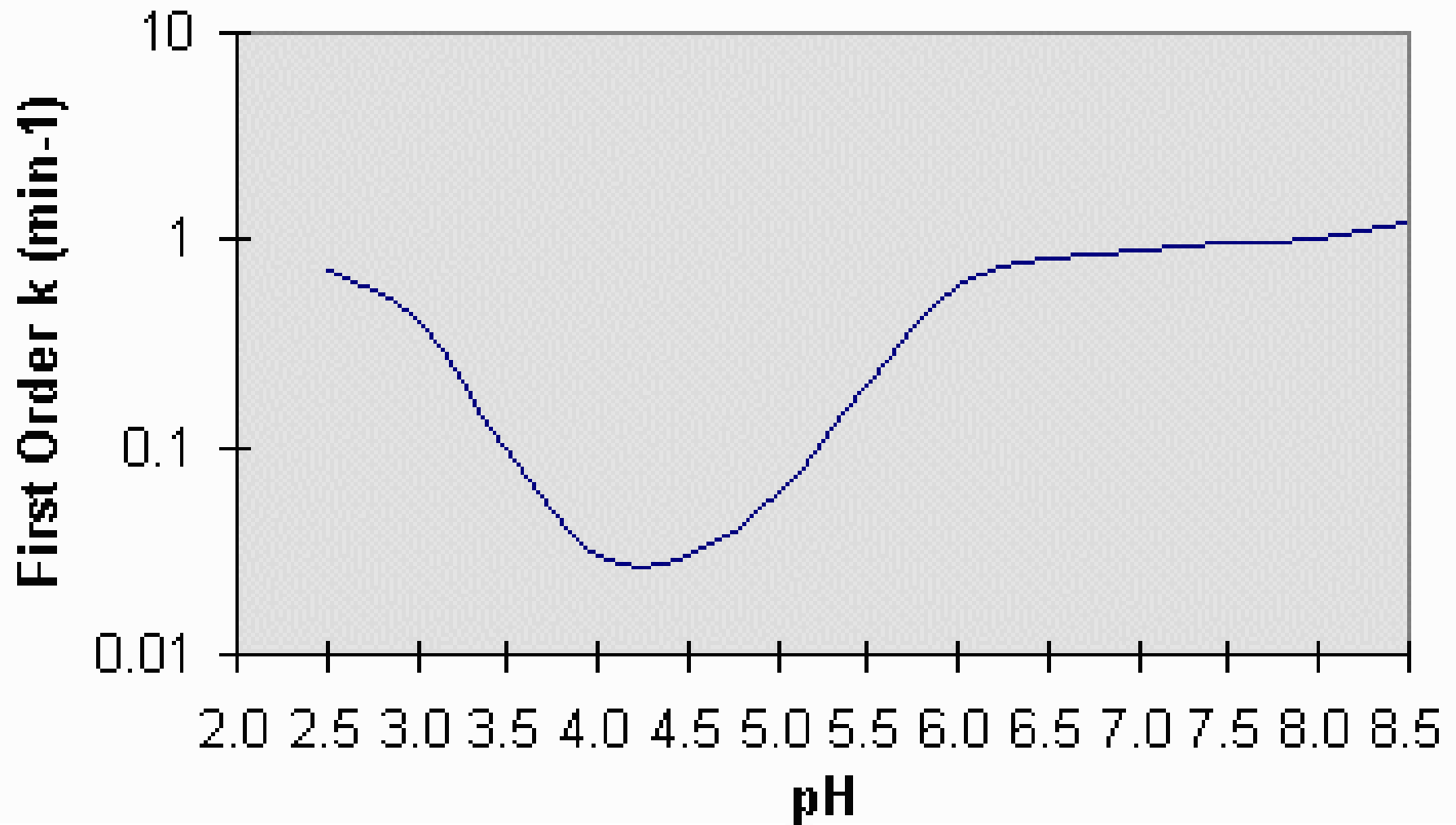
The combination of the above reactions results in a redox cycle where ferrous iron (Fe^{+2}) is converted to ferric iron (Fe^{+3}) and ferric iron is reduced back to ferrous iron. The rate of Fe^{+2} - H_2O_2 oxidation is significantly greater than Fe^{+3} - H_2O_2 reduction. Therefore, the generation rate of hydroxyl radical in solution is often rate limited by the regeneration of ferrous ion.

The procedure requires:

- adjusting the wastewater to pH 3-5;
- adding the iron catalyst (as a solution of FeSO_4);
- adding slowly the H_2O_2 . If the pH is too high, the iron precipitates as $\text{Fe}(\text{OH})_3$ and catalytically decomposes the H_2O_2 to oxygen

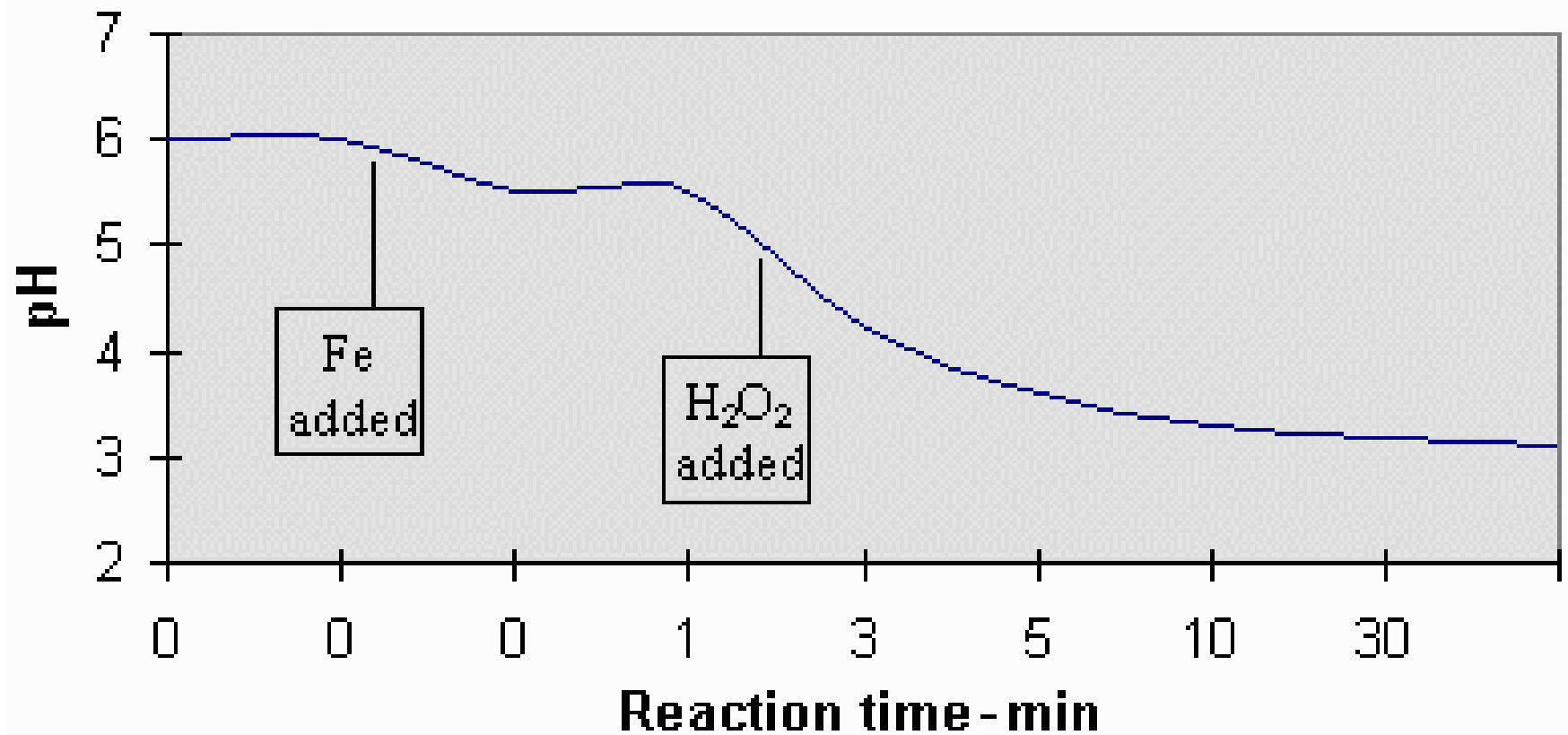
Typical Fe:H₂O₂ ratios are 1:5-10 wt/wt, though iron levels < 25-50 mg/L can require excessive reaction times (10-24 hours). This is particularly true where the oxidation products (organic acids) sequester the iron and remove it from the catalytic cycle. Fenton's Reagent is most effective as a pretreatment tool, where COD's are > 500 mg/L.

Effect of pH on Fenton's Reagent



pH will change during the dosing process as shown in the following figure. The first inflection is caused by the addition of FeSO_4 catalyst which typically contains residual H_2SO_4 . A second, more pronounced, drop in pH occurs as the H_2O_2 is added, and continues gradually. This drop in pH is attributed to the fragmenting of organic material into organic acids. The absence of such a pH decrease may mean that the reaction is inhibited.

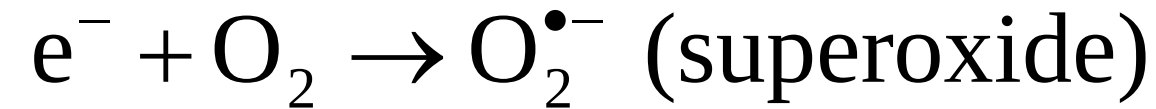
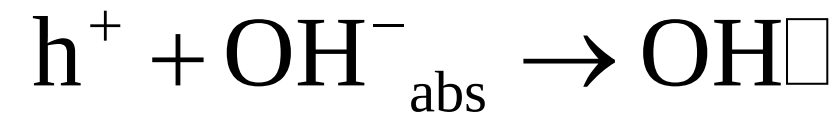
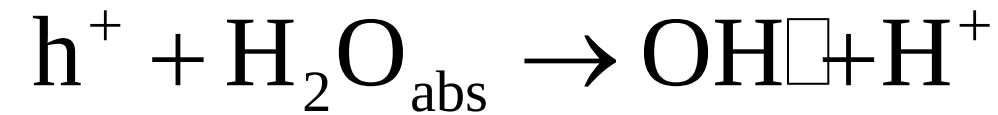
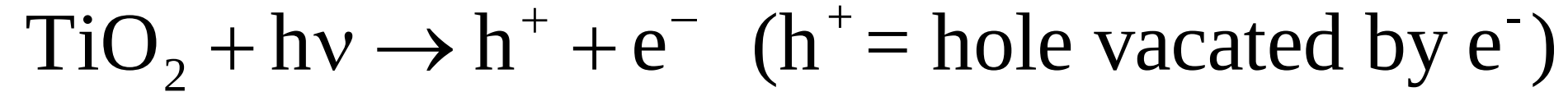
Typical pH Profile of Fenton Reactions



- Photocatalysis:

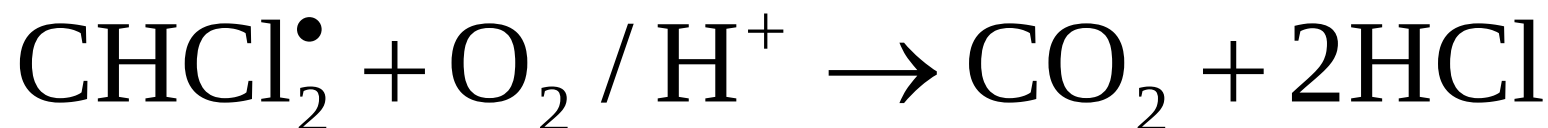
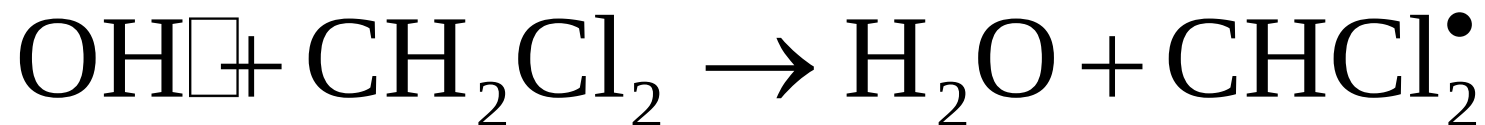
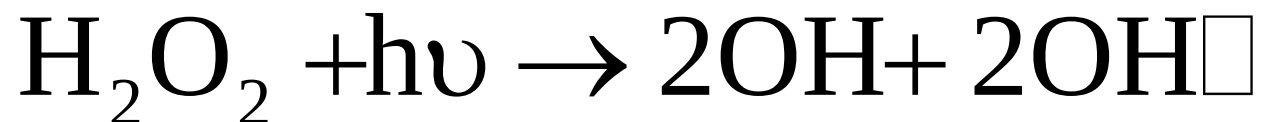
TiO_2 and UV produce hydroxyl radical

The process involves illumination of an aqueous suspension of a semiconductor. The light energy photogenerates electron hole pairs which can migrate to the interface where they react with adsorbed redox species. The process can be represented as:



Wavelength of irradiation is about 400 nm. Anatase TiO_2 is generally used. The process is subject to fouling and is limited to dilute solutions. Another problem is that the TiO_2 must be separated from the process water (to be reused). Applications are still in the developmental stage.

The following is an example of how the hydroxyl radical reacts with an organic (UV + peroxide oxidation of dichloromethane)



Advantages of AOP

- Effective in removing resistant organic compounds
- Capable of complete mineralization of organic compounds to CO₂.
- Not susceptible to the presence of toxic chemicals
- Generally produce innocuous end products
- Can be used to pretreat toxic compounds so that they can be bio-treated

Applications

$\text{O}_3/\text{H}_2\text{O}_2$ has gained the widest acceptance because of effectiveness and low cost.

$\text{H}_2\text{O}_2/\text{UV}$ has the advantage of simplicity (only chemical is H_2O_2 , cheap and soluble). Suited to small, minimum maintenance or intermittent operation systems. Some problems if materials in water absorb UV.

O₃/UV considered less favorable because of high pH requirement (chemical costs) but okay for low flows.

Least used are the TiO₂ systems although they have some advantages such as photocatalysts made be used, natural light may be used as a UV source, additional radical initiators are not required.

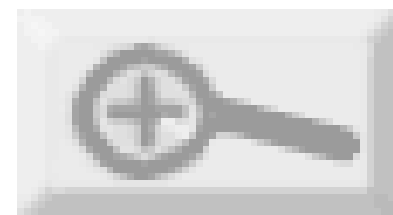
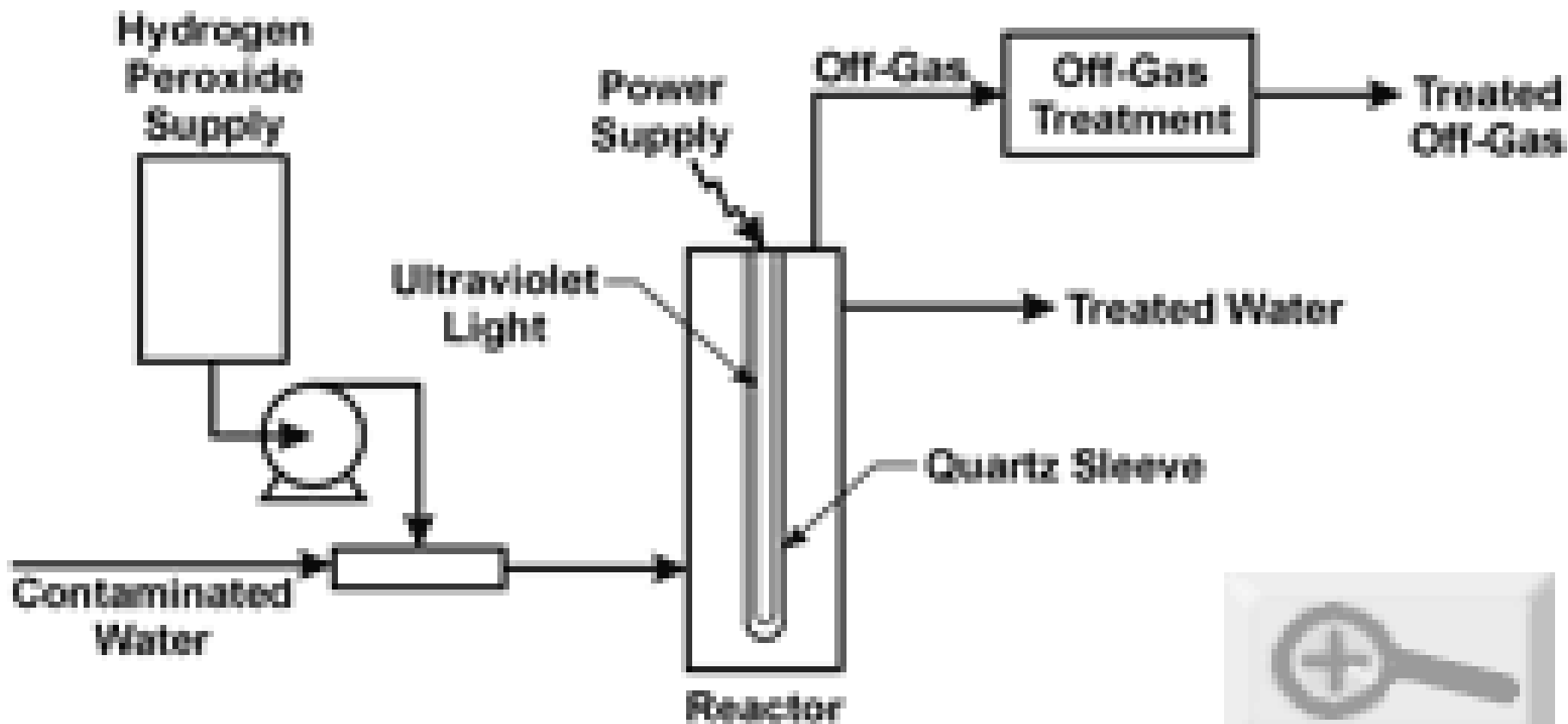
One of the operating issues that must be taken into account is the quantity of hydroxyl radical produced versus oxidant consumed. The following table list these theoretical amounts.

Table 7. Theoretical molar ratio of oxidants consumed to $\cdot\text{OH}$ radicals generated.

Process	O_3	H_2O_2	UV
$\text{O}_3\text{-OH}^-$	1.5	—	—
$\text{O}_3\text{-UV}$	1.5	(0.5)*	0.52 [†]
$\text{O}_3\text{-H}_2\text{O}_2$	1	0.5	—
$\text{H}_2\text{O}_2\text{-UV}$	—	0.5	0.5

*Hydrogen peroxide formed in situ.

[†]Moles of photon required for each mole of $\cdot\text{OH}$ radicals.



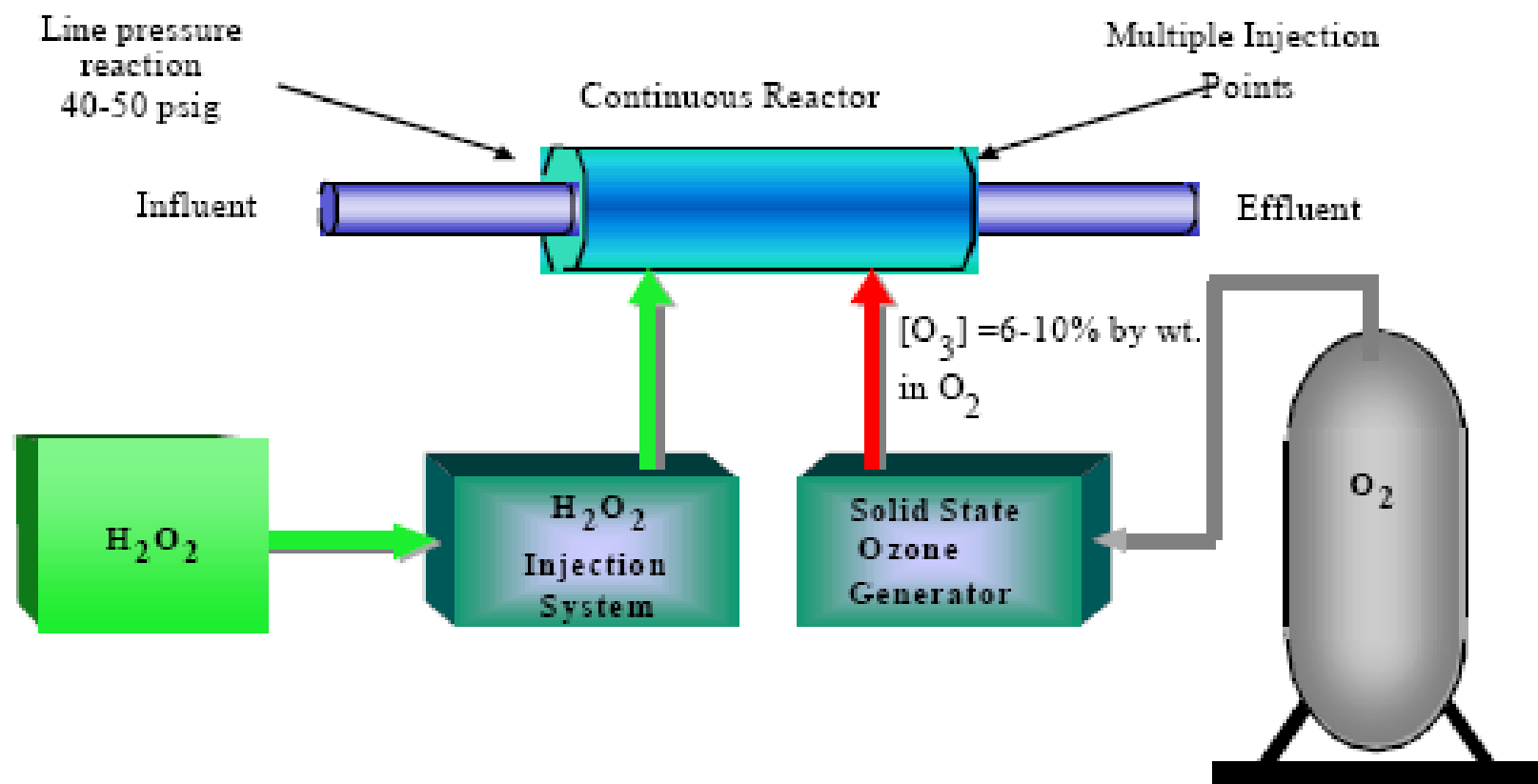


FIGURE 1. Schematic of HiPOx advanced oxidation system.

The following tables compare the effectiveness of various AOP's on the degradation of phenol (approx 100 mg/L).

Process	pH	Time (min)	% Reduction
O₃	5 – 3.4	80	80.6
O₃	5 – 3.4	80	58.3
O₃	6.8	80	90.4
O₃/UV	6.8	80	80.9
O₃/UV	9.3	80	92.5
O₃/UV	9.3	80	88.8

Process	pH	H₂O₂ (mM)	Fe(II) (mM)	Time (min)	% Reduction
Fenton	5-3	1.07	0.054	9	32.2
Fenton	5-3	2.45	0.054	9	58.0
Fenton	5-3	5.34	0.054	9	90.0
Fenton	5-3	10.7	0.054	9	100
Fenton	5-3	2.45	0.13	9	84.7
Fenton	5-3	2.45	0.26	9	87.2

Process	pH	TiO₂ (mM)	Time (min)	% Reduction
Photocatalysis	~6	0.05	150	42.2
Photocatalysis	~6	0.2	150	58.6
Photocatalysis	~6	0.6	150	74.4
Photocatalysis	~6	0.8	150	73.1
Photocatalysis	~6	2	150	73.4
Photocatalysis	~6	5	150	74.6

Approximate cost per kg of phenol destruction:

Process	Cost (\$/kg)
O_3/H_2O_2	2.93
O_3/UV	11.7
O_3	1.09
UV/H_2O_2	28.7
Fenton	2.61

Because the chemistry of wastewater matrices can be very different pilot testing is almost always required to test the technical feasibility of a specific AOP for a specific wastewater.