

P.G.SEMESTER-III

CC-XII

Environmental Chemistry and Green Chemistry

Unit-IV Green Chemistry : Def. & Obj.

Topic- Organic Waste Management (Part 2)

Dr. Jasmine Singh

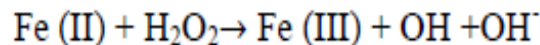
Assistant Professor

Department of Chemistry

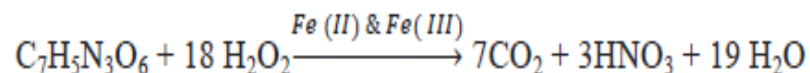
Maharaja College, Ara

Fenton reaction

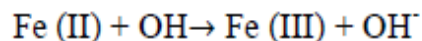
Fenton reaction is a chemical reaction involving the reaction of Fe (II) ions with hydrogen peroxide



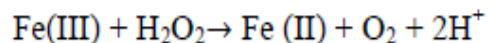
This reaction has a rate constant of about $70 \text{ M}^{-1} \text{ s}^{-1}$ at normal temperatures and a pH of 2-3. OH radicals can attack not only organics but also Fe (II), H_2O_2 at rates of the order of 10^7 - $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at normal temperatures. Because of their non-selective rapid reactions with various reducing agents in the solution, their steady-state concentration is very low (< nanomolar). TNT mineralization reaction is coupled with a Fenton reaction. It means that OH and HO_2 radicals, H_2O_2 , oxygen, and ferric ion formed in Fenton reaction degrades TNT. It is challenging to write the stoichiometric reaction in this multi-oxidant reaction system. Ideally, the stoichiometric reaction of TNT with H_2O_2 can be expressed as follows:



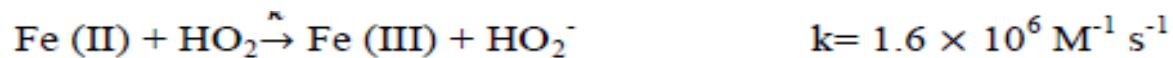
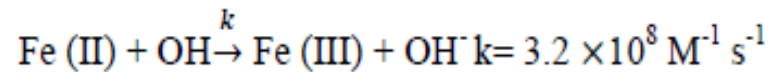
The above reaction does not take place directly without the presence of compounds such as ferrous salt in the reaction mixture to form OH radicals, which, in turn, form organic radicals. OH radicals also undergo single-electron reduction reactions such as the following:



Iron in the form of ferrous and ferric salts constitute the catalyst system for this reaction. Fe (III) can, slowly, reduce H_2O_2 by the following reaction with a rate constant value of $4.3 \cdot 10^{-3} \text{ s}^{-1}$ at 25°C : Activation energy of the reaction is 85.6 kJ/mol.



- HO₂ radicals, mentioned above, form as intermediates in this reaction. They are less reactive than OH radicals as exemplified below:



- No rational basis exists for selecting optimum reaction conditions for mineralization of a given organic compound in wastewater by AOP. Optimum conditions are determined based on experimentation. However, some commonalities, such as the following exist:
- Since OH radicals are non-selective, their loss through unwanted reactions is a definite possibility. Therefore, their generation in a sustained manner is a requirement for rapid mineralization. Reaction (2) is a non-stoichiometric source of OH radicals. Thus, iron in the divalent state is to be maintained for high OH concentration in solution. Fe (III) in the reaction (2) can be reduced back to Fe (II) by H₂O₂(reaction 5). The reaction rate is much slower. This **limitation** of Fenton reaction can be **overcome** by using photo-Fenton reaction as discussed below:
- TNT mineralization reaction involves the formation of different carboxylic acids as intermediates. A detailed mineralization mechanism was discussed. This fact can be taken advantage of in photo- Fenton reaction. Fe (III) forms complexes with carboxylic acids, and upon irradiation with U.V. or visible radiation, these complexes photolyze with a high quantum yield to produce Fe (II) and CO₂.

- This photolytic reaction contributes to CO₂ formation and TOC reduction directly. The best example is the oxalate complex of Fe(III), which decomposes with a quantum yield of nearly 1.0 upon irradiation in the UV-visible range. This principle is used in chemical actinometric measurements. Because of these factors, the photo-Fenton reaction was chosen for the mineralization of TNT. The reaction was monitored using total organic carbon (TOC) as the global parameter. The experiments revealed that mineralization could be achieved using photo-Fenton reaction, and TNT concentration could be reduced to below one ppm.
- Based on successful laboratory studies, a scaled-up facility of one cubic meter batch was installed with U.V.(253.7 nm) lamps of 75W each. The wastewater was brought to a pH of 2.5-3.0 using sulfuric acid to avoid hydrolysis of iron salts. Fe (II) concentration was initially maintained at 100 ppm. 30% hydrogen peroxide (250-300 mL of 30% strength) was introduced into the irradiated reaction mixture slowly in about an hour to avoid the accumulation of H₂O₂ in the reaction mixture, leading to its wasteful reaction with OH radicals as follows:



- Air sparging was done to mix the contents. Moreover, oxygen also reacts with carbon centered-radical intermediates to promote oxidation.

- The pilot experiments showed that TNT could be quantitatively mineralized to less than one ppm with a light energy expenditure of about two kWh/m³ of wastewater. Photo-Fenton reaction is quite versatile to mineralize a wide variety of organic compounds. Our studies showed that besides TNT, RDX and tetryl could also be mineralized.
- The authors have also developed methods to mineralize organic ion exchange resins used in demineralization applications using a photo-Fenton reaction. In this study, the solid resin was reactively solubilized using H₂O₂ under Fenton type reaction conditions to produce linear chains of the solubilized polymer. This was subjected to photo-Fenton reaction mineralization at room temperature quantitatively. The experiments were scaled to 20 liters Nuclear reactor decontamination aqueous formulations containing EDTA, ascorbic acid, and citric acid was also mineralized using photo-Fenton reaction in our studies. It is noteworthy that the carboxylic acids present in this mixture make photo-Fenton reaction an ideal choice for mineralization.
- In conclusion, the photo-Fenton reaction is a versatile green option for the treatment of wastewaters. There is a scope for using solar light in photo-Fenton reaction because the absorption of carboxylate complexes of ferric ion extends to the visible region. This aspect is being pursued further.
- AOP by photocatalytic oxidation using TiO₂ is handicapped by low quantum efficiency (<3%) for OH radical generation. It is in the state of development to be used for commercial applications.

TO BE CONTINUED.....