



ADVANCED OXIDATION PROCESS FOR WASTEWATER TREATMENT: A REVIEW

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Abstract: Advanced oxidation processes holds a promising future for the treatment of wastewater containing organic compounds that are not easily removable. All AOPs are designed to produce hydroxyl radicals. It is the hydroxyl radical that reacts to disintegrate organic compounds. AOP combine ozone, UV, hydrogen peroxide and/or catalyst to offer effective wastewater treatment solution for the reduction and/or removal of residual organic compounds that are measured by COD, BOD or TOC. This paper presents basic review of efficient AOPs developed to decolorize and/or degrade organic pollutants for environmental protection. Fundamentals of typical methods such as fenton, electro-fenton and photo-fenton, are discussed.

I. INTRODUCTION

Research activities devoted to environmental protection has gained rapid momentum as a consequence of paid attention to the environmental by political, social and legislative authorities delivering severe regulations. The fulfilment of severe quality standards is especially claimed for those substances that have detrimental impact on the biological sphere. Several conventional technologies exist for its treatment that include phase separation techniques (adsorption processes, stripping techniques) and methods that eliminate the contaminants (chemical oxidation/reduction). Chemical oxidation aims at the conversion of the contaminants to CO₂, water, inorganics or at least into harmless products. Apparently, techniques based on chemical destruction yields acceptable results, but sometimes, complete elimination of the contaminant is not possible by conventional way of chemical oxidation. Such systems require more effective oxidising medium in order to completely eliminate the pollutant. Intense research and quest has converged on the use of advanced oxidation processes (AOPs). Although advanced oxidation makes use of different reacting system, it is characterized by the same chemical feature i.e. production of OH radical and operates at near ambient temperature and pressure. The versatility of AOP is enhanced by the fact that they offer different possible ways for OH radical production thus allowing a better compliance with the specific treatment requirements. AOPs can provide effective technological solutions for wastewater treatment. Applications of AOPs to treat wastewater must consider that they make use of expensive reactants as H₂O₂ and/or O₃, so its economic viability must be considered before it is put to use.

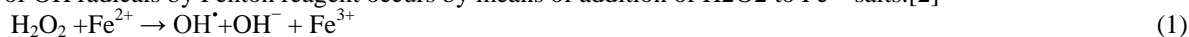
Advanced oxidation processes by definition refers to a set of chemical treatment techniques designed to remove organic and inorganic materials in wastewater. One such type of process is called In Situ Chemical oxidation. Contaminants are oxidized by four different reagents: ozone, H₂O₂, O₂, and air. These technique can be combined with UV irradiation and specific catalysts. This yields hydroxyl radicals. A commonly known example of AOP is the use of fenton's reagent. The AOP procedure is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic matter in wastewater. The contaminants are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts.

The main mechanism of AOPs is generally the formation of highly reactive free radicals. Hydroxyl radicals are effective in destroying organic chemicals because they are reactive electrophiles that rapidly reacts with electron-rich organic contaminants.

II. ADVANCED OXIDATION PROCESSES

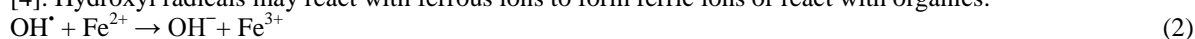
A. Fenton's process

It has been demonstrated that Fenton's reagent is able to destroy toxic compounds in waste waters such as phenols and herbicides. Generation of OH radical occurs by means of addition of H₂O₂ to Fe²⁺ salts. Production of OH radicals by Fenton reagent occurs by means of addition of H₂O₂ to Fe²⁺ salts.[2]

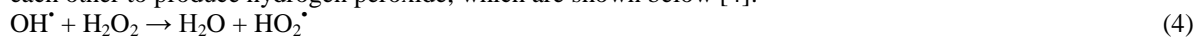


This is a very simple way of producing OH radicals neither special reactants nor special apparatus being required. This reactant is an attractive oxidative system for waste water treatment due to the fact that iron is very

abundant and nontoxic element and hydrogen peroxide is easy to handle and environmentally safe. The oxidation using Fenton's reagent has proven a promising and attractive treatment method for the effective decolorization and degradation of dyes [3]. The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants [4]. Hydroxyl radicals may react with ferrous ions to form ferric ions or react with organics:



Hydroxyl radicals can also react with hydrogen peroxide to produce other radicals, and may also combine with each other to produce hydrogen peroxide, which are shown below [4]:



Ferrous ions and radicals are produced during the reactions. The reactions are shown in Eqs. (6)–(9) [4]:



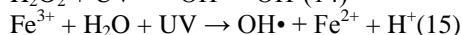
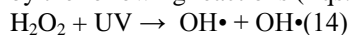
B. Electro-Fenton Process

There is a need to develop effective methods for the degradation of such organic pollutants, either to less harmful compounds or, more desirable, to their complete decolorization. Recently, mainly because of its amenability to automation, high efficiency and environmental compatibility, there is a growing interest in the use of effective direct or indirect electrochemical degradation of organic pollutants in waters [5]. In the presence of ferrous ions and in acidic aqueous medium the oxidation power will be enhanced due to the production of a very reactive one-electron oxidizing agent hydroxyl radical ($\bullet\text{OH}$) from the Fenton reaction. This electro-Fenton process can generate $\bullet\text{OH}$ by the simultaneous electrochemical reduction of O_2 in the presence of catalytic amounts of ferrous ions [3].



C. Photo-Fenton Process

In photo-Fenton process in addition to the above Fenton reactions the formation of hydroxyl radical also occurs by the following reactions (Eqs. (14) and (15)):



The addition of UV to Fenton's process could be an interesting allied in dye decolorization due to its capacity to influence the direct formation of $\bullet\text{OH}$ radicals [7]. The rate of organic pollutant degradation could be increased by irradiation of Fenton with UV light (photo-Fenton process). UV light leads not only to the formation of additional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe^{3+} . In this way, the concentration of Fe^{2+} is increased and the overall reaction is accelerated. Among the AOPs, the oxidation using Fenton's reagent and photo-Fenton's reagent has been found to be a promising and attractive treatment method for the effective decolorization and degradation of dyes. Malik and Saha [7] reported that the removal rate is strongly dependent on the initial concentration of the dye, Fe^{2+} and H_2O_2 . Muruganandham and Swaminathan [8] have carried out studies where similar results were obtained; they suggested a pH of 3 is optimum for fenton and photo-fenton processes.

Advantages of Advanced Oxidation Processes

- a) Rapid reaction rates.
- b) Small footprint.
- c) Potential to reduce toxicity and possibly complete mineralization of organics treated.
- d) Does not concentrate waste for further treatment with methods such as membranes.
- e) Does not produce materials that require further treatment such as "spent carbon" from activated carbon absorption.
- f) Does not create sludge as with physical chemical process or biological processes (waste biological sludge).

Disadvantages of Advanced Oxidation Processes

- a) Capital intensive.
- b) Complex chemistry must be tailored to specific application.

c) For some applications quenching of excess peroxide is required.

III. CLOSING THOUGHT

Advanced oxidation processes seem to be an environmentally friendly process for decolorization of real dyeing wastewater. Advanced oxidation processes represent a powerful means for the abatement of refractory and/or toxic pollutants in wastewater. Different AOP techniques have been developed thus allowing to make choices the most appropriate for the specific treatment problems. Major attention should be devoted in the future by researchers to fill some specific gap which exists for these techniques in the areas such as identification of reaction intermediates, development of rate expressions based on established reaction mechanisms, identification of scale-up parameters and criteria for cost effectiveness and maximum destruction efficiency. Moreover, the improvement of these techniques for a more efficient exploitation of sun radiation could ensure more economic solutions to the problem of water purification and recovery.

References

- [1] R. Andeozzi, V. Caprio, A. Insola, R. Marotta, -Advanced oxidation processes (AOP) for water purification and recovery, *Cat. Today* 53, pp. 51-59, 1999.
- [2] F. Haber, J. Weiss, -The catalytic decomposition of hydrogen peroxide by iron salts, *Proc. R. Soc. Series A* 147, pp. 332.
- [3] A. Wang, J. Qu, J. Ru, H. Liu, J. Ge, -Mineralization of azo dye Acid Red by electro-Fenton's reagent using an activated carbon fiber cathode, *Dyes and Pig.* 65, pp. 227-233, 2005.
- [4] M.P. Titus, V.G. Molina, M.A. Baños, J. Giménez, S. Plugas, -Degradation of chlorophenols by means of advanced oxidation processes: a general review, *App. Cat. B: Env.* 47, pp. 219-256, 2004.
- [5] S. Trasatti, -Electrochemistry and environment: the role of electrocatalysis, *Dep. of Physical Chemistry and Electrochemistry, Uni. of Milan, Via Venezian* 21, 20133 Milan, Italy.
- [6] M.S. Lucas, J.A. Peres, -Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes and Pig.* 71, pp. 236-244, 2006.
- [7] P. K. Malik, S. K. Saha, -Oxidation of direct dyes with hydrogen peroxide using ferrous ion catalyst, *Sep. Purif. Technol.* 31: 241-50, 2003.
- [8] M. Muruganandham, M. Swaminathan, -Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology, *Dyes Pig.* 63, pp. 315-21, 2004.
- [9] C.H. Wu, H.Y. Ng, -Degradation of C.I. Reactive Red 2 (RR2) using ozone-based systems: Comparisons of decolorization efficiency and power consumption, *Jr. of Haz. Mat.* 152, pp. 120-127, 2008.
- [10] M.S. Lucas, J.A. Peres, G.L. Puma, -Treatment of winery wastewater by ozone-based advanced oxidation processes (O₃, O₃/UV and O₃/UV/H₂O₂) in a pilot-scale bubble column reactor and process economics, *Sep. and Pur. Tech.* 72, pp. 235-241, 2010.