Impact Factor (SJIF): 4.542

International Journal of Advance Research in Engineering, Science & Technology

e-ISSN: 2393-9877, p-ISSN: 2394-2444

Volume 4, Issue 4, April-2017

Overview of Advance oxidation process for the tertiary treatment of pulp and paper industry wastewater

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Abstract* — the wastewater generated from the pulp and paper industry are potentially pollutant, because of their large volume and their refractory nature. Biological treatment generally is not capable to remove these compounds. Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of pulp and paper industry wastewaters containing non removable organic compounds. All AOP are designed to produce hydroxyl radicals HO•. It is the hydroxyl radicals that act with high efficiency to destroy organic compounds. Generation of HO• is commonly accelerated by combining oxidizing agents. AOP combine ozone (O3), ultraviolet (UV), hydrogen peroxide (H_2O_2) and/or catalyst to offer a powerful wastewater treatment solution for the reduction and/or removal of residual organic compounds as measured by COD. This paper presents a general review of efficient advanced oxidation processes developed to decolorize and/or degrade organic pollutants for environmental protection. Fundamentals and main applications of typical methods such as UV radiation plus hydrogen peroxide (UV/H_2O_2), Fenton's reagent (H_2O_2/Fe^{+2}), photo-Fenton ($UV/H_2O_2/Fe^{+2}$), and ozone in different combinations (O_3/UV; O_3/H_2O_2) is discussed.

***Keywords-* Pulp and paper industry wastewater, Advance Oxidation processes, COD removal.**

I. INTRODUCTION

The paper industry is the largest industry in India. India holds 15th rank among paper producing countries in the world. The Indian paper industry accounts for about 3% of global paper production. The industry is fragmented with over 750 paper mills, of which only 50 mills have a capacity of 50,000 TPA or more. About 70% of the total installed capacity of paper production in India is accounted by Gujarat, West Bengal, Orissa, Andhra Pradesh, Karnataka and Maharashtra. Uttar Pradesh, Tamil Nadu, Haryana, Kerala, Bihar and Assam together account for about 25% of the total paper production in India. The industry is working at 89 per cent capacity utilization.

The pulp and paper industry is use natural resources (wood, water), energy (electricity and fossil fuels) as a raw materials and major contributor of pollutants discharge to the environment. During the pulping and manufacture of paper products, there is generation of large amount of contaminants, whose composition varies depending on the manufacturing process. The main work of all pulping processes is to separate the fibers, producing a fiber suspension in water. Depending on the process wood preparation, pulping, pulp washing, screening, bleaching, papermaking and coating operations are the most important sources of contamination. The characteristics of the generated wastewater is depends on the type of wood, the type of process, the amount of water that the mill is able to circulate, the technology used and the selected management practices. Depending on the raw material use and the process involved for the manufacturing of paper product untreated wastewater can have high biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (mainly fibers), fatty acids, tannins, resin acids, lignin, and its derivatives. Some of them are naturally occurring pollutants and others are formed during the pulp and paper manufacturing process. Some substances are recalcitrant to biological degradation and toxic to aquatic species.

The wastewaters of pulping processes are characterized by their suspended solids content, organic substances, chromophoric compounds, inorganic compounds and salts. Semi chemical processes contain lingo sulfonates and also the characterization mention for the pulping processes. The Kraft process wastewaters are characterized by their content of solids (including particles of bark), dissolved organics, chromophoric compounds (mainly derived from lignin). If Kraft pulps are bleached with chlorine compounds, they can present organochlorine compounds (dioxins and furans). Although chromophoric groups are not well defined, they are basically composed by conjugated olefins and quinines, methodic quinines and aromatic rings. While bleaching of high yield processes uses oxygen as oxidizing agent, in the case of Kraft pulps, chlorine was historically used. The improvements that have been made in the bleaching process in the last 20 years consisted on the complete removal of elemental chlorine by developing technologies as Elemental Chlorine Free (Elemental Chlorine Free, ECF) or Totally Chlorine Free (Totally-Chlorine Free, TCF), combined with oxygen delignification, which reduces the amount of organochlorine compounds released into the environment. The initial values of COD of pulping processes are very different, depending on the origin of the effluent and the type of raw material [1]. Examples of initial COD of high yield pulping [TMP, CTMP, BCTMP, and NSSC] and Kraft pulping are shown in Table 1.

Table 1. COD of effluents from high yield and chemical pulping processes

Effluent	Process	COD [mg/L]
Pulp mills	TMP	3340; 3500; 5600; 7210; 3340
	BCTMP – TMP	2520; 7930
	TMP – CTMP	4000 – 7800
	CTMP	4800; 7900; 6000 – 9000; 12000
	NSSC	1000 – 5600
	Kraft bleaching	500 – 700; 1100 – 1700; 1254; 1200
Pulp and paper mills	TMP	1000 - 5600
	CTMP	2500 – 13000; 9521
	NSSC	5020
	Kraft	1000; 1400; 2210; 1130

TMP: Thermo mechanical pulping, CTMP: chemi thermo mechanical pulping, BCTMP: Bleached chemi thermo mechanical pulping, NSSC: neutral sulfite semi chemical process [1].

II. ADVANCED OXIDATION PROCESSES

In India conventional technologies like biological, thermal and physicochemical treatments are most commonly used to remove contaminants from the wastewater. Other treatment systems such as flocculation, precipitation, adsorption, extraction, and reverse osmosis required post-treatments to dispose the separated contaminants. These conventional treatments have been successful in lowering the chemical and biological oxygen demands, but their applicability is limited by a number of problems [2]. Some of the pollutants in industrial effluents are not biodegradable, conventional treatment processes are not sufficient. In order to meet the increasingly stringent discharge limits, mills are forced to adopt unconventional and technologically advanced treatment systems to reduce refractory organic compounds and color of wastewater processes [1]. Effluents from pulp and paper industry are highly colored. Biological treatments, such as activated sludge process, remain the most suitable treatment for the degradable organic matter (measured as BOD5), but the ability of these methods for removing refractory compounds is negligible. It is therefore necessary to identify alternative methods that can degrade these compounds.

Advanced Oxidation Processes (AOP) are used to oxidize complex organic constituents found in wastewater that are difficult to degrade biologically into simple end products. AOP are produce a total mineralization, transforming recalcitrant compounds into inorganic substances (CO2 and H2O2), or partial mineralization, transforming them into more biodegradable substances [1]. The oxidation of specific compounds may be characterized by the extent of degradation of the final oxidation products as follows: (i) primary degradation, which causes a structural change in the compound, allowing it to be more easily removed by other processes (for example, biological treatment, adsorption, etc.), (ii) acceptable degradation (defusing), which involves the decomposition of the compounds, reducing their toxicity, (iii) ultimate degradation, the last step comprising the mineralization of organic compound [1].

Advanced Oxidation Processes are capable of transforming pollutants into harmless substances in a short reaction time and can be used to treat effluents from the pulp and paper mills and other industry like chemical, petrochemical, textile etc. AOP typically involve the generation and use of the hydroxyl free radical ($HO^{\cdot}$) as a strong oxidant to destroy compounds that cannot be oxidized by conventional oxidants such as oxygen, ozone, and chlorine. The high reactivity of these radicals and their low oxidation selectivity are useful attributes that made this process a promising technology for the treatment of effluents containing refractory organic compounds [1]. The main strengths and objective of the oxidative processes are that they do not transfer contaminants from one medium to another. The formation of sludge does not happen during the process, and in some cases complete mineralization of refractory compounds occurs. The negative aspects of these processes are the high investment and operating costs and the generation of undesirable byproducts. The combination of biological and chemical processes is more economical option to increase the treatability of refractory effluents, by increasing the BOD5/COD ratio and /or by the better utilization of the oxygen rate [1]. Therefore, chemical oxidation is affected by the amount of oxidizable organic compounds, the reaction rate between the oxidizing agents and the organic compounds, and by chemical conditions, such as pH and temperature, whereas the biological processes are affected mainly by the pH, the presence of toxic substances, the redox potential and the oxygen available [1]. The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential. The relative oxidizing power of the hydroxyl radical, along with other common oxidants, is summarized in Table 2.

Table 2. Comparison of oxidizing potential of various oxidizing agents

Oxidizing agent	Electrochemical oxidation potential (EOP), V	EOP relative to chlorine
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78

Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

From Metcalf and eddy.

Several technologies such as Fenton, photo-Fenton, ozonation, photocatalysis, etc. are use as the AOP and the main difference between them is the source of radical production. For the effective oxidation of refractory organic compounds, hydroxyl radicals should be generated continuously through photochemical reactions due to its chemical instability. Generation of HO• is commonly accelerated by combining some oxidizing agents such as ozone (O3), hydrogen peroxide (H2O2), UV radiation, and ferrous and ferric salts (Fe^{+2} and Fe^{+3}) [1], and also by radiation sources such as ultrasound, visible, solar and thermal energy. By adjusting the reaction conditions, the HO• radicals with a significant oxidation potential up to 2.8 V, can attack a wide variety of contaminants. Among these treatments, UV radiation plus hydrogen peroxide (UV/H_2O_2), Fenton's reagent (H_2O_2/Fe^{+2}), photo-Fenton ($UV/\ H_2O_2/Fe^{+2}$), and ozone combinations (O_3/UV, O_3/H_2O_2) are considered to be effective for the oxidation of effluents from the pulp and paper industries [1], [2].

2.1 Advanced Oxidation using Ozone

Ozone is use as an oxidizing gas which reacts with inorganic and organic compounds of wastewater, directly or indirectly, through the formation of hydroxyl radicals. It is poorly soluble in water (12 mg dm-3, 25°C), but once in contact with water, it becomes highly unstable and rapidly decomposes through a complex series of reactions, in accordance with the mechanism of hydroxide ions (HO-) [1]:

$$O_3 + HO^- \rightarrow HO_2^- + O_2$$
$$HO_2^- + O_3 \rightarrow O_3^-\bullet + HO_2\bullet$$
$$HO_2\bullet \rightarrow O_2\bullet + H^+$$
$$O_3 + O_2\bullet \rightarrow O_3^-\bullet + O_2$$
$$O_3^-\bullet + H^+ \rightarrow HO_3\bullet$$
$$HO_3\bullet \rightarrow HO\bullet + O_2$$
$$O_3 + HO\bullet \rightarrow O_2 + HO_2\bullet$$

The chain reaction is sustained by the formation of the $HO_2\bullet$ radical, which can use for then initiate further reactions. The hydroxyl radical (HO•) is the most important parameter formed during the ozone decomposition. pH, the nature and concentration of oxidisable organic compounds, ozone dose, competition between the target compound and biodegradable by-products, the presence of oxidant scavengers, and the efficiency of ozone mass transfer are the main factors affecting the ozonation process. Ozone is effective to decolorize effluents, and convert refractory compounds into biodegradable compounds from the wastewater. The ozone dosage played an important role in discoloration. The increase of the ozone dosage in 10-fold produces a 19-fold increase of the discoloration rate [1], [2], [3].

Ozonation process give best result at alkaline pH, and it is due to the reaction between all organic and inorganic compounds with the molecular ozone and the oxygen radicals, including the hydroxyl radical. These hydroxyl radicals have an oxidation potential (E° = 2.80) higher than O_3 (E° = 2.07) in the direct reaction under acidic conditions. Removal of color and COD has been favored at pH higher than 9.

The combination of ozonation with biological treatment reduces biological regrowth potential, because biological treatment can remove biodegradable organic matter selectively. Ozonation transforms large molecules into smaller ones, thus increasing the biodegradability of the organic matter [1]. Ozonation combined with biological treatment is an effective method for treating effluent from several pulping processes. By using ozonation process 50% of COD value was decrease two different TMP effluents. A reduction of 12% of TOC, 70% of total phenols, and a 35% in color after 60 minutes of ozonation have been reported for an industry that produces bleached Kraft pulp. Ozonation of wastewater from a similar industry with doses of 0.7 to 0.8 mg/L for 120 min resulted in a COD removal of about 21% (± 5%). It has been found that the use of ozone (dose: 50 - 250 mg/L) as a pretreatment of a biological reactor is effective for the treatment of a bleached Kraft pulp effluent, as it increase the effluent biodegradability, checked by increasing BOD along with the reduction in COD (reductions close to 11%). With the use of ozone as a post treatment, the reduction percentages were much lower [1], [3], [5].

2.2 Advanced Oxidation using Hydrogen Peroxide

Hydrogen peroxide is also use as the oxidizing agent for the treatment of pulp and paper industry wastewater. By using hydrogen peroxide, the reaction between the generated HO• and many organic contaminants occurs rapidly. It produces the oxidation of organic products, which can turn in react with the HO• radical. The use of this agent has emerged as a viable alternative among other advanced oxidation processes, because it is a non-toxic reagent that does not form any harmful by-product, improves the efficiency and reduces the critical conditions of the oxidation reaction [1]. For a given concentration of H_2O_2 and pH, hydroxyl radical production mainly depends on catalyst concentration and reaction temperature. Once the radical is formed, it can react with the unreacted H_2O_2 or the organic matter, resulting in oxidized species.

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O$$
$$HO_2\bullet + HO\bullet \rightarrow O_2 + H_2O$$

The first reaction is favored when the effluent contains high levels of organic matter, and leads to a high degree of mineralization (desired reaction.) The second is favored when the H_2O_2 is present in large amounts or the load of catalyst is low. This reaction affects the efficiency of the overall degradation and acts as a radical scavenger, resulting in a significant increase in operating costs, and inhibitory effects on degradation of the compounds [1]. Hydrogen peroxide is not able to oxidize the dissolved matter; radicals should be generated from the direct reaction of another oxidant and the ionic form of hydrogen peroxide, which is the initiation stage of a radical mechanism [1]. The catalyzed reaction of ozone with hydroxyl ion must be considered as a second step of the radical initiation mechanism, leading to the formation of hydroxyl radicals. The rate of initiation of the reaction of radical generation becomes more important at high pH [1]. The combination of these two oxidizing agents is also beneficial in the treatment of compounds that show little or no reactivity towards the direct attack of the ozone molecule [1].

2.3 Advanced Oxidation using catalyzed H_2O_2 (Fenton process)

The renewed interest of researchers for this classic, old reactive system, discovered by Fenton the last century, is today underlined by a significant number of investigations devoted to its applications in wastewater treatments. It has been demonstrated that Fenton's reagent is able to destroy toxic compounds in waste waters such as phenols and herbicides. Production of OH radicals by Fenton reagent occurs by means of addition of H2O2 to Fe_2^+ salts.

$$H_2O_2 + Fe_2^+ \rightarrow OH\bullet + OH^- + Fe_3^+$$

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 non toxic 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 organic and inorganic matter [4]. The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants [1]. Hydroxyl radicals may react with ferrous ions to form ferric ions or react with organics:

$$OH\bullet + Fe_2^+ \rightarrow OH^- + Fe_3^+$$
$$OH\bullet + \text{organics} \rightarrow \text{products}$$

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:

$$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$$
$$OH\bullet + OH\bullet \rightarrow H_2O_2$$

Ferrous ions and radicals are produced during the reactions. The reactions are shown in below equation:

$$H_2O_2 + Fe_3^+ \leftrightarrow H^+ + FeOOH_2^+$$
$$FeOOH_2+ \rightarrow HO_2\bullet + Fe_2^+$$
$$HO_2\bullet + Fe_2^+ \rightarrow HO_2^- + Fe_3^+$$
$$HO_2\bullet + Fe_3^+ \rightarrow O_2 + Fe_2^+ + H^+$$

The efficiency of Fenton process depends on the generation rate and the concentration of oxidizing agents formed during Fenton reaction. Operational parameters that directly affect the efficiency of the process are: the source of iron catalyst (e.g. ferrous or ferric salt), iron and hydrogen peroxide concentrations, their ratio, pH, temperature and treatment time. The main advantage of the Fenton process is that the reagents are safe to handle and environmentally benign. It does not require highly complicated devices or pressurized systems for the oxidation process, making it technologically a viable for direct application on any scale. The potential application of Fenton technology for the treatment of highly polluted industrial effluents requires achieving high efficiencies of H_2O_2 consumption, since this is the critical component of the operating costs. High temperatures increase TOC and COD removal, since H_2O_2 consumption is more efficient in these conditions. For example, COD removal was 92% at 90ºC compared to 67% at 50ºC. Fenton's reagent is used to produce hydroxyl radicals in an electrolytic cell and ferrous ion is regenerated by the reduction of ferric ions at the cathode. Using this method, COD reduction up to 96% in a Kraft pulp mill effluent was achieved [1].

2.4 Advanced Oxidation using UV radiation

UV radiation with the combination of different catalyst is use for the treatment of wastewater of pulp and paper industry. UV/H_2O_2, UV/O_3, and their combinations are suitable for treating the organic components of the effluents. UV/H_2O_2 treatment is based on the formation of radicals HO• by photolysis of the hydrogen peroxide:

$$H_2O_2 + UV \rightarrow 2HO\bullet$$

UV/ H_2O_2 technique requires a relatively higher dose of H_2O_2 and / or longer exposure to UV rays. The speed of photolysis of hydrogen peroxide is pH dependent and increases in alkaline conditions, because of the formation of HO_2^- anions, which show a molar absorptivity of $240M^{-1}$ cm^{-1} at 253.7 nm, which is higher than the hydrogen peroxide, by the reaction:

$$HO_2^- + UV \rightarrow HO\bullet + O\bullet^-$$

Ozone alone for the treatment of wastewater was not effective, however, by using UV/O3 treatment reductions of 95% and 98% in COD was achieved. In the treatment of an effluent from a bleaching process, the color removal was more influenced by the pH than by UV. It was verified that the discoloration constant depends on pH rise, contributing favorably to increase the reaction rate [1]. O_3/UV process is effective for oxidation and destruction of toxic and water-refractory organic compounds. It consists basically of an aqueous system saturated with ozone, which is irradiated with UV light at 253.7 nm. The extinction coefficient of ozone at 253.7nm is $3300m^{-1}cm^{-1}$, much higher than that of hydrogen peroxide and its decomposition rate is about 1000 times greater than that of the same reagent. Irradiation of ozone in water produces H2O2 quantitatively. Hydrogen peroxide generated is in turn photolyzed, generating radicals HO• and reacts with the excess of ozone generating radicals which contribute to oxidation, according to equation:

$$O_3 + H_2O + UV \rightarrow O_2 + H_2O_2 + UV \rightarrow 2HO\bullet$$
$$(HO_2^-) \rightarrow HO\bullet$$
$$HO^- \rightarrow HO\bullet$$

Fenton's reagent resulted in a degradation 40-fold faster than the UV process. The highest percentages of reduction achieved were, O_3: 100%; O_3/ H_2O_2: 92.5% UV: 24.2%; UV/ H_2O_2: 90.6%; O_3/UV/ H_2O_2: 99.4% Fe (II) / H_2O_2: 100% various oxidative systems have been evaluated on different streams of wastewaters from pulp and paper mills [1]. Applying different iron doses (1.3, 20, and 50 mgL-1) in the Fenton's reagent on an outgoing effluent from a biological treatment (initial COD: 898.9 mg/L), COD removal achieved was 4, 18, and 36%, respectively. On the contrary, when photo-Fenton was applied with 5 and 10 mgL-1 of Fe(II), COD removal rates exceeded 90% [1].

The effect of the initial concentration of hydrogen peroxide in UV/ H_2O_2, Fenton and Photo-Fenton in the treatment of the effluent from a recycled cardboard mill (COD: 10300 mgL-1) has been reported. Photo-Fenton treatment produced the greatest reduction in COD (76%) compared with UV/ H_2O_2 and Fenton, in 45 minutes. With the same purpose, a papermaking effluent with a COD of 950 mg/L was treated by the Fenton method, obtaining color and COD reductions of 95% and 50% respectively [1].

2.5 Advantages of Advanced Oxidation Processes

a) Rapid reaction rates.
b) Small foot print.
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 (wasted biological sludge).

2.6 Disadvantages of Advanced Oxidation Processes

a) Capital Intensive.
b) Complex chemistry must be trilored to specific application.
c) For some applications quenching of excess peroxide is require.

III. CONCLUSIONS

Advanced oxidation processes seems to be an environmental friendly process for removal of refractory organic and inorganic matter and also for the reduction of color of wastewater generated from the different paper mill processes. Advanced oxidation processes represent a powerful mean for the abatement of refractory and/or toxic pollutants in wastewaters. Different AOP techniques have been developed thus allow to making 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.

The pulp and paper industry is a complex activity which involves many different processes and products. Pollution of water bodies is major concern because it is an industry that generates large volumes of waste water per ton of pulp or paper produced, depending on the nature of the raw material, the final product and the extent of reused water. In all advanced oxidation processes, the most important parameter or oxidizing agent is hydroxyl radical. By using this agent no contaminants are transfer from one phase to the other phase and also no sludge will produce from the treatment. During the treatment by H_2O_2 the dose of H_2O_2 is very critical. By increasing H_2O_2 concentration, hydroxyl radicals are more available for the oxidation of pollutants and the efficiency of removal of recalcitrant compounds also increases [1].

In the pulp and paper industry different raw materials are use for the production of paper products so there is variation in the generated wastewater from the process. Different AOP are use for the treatment of generated wastewater. All the AOP are give different efficiency to treat the effluent. It has been conclude that the combination of biological treatment and advanced oxidation processes are more effective than the AOP alone. It is clear that advanced oxidation processes are technically applicable for the removal of recalcitrant compounds and refractory compounds from effluents of pulp and paper mills. This technology is to improve biodegradability, reduce toxicity, enhance color removal and disposal of organic compounds, increasing the possibility of discharge those wastewaters into the receiving bodies without causing any damage. Due to the differences between the effluents from the various processes and operations of these industries, some oxidative processes must be combined to improve the efficiency of removal, though it can mean an increase in operating costs.

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