Review Paper:

Reduction of Colour from effluents of Pulp and Paper Industry by Ozonation: A Review

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Abstract

Pulp and paper making is the major old process industry in India which is water intensive and generates heavy water pollution. Pulp and paper industries are the fifth largest contributor to industrial water pollution. Waste water is generated from each and every section of paper making process and depends upon the type of pulping and bleaching process. Presently, primary and secondary (Biological) treatment systems based on activated sludge process are widely used by paper industry for effluent treatment.

The process requires high energy and chemical inputs and involves high operational costs. One of the novel processes for treating effluent is its oxidation through ozonation which is a greener way of degrading pollutants. Ozonation of intermediate stage effluents having high colour load is more effective for industrial application and re-utilization.

Keywords: Ozonation, Colour, Effluent, COD, BOD, AOX.

Introduction

The relationship of man with the environment is from the very beginning of ancient history. The equilibrium between the two must be maintained at all costs throughout the existence of human beings on the earth. Paper industry plays an important role in socio-economic development of a country. It is one of the essential commodities even after the growth of electronic media. The global demand of paper is continuously increasing.

During the past few decades, industries have registered a quantum jump which has contributed to high economic growth but simultaneously these create a lot of environmental pollution.

The pulp and paper industry has been considered to be a major consumer of natural resources (wood, water) and energy (fossil fuels, electricity) and a significant contributor of pollutant discharges to the environment. The water quality is seriously affected which is far lower in comparison to the international standards.

It is found that one-third of the total water pollution comes in the form of effluent discharge, solid wastes and other hazardous wastes. The surface water is the main source of paper industries for waste disposal. Although all industries function under the strict guidelines of the Central Pollution Control Board (CPCB), but still the environmental situation is far from satisfactory. Different norms and guidelines are given for all the industries depending upon their pollution potentials. When paper industry is concern, it eliminates highly coloured effluent with significant amount of COD, BOD, suspended and dissolved particles.

It has been observed that the coloured effluents of paper industry after mixing with the public sewage carry over above 50 kilometres. Effluents of the pulp and paper industry contain a number of toxic compounds and cause deleterious environmental impacts upon direct discharge to receiving waters.

The most significant sources of pollution in pulp and paper industry are wood preparation, pulping, screening, pulp washing, bleaching and coating operations. Among the various processing steps, pulping generates high-strength waste water containing toxic chemicals such as phenolics[2,7].

Three main groups of organic compounds are present in paper industry effluents which include: (a) Starch degradation products such as saccharides or carboxylic acids (b) Phenolic compounds arising from lignin and (c) Other pollutants which may be present in the fresh waters such as surfactants. Major problems due to the pollutants present in the effluents of paper industry are high suspended solids, chemical oxygen demand (COD), toxicity, absorbable organic halogens (AOX) etc. The different sources of pollutants in pulp and paper industry are given in figure 1.

Effluent generation in paper mill process

The paper industries are mainly water intensive and highly polluted waste water is discharged from all unit operations. In large paper mills, the waste water is segregated into two streams[19]. Coloured stream (due to presence of lignin) comprises of waste water from pulp washing, caustic extraction, oxygen delignification back water and chemical recovery sections and colourless or light-coloured stream comprises of waste water from chipper house, chlorination, hypochlorite, dioxide stage and paper machine sections.

In a large scale paper industry, generally the coloured effluents are produced from chipper house, pulp mill and soda recovery while the less effluents are released from stock preparation and paper machine. The effluents of pulp and paper mill have been recognized to cause environmental hazards for many years.

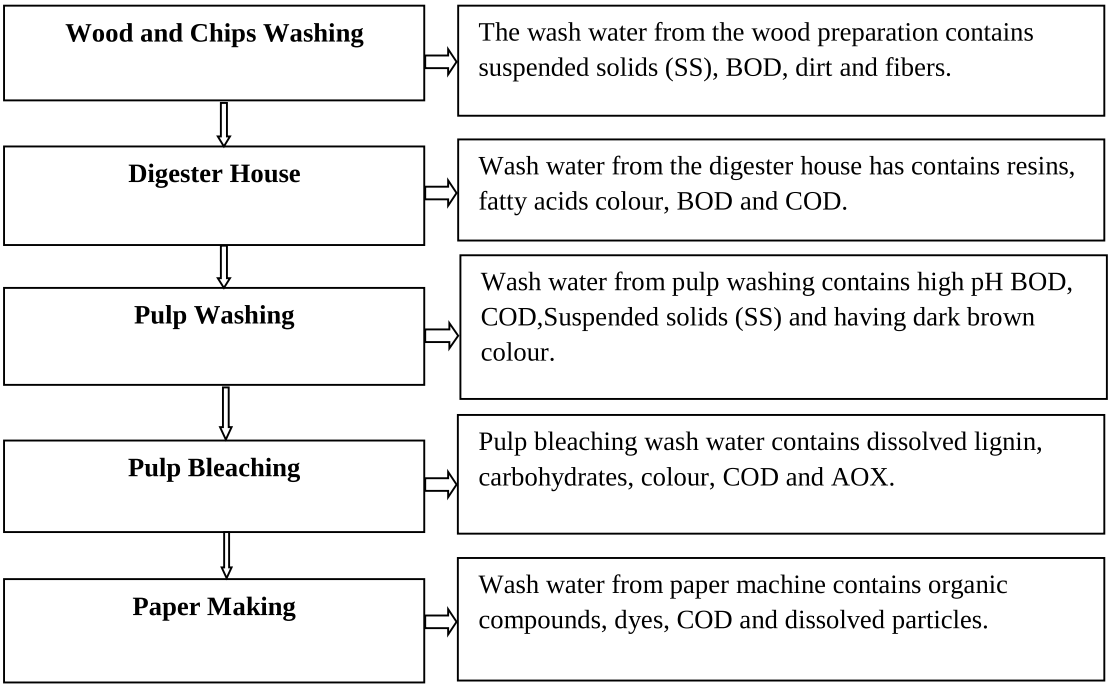

Fig. 1: Sources of Pollutant in different stage of pulp and paper industry

The chemical composition of these effluents depends upon the raw materials used and pulping and bleaching process employed. Indian paper industry uses an average of 150-200 m^3 of fresh water per ton of paper and nearly 50-75% of which is discharged as effluent[6,15,20]. The water pollution in pulp and paper mills include a wide variety of chemicals like lignin and other organics like extractives, degraded lignin and celluloses from wood and bamboo etc., caustic soda, sodium sulphate, sodium sulphite, chlorine, chlorine dioxide, fillers like talcum, precipitated calcium carbonate, titanium dioxide, aluminium sulphate etc.

The present effluent treatment technologies significantly reduce the COD, BOD, TSS and TDS but not the colour[3,18,24]. In order to treat the effluents properly, the colour load from the effluent must be removed. Colour is a visible pollutant which can be easily identified by the public authorities. So modification for effluent treatment is essential either from the very beginning where the colour effluent is generated or after the recent treatment process before discharge.

Characterization of pulp and paper mill wastewater

Wood and bamboo, the main raw materials used for pulping contain cellulose, hemicelluloses, lignin and extractives. The principal source of colour in pulp and paper mill effluent is due to presence of lignin in wood which is separated from cellulose fibres in pulping and bleaching process.

Oxygen delignification is the most popular process, next to pulping in paper industry to remove most of the lignin content and reduce the bleach chemicals. The pulp from post oxygen stage is subjected to different bleaching sequences to produce the bleached pulp. The washing liquors from post oxygen stage contain large amount of dissolved organic materials from the degradation of lignin and are mainly responsible for colour load in pulp and paper industry effluent.

The pulp and paper industry produces effluents with large BOD, COD and colour. The main pollutants in pulp and paper industry effluent can be classified into three main categories as floating, suspended and dissolved matter as shown in figure 2. Effluents of kraft pulping are highly polluted and bleaching stage wastes contain colour and adsorbable organic halides (AOX), which depend upon the pulping and bleaching process adopted. During the past decade, a number of studies have been addressed to lignin oxidation with molecular oxygen under alkaline condition[2,4,10,17,23].

Based on the accumulated data, Gierer et al[5] proposed a reaction mechanism which involves the phenolate anions formed under the alkaline conditions of the process, being converted into phenoxy radicals followed by the formation of hydroperoxides and the eventual degradation of aromatic rings to muconic acids**.** Kaneko et al[8] reported on degradation of lignin and reactivity of lignin model compound with ozone. In order to elucidate the reactivity of different types of lignin-structural units toward ozone, they applied ozone in various lignin model compounds. A α-carbonyl type structure is much more stable against ozone than a benzyl alcohol type structure. A guaiacyl nucleus reacts faster with ozone. Biphenyl and phenyl coumaran structures react readily with ozone.

Ksenofontova et al[9] reported on ozone application for modification of humates and lignins. Their literature data concerns about the kinetics and mechanism of ozonation of such complicated macromolecular compounds. The problem is that the ozonation is multistage process and a wide varieties of intermediates are formed. For example, the ozonation pathways of phenolic compounds depend greatly on pH. It is known that molecular ozone preferably oxidizes electron-rich sites [12]. The application of small doses of ozone was shown to result in polymerization processes. The major end products of lignin ozonation are reported to be carbonyl compounds, low molecular weight (MW) carboxylic acids mainly acetic, formic and oxalic acids which are stable to ozonation.

In spite of many studies on the structure of humates (HS) and of their oxidation products, the reaction pathways that HS undergo during ozonation process, remain poorly understood. The production of lower MW fulvic acid (FA) using ozone oxidation of higher MW humic acid (HA) has been discussed by several researchers. The obtained FA showed a high content of oxygen and carboxylic groups. It is known that during ozonation in water solutions, hydroxyl radicals ($OH^•$) reactions proceed along with direct ozonation.

The reactions with $OH^•$ radicals may bring about substantial structural changes in macromolecules including hydroxylation, decarboxylation and depolymerisation of the initial materials, producing oxidized structures that are less hydrophobic and less aromatic. [1,14].

Colour measurement: Colour can be measured on digital UV-Vis spectrophotometer at the wave length 465nm. For that 1.245gm potassium chloroplatinate and 1.0gm of crystalline cobaltous chloride were dissolved in distilled water and 100ml of concentrated hydrochloric acid was added to it and then make up the volume to one litre. This has a colour of 500 Pt cobalt colour unit. Standard solutions of 10,20,30,40,50,60,70,80,90 and 100 Pt Co units were prepared by diluting 1,2,3,4,5,6,7,8,9,10 ml of the standard stock solutions to 50ml in a volumetric flask. Absorbance of the different standard solutions was determined at 465 nm. The effluent pH was adjusted to 7.6 by adding NaOH or H_2SO_4 and then centrifuged for 5 minutes at 1500 RPM or filtered through 80µ filter paper. The absorbance of the solution was then determined at 465nm and the colour of the effluent was computed from the calibration curve:

$$\text{Colour in Pt Co Unit} = 500\ [A_1/A_2]$$

where A_1 = Absorbance of the sample and A_2 = Absorbance of 500 units of Pt Co Standard and [A_{465} = 0 .132].

Application of ozone for effluent treatment

Ozone is a highly reactive allotrope of oxygen containing three atoms per molecule and a powerful oxidizing agent which reacts with organic as well as inorganic compounds directly or indirectly through the formation of hydroxyl radicals. It is a strongest commercially oxidant after fluorine and is commonly used for the treatment of water and industrial applications. It reacts with both inorganic and organic compounds. In the pulp and paper industry effluent, the principal colour bodies include tannins, humic acids and humates from the decomposition of lignin. These lignin bodies are highly coloured and quite resistant to biological attack resulting in their long persistence to the environment. Recently ozonation has been considered as a greener technique for colour removal of colour.

The process also does not generate any toxic by-products. The application of ozone in pulp and paper industries has become more popular after the development of technology in producing low cost ozone which can be safely used for the production of total chlorine free (T.C.F) or elementally chlorine free (E.C.F) pulp. Although ozonization is a very good choice for the physical and chemical treatment of effluents released from pulp and paper industry, it cannot be used for effluent treatment due to its high cost.

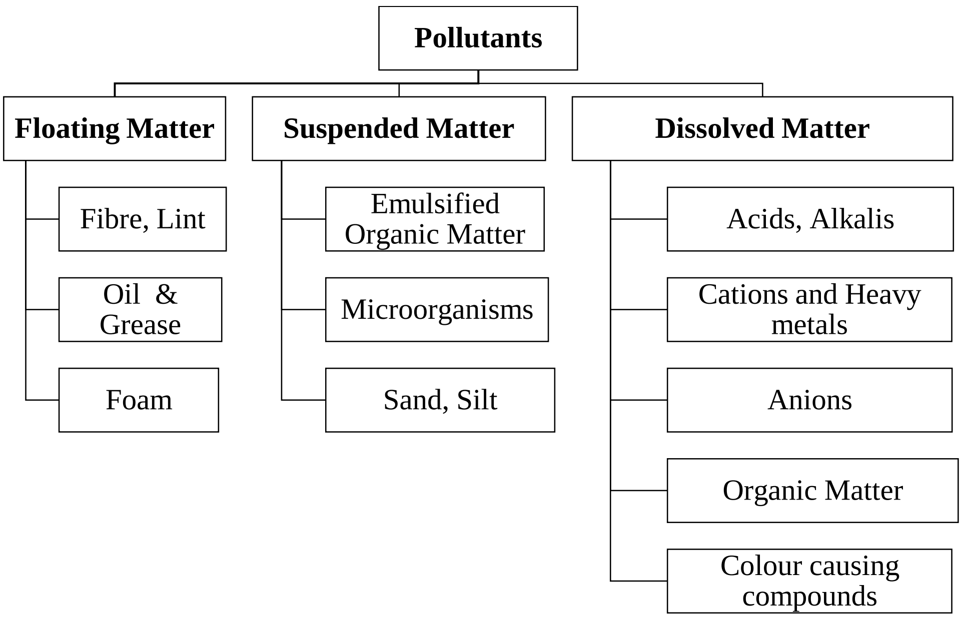

Fig. 2: Classification of pollutants of pulp and paper industry

Rosner[16] reported about the art of ozone system for paper mill effluent treatment. He reported that due to increasing COD discharge loads mainly caused by lignin compounds, were not tolerated by public authorities and further purification by means of biological process alone was not possible to treat the effluent properly.

Teramoto et al[21] studied the ozonation of aqueous cyanide solution using semi-continuous bubble column as well as continuous bubble column. It was found that overall reaction rate is controlled by liquid-film mass transfer resistance. The experimental data were explained on the basis of theory of gas absorption with chemical reaction. A method for evaluating capacity coefficient of liquid-phase mass transfer from absorption rate of ozone into water of high pH was also presented[21].

Lindholm et al[11] reported on the molecular mass distribution of bleaching filtrates used for studding the tendency of ozone to react with already stable lignin fragments under various bleaching conditions. Ozone can break down lignin into fragments soluble in water or alkali.

The main reaction products are different muconic acid derivatives. Ozone can be generated by applying high electrical energy to molecular oxygen. At first, the molecular oxygen decomposes and forms oxygen free radical which further reacts with molecular oxygen and forms ozone. These are compounds of polyaromatic structure, substituted aromatic structure, concentrated hetero-circular molecules or perplex ions. Ozone has the property to decompose in water in a self-sustaining radical chain reaction initiated by hydroxyl radical.

Advanced oxidation process (AOP): Oxidation reaction can be enhanced by using some other reagents with ozone. Advanced oxidation process (AOP) is a promising alternative technology in pollution control for several contaminated effluents and the performance of the different AOP-systems such as O_3/H_2O_2, UV/H_2O_2, Fe^{2+}/H_2O_2 (Fenton's reagent), UV/O_3, UV/TiO_2. Ozonation of pulp and paper industry effluent involves two types of oxidation reactions with molecular ozone (O_3; Ozonolysis) or indirect reactions with free radicals that are formed during ozone decomposition. Ozone decomposition is a function of several factors including pH and the presence of inorganic and organic compounds. Molecular ozone reactions are extremely selective and limited to unsaturated aromatic and aliphatic compounds. On the other hand, in presence of hydroxyl ions (OH^-) at alkaline pH (> 9), ozone decomposes in water and forms $OH\cdot$.

$$O_3 + H_2O \longrightarrow 2HO^{\cdot} + O_2$$
$$O_3 + OH^{-} \longrightarrow O_2 + OH_2^{\cdot}$$
$$O_3 + OH^{\cdot} \longrightarrow O_2 + OH_2^{\cdot} \longleftrightarrow O_2 + H^{+}$$
$$O_3 + HO_2^{\cdot} \rightleftharpoons 2O_2 + HO^{\cdot}$$
$$2\,HO_2^{\cdot} \longrightarrow O_2 + H_2O_2$$

In peroxone process (O_3/H_2O_2), $OH\cdot$ radicals are generated by free radical chain reaction mechanism by the reaction between ozone and hydrogen peroxide[22]:

$$H_2O_2 + 2O_3 \longrightarrow 2OH^{\cdot} + 3O_2$$

Catalytic ozonation: The ozonation process can again be enhanced by using some catalyst. Catalytic ozonation can be devided into homogeneous and heterogeneous process. In homogeneous catalytic ozonation, transitional metal ions such as Fe(II), Mn(II), Ni(II), Co(II), Cd(II), Cu(II), Ag(II), Cr(II) and Zn(II) are used with ozone. In homogenous reactions, transition metal ions present in the reaction solution initiate ozone decomposition by the generation of superoxide radicals ($O_2\cdot$). The transfer of one electron from the ($O_2\cdot$) molecule to O_3 results in the formation of ozonide. Heterogeneous catalytic ozonation involves the use of metal oxides or metals or novel metals supported on metal oxides like TiO_2, Al_2O_3, SiO_2, MnO_2 and Fe_2O_3 or Cu, Ru, Pt, Pb, Pd, Co metals mounted on these catalyst supports by several ways are used in the catalytic ozonation. The activity of these catalysts is based on the catalytic decomposition of ozone and the enhanced generation of $HO\cdot$.

The efficiency of catalytic ozonation depends to a great extent on the catalyst, its surface properties and solution pH.The ozone-electrolysis is an another advanced oxidation process. The mechanism for ozone-electrolysis is given bellow

$$O_3 + e^{\ominus} \longrightarrow O_3^{\ominus} \quad \text{(At cathod)}$$
$$O_3^{\ominus} + H_2O \longrightarrow OH + O_2 + OH^{\ominus}$$

Naoyuki et al[13] reported that ozonation combined with electrolysis is better than ozonation for removal of COD and suspended solids.

Advantages of ozonation: Ozone is more effective than chlorine in destroying viruses and bacteria. The ozonation process utilizes a short contact time (approximately 10 to 30 minutes). There are no harmful residuals that need to be removed after ozonation because ozone decomposes rapidly.

After ozonation, there is no re-growth of micro-organisms except for those protected by the particulates in the wastewater stream. Ozone is generated onsite and thus, there are fewer safety problems associated with shipping and handling. Ozonation elevates the dissolved oxygen (DO) concentration of the effluent.

Conclusion

The ozonation with the application of catalyst is more efficient for the reduction of colour and COD from pulp and paper industry effluents. Again, AOP and ozonation with electrolysis are also very useful for reduction of COD and colour. The colour of pulp mill effluents is mainly due to degraded lignin-based chromophore compounds.

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