Characteristics and Treatment of Pulp and Paper Mill Effluents – A Review

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***Abstract*—Pulp and paper mills generate huge amount of wastewater depending on the type of processes used in the plant whose unsafe disposal can be very hazardous to environment and human health. Such wastewater need be treated properly prior to release into environment. In view of the fact there has been substantial research and development worldwide concerning wastewater treatment thereby limiting the discharge of pollutants to receiving environment. The present review covers a variety of wastewater treatment methods and research carried out on removal of various toxic pollutants so as to limit the release of pollutant load. Various treatment processes for pulp and paper industrial effluents, including aerobic, anaerobic, photo-catalysis, electrochemical, ozonation, coagulation–flocculation and adsorption treatment processes have been presented. Though, the conventional wastewater treatment systems widely practiced in pulp and paper industry generally involve primary clarification followed by activated sludge processes. However, supplementary treatments including advanced oxidation processes, biological treatments, membrane filtration, etc. are needed to eliminate higher levels of pollutant. In order to reduce the use of freshwater, recycling and reuse of the properly treated wastewater has been emphasized. Best treatment strategy should be devised considering the type, amount and characteristics of wastewaters. Further, an effective treatment system need to be inexpensive and should integrate a series of physicochemical, biological, and hybrid treatment processes.**

***Index Terms:* Pulp and paper industry, Wastewater characteristics, Physicochemical treatment, Coagulation-flocculation, Biological treatment**

I. INTRODUCTION

Industrialization have not only increased the demand for clean water but also posed problems of wastewater disposal thereby making the water resource more and more scare. The world demand for paper has grown rapidly to tune of 5-6% annually. It is estimated that the capacity of the mills increases from 8.3 million tonnes in 2010 to 14 million tonnes in 2020. In a pulp and paper manufacturing process, water acts as a disintegration medium for the raw materials, a transport for fibers, and for paper formation and gets contaminated during various processes. The industry utilizes a high quantity of fresh water (60 - 230m^3 per ton of paper production), resulting in the generation of large amounts of wastewater [1].

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It is the sixth largest polluter (after oil, cement, leather, textile and steel industries), discharging a variety of wastes into the environment [2]. The high consumption of fresh water and generation of a huge volume of toxic wastewater are the most important environmental concerns related to the pulp and paper industry. Even with the most modern and efficient operational techniques, about 60 m^3 of water is required to produce a ton of paper, resulting in the generation of at least 50 m^3 of wastewater [3,4]. However, the required quantity of water is dependent on the type of process and chemicals used in the process [5]. According to an estimate, the pulp and paper industries every year generate more than 7000 billion gallons of highly colored and toxic waste effluents mainly containing high molecular weight, modified and chlorinated lignins [6,7].

Most of Indian paper and pulp mills discharge their effluents, containing bleach and black liquor, directly into the receiving water bodies, and thus cause serious environmental concerns [8]. The pulp and paper production generates a significantly large amount of pollutants characterized by this high concentration of total suspended solids (TSS), Chemical oxygen demand (COD), biological oxygen demand (BOD) and (BOD) and many other toxic substances viz., phenols, aldehydes, ketones, amines, cynide, metallic wastes, plasticizer, corrosive alkalis, oils, greases, dyes, biocides, suspended solid, non biodegradable matter, radioactive wastes and thermal pollutants [9]. The volume and pollution load of the generated wastewater depends upon different combinations of unit processes involved in the production, type of raw materials and chemicals used, kind of paper produced, and the degree of water recovery [10]. The pollutants discharged from the paper industry affect aquatic and land ecosystems. Many research studies reported toxic effects on various fish species due to the exposure of pulp and paper industrial wastewater, including liver damage, mixed function oxygenase activity, physiological changes, respiratory stress, toxicity and lethal effects [11-13]. The wastewater contains high concentrations of recalcitrant dissolved organic matter, and when aquatic systems are overloaded it can induce high biochemical oxygen demand [14]. Pulp mill effluent treatment plants produce primary and secondary sludges that pose several environmental challenges. The extent of pollution due to discharge of wastewater to the receiving water body has been extensively studied [15-22].

II. CHARACTERISTICS OF PAPER MILL EFFLUENTS

Among various stages of paper making, raw material processing, pulping, pulp washing, screening, washing, bleaching, paper machine and coating operations are the important pollution sources [23]. The effluent is characterized by dark color, foul odour, high organic content and extreme levels of COD, BOD, and pH [24]. In general, high organic matter and suspended solid contents are considered major pollutants of pulp and paper industry effluents. Among the paper making processes, pulping especially by chemical pulping generates high strength wastewater which contains wood debris and soluble wood materials, organic material and suspended solid [1]. Also, Chlorine used for bleaching of pulp generates enormous toxic chemicals as it utilizes chlorine for brightening the pulp [17]. The wastewater generated from pulping process also consist various wooden compounds such as lignin, carbohydrate and extractives. Chlorination is generally the first stage in kraft bleaching and during this treatment chlorinated organic compounds are produced [25]. Chloro-organic compounds tend to persist in nature because of their inherent recalcitrance. They are often toxic to aquatic life; many are genotoxic and have the potential to migrate widely throughout the ecosystem. The colour in paper mill effluent is caused by organic legends such as wood extractives, resins, synthetic dyes, tannins, lignin and their degradation products [26,27]. Addition of toxic compounds such as resin acids, unsaturated fatty acids, diterpene alcohols, chlorinated resin acids and others can exist in the wastewaters subjecting to the process [24]. The different bleaching sequence adopted by pulp and paper industry are especially problematic due to the presence of adsorbable organic halides (AOX), total organic chlorides (TOCl) and wood extractives in the effluents. The most important reaction in the bleaching step is oxidation of chlorine and the main problem about the wastewater content is the generation of chlorinated organic compounds [28]. The wastewater generated from paper making process include large number of degraded organic and inorganic contaminants depending upon the type of raw materials, end product, high concentration of chemicals such as sodium carbonate, sodium sulphide, bisulfites elemental chlorine dioxide, calcium oxide, hydrochloric acid, etc [29].

Due to the severe toxic effects of pulp and paper mill effluents, reduction and/or removal of pollution load prior to their discharge into the environment is crucial. For efficient treatment of paper mill effluents, assessment of the actual pollution load exerted by each individual processing unit in terms of certain physicochemical parameters is considered essential. Das and Patnaik analyzed the physicochemical characteristics of hard wood based kraft pulp and paper mill effluent and reported the value of pH, lignin and COD as 7.08, 145.0 and 816 ppm respectively. The result revealed that both raw and treated effluent possessed high value of solids, BOD, COD, chlorides etc [30]. Kamalakar et al. reported the physicochemical characteristics of the effluent of century pulp and paper mill and found that the values of pH, BOD, COD, suspended solid and total dissolved solids were 7.6, 1140 mg/L, 3288 mg/L, 185 mg/L and 655 mg/L respectively. The concentration of Na^+, K^+, Ca^{+2}, Mg^{+2} , Cl^-, NO_2 and bicarbonates was 84.4, 131.0, 204.8, 43.95, 252.5, 0.25 and 162.5mg/L respectively [31]. Analysis of physicochemical characteristics viz., pH, colour, TS, TDS, TSS, turbidity, BOD, COD, and AOX of effluents collected from different processing units of an agro-based paper mills located in Uttarakhand state of India found to vary considerably across the discharge streams. The mean values pH, colour, TS, TDS, TSS, turbidity, BOD, COD, and AOX were found in the range of 2.55–9.8±0.05, 410– 2802 PCU, 1980.65–2785.79 ppm, 1650.67–2470.35 ppm, 315.44–401.35 ppm, 73.22–349.37 NTU, 170.32–670.42, 705.52–2000.55 ppm, and 14.98–40.82 respectively [32]. Further, the same characteristics of effluents from another agro-based paper mills located in Uttar Pradesh state of India ranged from 1.82±0.03 to 9.84±0.06, 481.44±0.58 to 3936.16±5.76 PCU, 1718.49±0.65 to 4252.29±4.46 ppm, 1518.27±2.65 to 3032.14±3.32 ppm, 200.22±2.01 to 1220.15±3.15 ppm, 113.23±1.46 to 481.22±2.61 NTU, 355.65±3.50 to 1342.22±3.50 ppm, 881.52±3.19 to 2710.12±4.52 ppm, and 15.75±0.51 to 38.35±0.21 ppm respectively [32]. The higher values of all physicochemical parameters of effluents from various processing units of the paper mill than the permissible limit necessitate appropriate treatment prior to their discharge in the environment.

III. HAZARDS OF WASTEWATER DISCHARGE

Most pulp and paper mills dispose wastewater into nearby water bodies. The deliberate discharge of such harmful chemicals into the environment has enough potential to disrupt the structure and functioning of the natural ecosystem. Such effluents are believed to contain some naturally occurring endocrine disrupting chemicals such as phytosterols, which may be related to a variety of physiological and morphological abnormalities in fish inhabiting receiving waters [34]. Some of which are toxic, mutagenic, persistent, bio-accumulating, thus causing numerous harmful disturbance in biological system [35,36]. Studies on impact of water quality demonstrated a variety of responses in fish populations living downstream of bleached kraft pulp mills. Studies demonstrated a variety of responses in fish populations living downstream of bleached pulp mills. These included delayed sexual maturity, smaller gonads, changes in fish reproduction and a depression in secondary sexual characteristics [13]. Some of toxins like chlorides, transition metals, chelating agents, and dioxins found in paper mill effluent have been shown to cause ailing effect in humans. Consumption of such contaminated water may result in ulceration of internal organ linings, severe diarrhea, and can be fatal [37]. The dark color and high turbidity due to suspended solids can cause the problems of both water opacity and blanketing of river or lakebeds. Severe blanketing may result in anaerobic decomposition under the blanket releasing hydrogen sulphide into aquatic ecosystems. The dark color and blanketing can reduce photosynthetic activity in aquatic plants. The effluents can also cause thermal impact, slime growth, scum formation and loss of aesthetic beauty in the environment [24].

IV. TREATMENT OF WASTEWATER

Treatment of the pulp and paper mill effluent is essential to reduce pollution load and to comply with environmental norms. Different methods have been practiced for the treatment of pulp and paper industry effluent which includes physical, chemical, electrochemical and biological methods. Pokhrel and Viraraghvan [24] and Savant et al. [2] extensively reviewed various treatment methods available for pulp and paper industry effluent. Furthermore, several other treatment processes including aerobic, anaerobic, photo-catalysis, electrochemical, ozonation, coagulation- flocculation and adsorption exist for treatment of pulp and paper mill effluents [38-40].

The main treatment processes are primary clarification by sedimentation or flotation, and secondary treatment with advanced oxidation. Reduction of COD index is usually considered as a measure of the effectiveness of the wastewater treatment process in the treatment plant. Studies have shown that traditional biological purification does not remove toxic compounds as well as the total content of organic compounds and may even lead to the formation of metabolites with even greater persistence and toxicity. Physicochemical treatment methods are commonly used. Physicochemical treatment of wastewater including viz., sedimentation, ultra-filtration [41], flotation [42], screening [43], coagulation, flocculation [44], ozonation and electrolysis [45] which are used to remove suspended solids, colloidal particles, toxic compounds, floating matters, and colours at the preliminary, primary, or tertiary stages of wastewater treatment. The concentration of contaminants present in wastewaters and their desired removal efficiencies are important factors in choosing the type of physicochemical treatment process. Coagulation and flocculation processes using aluminum, ferric chloride, lime, ferrous sulfate and poly aluminum chloride are considered as an efficient treatment method to reduce COD, total suspended solids (TSS) and colour of pulping effluent [46-48]. Several techniques including chemical precipitation, electro deposition, solvent extraction, ultra filtration, ion exchange distillation and microfiltration are available to reduce BOD, colour and total solids, etc. [49]. Adsorption, membrane filtration and chemical processes have been assessed for their efficacy and practicality [50-53]. The addition of various oxidation agents has been tested in the laboratory as a promising way to treat highly polluted effluents [54].

A. Decolouration

The colour in paper mill effluent is caused by organic ligands such as wood extractives, resins, synthetic dyes, tannins, lignin and its degradation products [26,27]. Colour and toxicity of effluent are also due to low and high molecular weight chlorinated organic compound generated during wood cooking, conventional bleaching of pulp [55]. Such wastewaters also contain high concentrations of suspended solids and floating matters. Therefore, sedimentation is applied as a primary treatment process which is reported to remove 80% of suspended matters from wastewater [56]. Sedimentation in combination with adsorption and ultra-filtration is reported to achieve 60% and 87% total solid removal respectively from the Kraft black liquor [41]. Despite its better removal efficiency, use of ultra-filtration in the pulp and paper mills is uncommon due to its high cost. A combination of ferrous sulphate, alum, ferric chloride, lime, magnesium sulphate, and calcium hypochlorite and chlorine water reported to be effective in reducing color of paper mill effluents. The combination of alum, lime and magnesium sulphate in presence of ferric chloride have been found to remove the colour, BOD and COD by 97%, 71% and 61% respectively [57]. The chemical precipitation of coloring matter and its subsequent removal using lime and salts of iron and aluminum is reported [58-60].

B. Chemical Coagulation and Flocculation

Coagulation technology involves the addition of a coagulant additive such as alum, ferric salt, calcium or polyamine to the waste water stream. It is frequently applied in the primary purification of industrial waste water. Applications of alum, ferric chloride, ferric sulphate and lime for chemical coagulation have been extensively studied for the treatment of pulp and paper mill wastewater [58,59,61]. Coagulation/flocculation treatment using alum and clay combinations reported to reduce colour up to 88%; however, showed poor settling characteristics [26]. Aluminum sulphate and ferric chloride were found to be equally efficient in removing turbidity from suspension at pH 8.0±0.2. Removal of organics from the wastewater by employing wet oxidation (WO) and catalytic wet oxidation (CWO) technique using a high pressure reaction system was investigated. Different types of catalysts prepared from single metals (transition/noble) were used for CWO studies. The single transition (CU, Mn) or noble metal (Pd) catalyst showed appreciable total organic removal, but the bi-metal catalysts (Cu/Mn, Cu/Pd, Mn/Pd) exhibited even higher activity for organics removal. A significant total organic carbon (TOC) removal (>84%) was achieved by using CWO process. The TOC removed by Cu/Pd catalyst was the highest, followed by the Mn/Pd and Cu/Mn catalytic system [62].

Chemical coagulation and flocculation followed by sedimentation are widely used processes for the removal of suspended solids and have been applied in pulp and paper effluents as a tertiary treatment [24]. It is a proven technique for treatment of high suspended solid wastewater, especially those formed by colloidal matters [63]. Flocculation can lower the pollution load and generate adequate water purity. Coagulation studies with alum and poly aluminium chloride (PAC) revealed its removal efficiency towards turbidity, TSS and COD as 99.8%, 99.4% and 91% respectively at optimum alum doses of 100mg/L and 6 pH. In addition, when treated with 500mg/L PAC, reduction of 99.9 % for turbidity, 99.5% for TSS and 91.3% for COD was recorded [64]. Orori et al. tested seven methods including chemical coagulation, ferric chloride, calcium oxide and alum, electrochemical alone and electrochemical combined with CaO or alum or with wood chelate for removal of color from waste water effluents of pulp and paper mill in Webuye, Kenya [65]. Electrochemical combination method found to be the best method to remove color from the effluent. This technique improved the physical properties of corrugated paper, reduced freshwater consumption, and lowered the impact of effluent water pollutants on the ambient environment [66].

Coagulation and flocculation treatment performed using various alum and clay combinations recorded almost 88% reduction in colour but showed poor settling characteristics [26]. However, chloride and sulphate salts of iron and aluminum, 88% reduction in total carbon and 98% in turbidity were achieved [58,59]. Removal of colour, TOC and AOX from pulp mill effluent was reported by advanced oxidation processes [67]. Also, TiO_2-assisted photo catalysis (UV/TiO_2) reported to remove 79.6% of TOC and 94% of toxicity [68]. The electrochemical oxidation of paper mill wastewater was studied by using a dimensionally stable anode. The result showed that the presence of NaCl is a determining factor in the purification process. Electrolysis of waste water containing 5mg/L NaCl at a cell potential difference of 6V for 120 minute, removed 99% of COD and for color and phenol removal was 95% after 15 minutes. Studies on removal of phenols using ferric chloride reported to precipitate phenols as well as coloring matter from waste water on [69]. Further, a two step sequential treatment was investigated to remove color and phenols from paper mill effluent [70].

Hearth et al. studied the colour and phenolic compounds reduction of Kraft pulp mill by ozonation with some pretreatments [71]. The study was performed with the treatment of Kraft pulp mill effluent by ozonation alone as well as by combined treatment of ozonation preceded by chemical coagulation, activated carbon adsorption or membrane filtration which is used in pulp and paper industry in a variety of applications, particularly in purification and recovery of water, raw material and energy [72]. Coagulation and the Fenton process were applied as a pretreatment step before ultrafiltration (UF) for the treatment of secondary effluent from a recycled paper mill. Results exhibited that

Fenton pretreatment combined with UF had the best performance and resulted in a COD reduction of 91.81%. The addition of PAC in the effluent and subsequent mixing creates proper flocculation condition and the floccs generated are denser than water. With the increase of concentration, the removal of COD and colour also increases [73].

C. Chemical Treatment

The chemical precipitation of coloring matter and its subsequent removal from paper mill effluent using lime and salts of iron and aluminum is reported by various authors [58-60]. The major advantage of chemical treatment is that most of the COD and TSS are being reduced during this process; therefore it can be more cost-effective before secondary treatment as well as removing the color from the effluent [74,75]. Among these, adsorption is one of the most promising, highly effective, cheap, single step and less troublesome technique to remove pollutants from waste water as no sludge is produced [76,77].

D. Activated Carbon Adsorption

Activated charcoal has a matrix of micropores which offers a surface area of $1400m^2/gm$ of material, thus making it suitable for adsorption as it can easily collect and hold compounds of lower volatility. Activated carbon is one of the most important chemical absorbents [78]. It is known to remove soluble and trace organics up to 90-95% and heavy metals and inorganics up to 95%. Hence activated carbon adsorption can be used for removal of organic compounds and colour from wastewaters [79]. Murthy et al. reported a high removal of color by activated charcoal, fuller's earth, and coal ash [80]. Sullivian found that the waste water can be treated by the activated carbon and ion exchange to reduce color and chloride to the acceptable level for reuse [81]. Comparative efficiency of commercial and indigenously prepared pyrochar (granular and activated) from paper mill sludge for removal of color and organic matter from distillery wastewater was investigated. Result showed colour removal up to 98, 83 and 93% at 10, 15 and 2 gm/L of activated pyrochar, granular pyrochar and commercial carbon respectively. Also, reductions in COD and TOC at the same does were 64% and 42.9%, 86.7% and 52.84%, 52.02% and 33.68% respectively indicating commercial carbon being highly effective at low does, but similar reduction could be obtained at large doses of pyrochar [82].

Removal of phenol and phenolic derivatives using activated carbon has been carried out by several researchers [83,84]. Fly ash as an adsorbing medium can be used to remove chlorinated organic and colour efficiently. Shawwa et al. reported the use of delayed petroleum coke for the efficient removal of AOX from bleaching waste water [85]. Temmink and Grolle obtained an excellent polishing with respect to colour and cationic demand in biologically treated wastewater from paper industry with activated carbon treatment [86].

However, high cost of activated carbon prompted research for cheaper substitutes such as flyash, peat, rice husk waste coir pith, orange peel, *Eichhornia sp.* roots and shoots [87], baggasse, tea dust, coir pith [88], corn cob [76] clay and coal [89] silk, cotton, coconut tree, saw dust, maize carbon, banana pith and cassava pith [90] for removal of colour.

E. Photo catalytic treatment

Torrades et al. described a photo catalytic treatment, which removed the entire color and most of the TOC, AOX, and COD in a highly loaded polluted effluent within 20 hours [91]. Moiseev et al. have shown that the use of photo catalytic oxidation as a pretreatment step enhances the biodegradability of waste water containing recalcitrant or inhibitory compounds and is an alternative to a long and energy intensive total pollutant mineralization [92].

F. Biological Treatment

Biological treatment of pulp and paper mill effluents involve used of microorganisms with lignolytic properties which are capable of degrading toxic and recalcitrant compounds [93]. Such lignolytic microorganisms including fungi, actinomycetes, yeast, bacteria, and algae, can produce enzymes responsible for lignocellulose degradation [94]. Application of enzymatic treatment alone or in combination with other physical and chemical methods has been widely reviewed [95-97]. The enzymatic treatment despite being a safe and ecofriendly process has limited commercial applications owing to high cost and long residence time [98].

Wastewater treatment plants commonly employ aerobic and/or anaerobic biological processes to remove organic contaminants in wastewaters. Of which, pulp and paper mills prefer to use aerobic processes owing to their relatively low cost and ease of operation. Anaerobic processes are though not so common, a number of mills use different anaerobic technologies due to lesser sludge production, renewable energy production, smaller area requirements and capacity for further degradation of pollutants [99]. Disadvantages of both aerobic and anaerobic processes include high sludge production in aerobic processes and sensitivity of anaerobic bacteria to toxic materials. Further, high sulphur content wastewater from chemical pulping had a detrimental effect on the contaminant removal capacity of anaerobic processes, especially at low pH [100].

G. Tertiary Treatments

For biologically resistant compounds, tertiary treatment process like adsorption, advance oxidation and membrane filtration are applied. Catalkya and Kargi (2008) obtained 79.6% TOC and 94% toxicity removals by TiO_2-assisted photocatalysis (UV/TiO_2) with a titanium dioxide concentration of 0.75 g/L at pH 11 within a time period of 60 minutes. Performances of membrane processes, such as microfiltration (MF), ultrafiltration (UF), nanofilteration (NF) and reverse osmosis (RO) in the treatment of pulp and paper industry effluents have been investigated by different researchers [101-103]. BOD, COD, TDS, TSS, AOX and color from pulp and paper effluents are effectively diminished [104[. Yao et al. found 99% reduction in AOX using ultra filtration. Reverse osmosis with pressures in the range of 3.5-4.5 MPa or higher can also be useful for AOX removal [105].

Nano-filtration in combination with electro dialysis at a pilot scale has removed 95% of the contaminating toxic halides, salts and colorants leaving the treated effluents suitable for process reuse [106]. Sandhya reported the technical feasibility of various low cost adsorbents for heavy metal removal instead of using commercial activated carbon. Adsorbants that stand out for high adsorption capacities are chitosan, zeolite, waste slurry and lignin [107]. Saravanan and Sreekrishnan studied bio-physicochemical treatment for removal of colour from pulp and paper mill effluents [108].

Despite availability of several tertiary treatment processes only a few are used in pulp and paper mills because of their high cost; as such, coagulation and flocculation are still considered as inexpensive process in pulp and paper industries for additional polishing of the effluent.

V. CONCLUSION

Treatment of the wastewater of pulp and paper mills is challenging due to varied complexity depending on the characteristic of the wastewater, required purity to be achieved in the treated water and fulfillment of regulatory norm for safe disposal the reclaimed effluents. A successful wastewater management system needs to clearly define water qualities for reuse in the industry, other uses and disposal. The pulp and paper mill effluent must be treated to achieve the discharge limits. In addition, it is important to achieve stable and reliable operations of both the pulp/papermaking process and the wastewater treatment system. The importance of efficient wastewater treatment in the pulp-and-paper industry is fueled by the growing concerns over the use of fresh water, increased economic consideration and stringent environmental regulations. In order to reduce the use of freshwater, recycling and reuse of the properly treated wastewater has been emphasized which will also reduce the volume of wastewater discharges to the environment. There are many existing treatment processes for pulp and paper industrial effluents, including aerobic, anaerobic, photo-catalysis, electrochemical, ozonation, coagulation–flocculation and adsorption treatment processes. The type, amount and characteristics of wastewaters are important to devise the best treatment strategy. An effective physicochemical treatment should be the economically viable for the required finishing treatment for the effluents. In view of the fact the wastewater treatment practice in pulp and paper mills need to integrate a series of physicochemical, biological, and hybrid treatment processes.

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