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Review Paper

Various Treatment Processes for the Removal of Absorbable Organic Halides (AOX) from Pulp and Paper Industry Wastewater

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Abstract- *Paper and pulp industry is one of the most important industries in India, not only for Economical purpose but also for Social purpose. The pulp and paper industry is the world's second largest consumer of chlorine and the greatest source of toxic organ-chlorine discharges directly into waterways. At first glance, a sheet of paper might seem harmless, closer look at paper production reveals toxic chlorine bleaching and reckless logging practices that are devastating our forests, our rivers and lakes, and our health. The paper demand is increasing day by day with put great pressure on these industries. When residual lignin from wood fibers and chlorine/chlorine compounds react then absorbable organic halides (AOX) is generated, in the bleaching process. They are proven very carcinogens and mutagens, bioaccumulative. (AOX) can cause severe effects on the health of people and wildlife and are implicated in local and global outbreaks of cancer, impaired reproduction and development, immune suppression, and other diseases. This paper reviews the various Physical, chemical and electrochemical methods reported to remove AOX compounds are available and also different types of aerobic, anaerobic and combined biological treatment processes have been developed for treatment of pulp and paper industry wastewater. There is a growing need for modernization and introduction of energy efficient and clean technologies for enhancing competitiveness and productivity*

Keywords: Absorbable organic halides, Pulp and paper industry, AOX, carcinogens, bioaccumulative Wastewater treatment.

Introduction

Paper manufacturing is a highly capital, energy and water intensive industry. It is also a highly polluting process and requires substantial investments in pollution control equipment. In India, around 905.8 million m3 of water is consumed and around 695.7 million m3 of wastewater is discharged annually by this sector. India's current average fresh specific water consumption of about 150 m3/tonne of product is far above the global best specific water consumption of 28.66 m3/tonne (for large scale wood based pulp and paper mill) and this large gap is primarily attributed to the use of obsolete technology / equipments and poor water management practices.

Plenty of published literature is available on various physical, chemical and biological treatment technologies that have aimed at removing AOX and colour from pulp and paper mill effluents. Physical techniques include adsorption, ultrafiltration, nanofiltration and reverse osmosis. Chemical treatment entails processes such as neutralization of bleach effluent, advanced oxidation processes (ozonation, peroxidation, photocatalysis) and supercritical water oxidation. Precipitation/coagulation has been studied for different types of pulp mill effluents using a wide variety of coagulants [3,5]. Alkaline sulfide and alkaline hydrolysis processes have been reported to achieve partial removal of AOX compounds through nucleophilic substitution by sulfide and hydroxide groups [6,8]. Major limitations of the above listed physico-chemical methods are cost and generation of secondary pollutants (air emissions or sludge). An emerging technology is the reductivedechlorination of AOX compounds using zero-valent metal (ZVM) and bimetallic systems [9,12]. Although such reactions are very efficient and faster, the presence of inhibitory co-pollutants may lead to the drastic reduction

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Although such reactions are very efficient and faster, the presence of inhibitory co-pollutants may lead to the drastic reduction of catalytic activity of metallic systems thereby precluding their field scale application. Aerobic and anaerobic biodegradation of AOX compounds, in particular PCP have been studied in great depth [2,13,18]. While biodegradation may prove economical, requirements for specific environmental conditions (methanogenic or sulfate reducing) in case of anaerobic degradation and long acclimation and retention times restricts its field application.

Over the past two decades there has been growing interest in the application of electrochemical methods for the treatment of potable water and industrial effluents laden with highly recalcitrant pollutants. Chen [19] published an exhaustive review article on the development, design and applications of various electrochemical technologies such as electrodeposition for the recovery of metals, electrocoagulation and electroflotation for the removal of suspended solids, oil and grease as well as colloids and electro-oxidation for the removal of refractory organic pollutants. Zhou et al. [20] observed a synergistic effect on COD removal using a fluidized electrochemical reactor that integrated electrochemical oxidation and adsorption on fluidized activated carbon into a single cell. In the combined process the model organic pollutant, *p*-nitrophenol could be directly oxidized at the PbO_2 anode surface or adsorbed onto activated carbon followed by oxidation. Ge et al. [21] developed a bipolar electrocoagulation – electroflotation process for the remediation of laundry wastewaters. The investigators sandwiched aluminium plates between two titanium electrodes with opposite charges. Al^{3+} produced from the anodic corrosion of aluminium enabled the removal of pollutants by charge neutralization and enmeshment in the cationic hydroxide precipitates while the ultra-fine bubbles of O_2 andH_2 generated at anodic and cathodic sides of Ti, respectively, encouraged separation (flotation) of the flocculated sludge. COD removal efficiency of 70% was noted while 90% removal of turbidity, surfactant and *p*-phosphate were achieved. TezcanUn et al. [22] employed electrocoagulation method using iron or aluminium as electrodes in the presence of 2.3% H_2O_2 as the oxidant and 0.5 g L−1 of polialuminium chloride as the coagulating agent for the treatment of olive mill wastewaters. The performance of the iron electrode was better in comparison to that of aluminium with 62–86% reduction in COD and 100% removal of oil–grease and turbidity. Yavuz [23] investigated electrocoagulation and electrofenton methods for the treatment of pretreated distillery wastewater using iron electrodes. Electrocoagulation was ineffective under the experimental conditions used by the authors. On the other hand, electrofenton achieved COD and TOC removal efficiencies of 93% and 89%, respectively, using 0.3M Na_2SO_4 and 60 g L−1of H_2O_2 at pH 4. Panizza et al. [24] compared direct and indirect electrochemical oxidation of a synthetic solution containing the basic dye, methylene blue. Direct oxidation was carried out usingthe boron-doped diamond anode through eneration of hydroxylradicals while indirect electrolysis was accomplished through electro generation of active chlorine species on a $TiRuO_2$ oxideanode. Indirect electrolyses achieved faster mineralization and decolourization of the dye solution. electrochemical oxidation/reduction can be direct (by sorption on anode/cathode followed by direct electron transfer)or indirect (through formation of reductive/oxidative species) in nature. Electrochemical reduction of chlorophenols which constitute a major fraction of AOX involves sequential dechlorination resulting in the accumulation of either partiallydechlorinated and/or hydrocarbon end product such as phenol [25–28].

On the other hand, complete destruction of chlorophenols can be achieved by electrochemical oxidation[29]. Reactions involving electrochemical reduction are generally carried out in a divided cell which necessitates the provision of cathode and anode separating membrane. However, membranes may be fouled when applied for the treatment of actual wastewater thereby limiting their field scale application.

In this respect electrochemical oxidation offers flexibility since it can be achieved in divided or un-divided cells [29–34]. The extent of follow-up treatment of electrochemically treated effluent depends mainly on the type of anode and reaction conditions (such as pH). A sacrificial anode such as iron or aluminium results in formation of electrochemical sludge made up of a wide variety of metal-hydroxide species [35]. On the other handa non-sacrificial anode eliminates the generation of chemical sludge. Thus, electrochemical oxidation processes employing undivided cells and non-sacrificial anodes may be simple in operation and low in operational cost. Electrochemical treatment of diluted/undiluted wastewaters such as olive oil mill [33,36]distillery [34] and, tannery [37] has been demonstrated using NaCl (4–40 g L−1) as an electrolyte as well as a source for theproduction of oxidative chlorine species.

However, to the best of our knowledge there is very little information on the electrochemical remediation of PCP or AOX in actual pulp bleaching wastewater, mediated by indirect oxidative route. In the present investigations we have evaluated an electrochemical treatment method for the removal of PCP from water since this is one of the most toxic pollutants in the AOX fraction. Subsequently we extended the process parameters to removal of PCP from actual pulp bleaching effluent. The major objectives of our investigations were to: (a) study the efficiency of removal of PCP fromwater by electrochemical treatment using NaCl as an electrolyte since chloride ions constitute major fraction of anions present in pulp bleaching effluent (where elemental chlorine is used for bleaching). (b) Study the effect of current density and elucidate the mechanism of PCP removal and (c) extend the application of electrochemical method for removal of PCP spiked into raw or pretreated pulp bleach effluent. To avoid problems related to divided cells and sludge generation, we conducted experiments in an undivided cell employing a non-sacrificial anode, graphite. Also electrolyte was not added into pulp bleaching effluent in order to minimize the concentration of dissolved solids in the treated effluent.

The findings from the Canadian research programme coupled with observations made in the Baltic sector focussed attention on natural plant components, particularly those capable of interfering with the endocrine systems responsible for hormone synthesis and metabolism. Landner et al. (1994) suggested that natural sterols present in the wood such as α- and β -sitosterol could be a factor since administration of these compounds to fish induced similar responses to pulp and paper mill effluent exposure. This theme was also taken up by Tana et al. (1994) who noted that a proportion of these chemicals extracted from wood would not be cycled through the recovery process, but would be passed to the bleach and effluent treatment plants. The current situation is analogous to that prevailing after regulatory initiatives to control BOD and COD discharges in the 1980's and before. Removal of BOD from effluents led to improvement in recipient quality, but allowed the identification of effects due to other agents present in discharges, specifically organochlorines, which had previously been obscured. Progressive reduction of organochlorine loading similarly, has allowed the identification of yet further impacts due to other chemicals. (see: eg. Owens 1991). In fact, laboratory studies as early as 1941 had established that it was possible to masculinise mosquito-fish using artificial hormones. It was reported in 1991 that androstenedione, androstanol and spironolactone could achieve the same result. In 1978 it had been reported that phytosterols present in tall oils recovered from wood could be converted by microbes to steroids. Tall oil consists of 25-25% phytosterols. Hence, the total phytosterol production by this route alone in the US was estimated at 20,000 tons. (see: Davis and Bortone 1992). These same changes can be produced by exposing fish to kraft mill effluent, although the authors do not specify whether this was derived from a chlorine chemical bleach line. As a result, there are now two distinct elements to the debate about environmental protection from pulp and paper operations. The Canadian findings have prompted the industry into large scale questioning of the utility of reducing AOX emissions any further. For example, Myreen (1994) cites the opinion of scientists in the Nordic countries and Canada that reductions of organochlorines below 1.5 kg AOX/ADT pulp represents an inefficient use of resources. The precise basis for this view is obscure. Malinen et al. (1994) advance a similar viewpoint in their analysis of the future of the industry in Finland. The views subsequently diverge markedly. While Malinen et al. (1994) propose the development of treatment plant to address the residual problems, Myreen (1994) considers that total effluent free (TEF) production is now accepted by the industry as the decisive step towards environmentally friendly pulp and paper production. In light of the Canadian findings and the realisation that all pulp mills can emit endocrine disruptive chemicals on a large scale, closure of the mill circuits may be seen as an environmental imperative for the industry, a theme taken up and discussed by Albert (1995b). In most geographical areas there appear to be clear present and likely future environmental, market and fiscal incentives to move towards TEF production.

Anaerobic treatment is a technically simple, relatively inexpensive technology and consumes little energy. It also requires less space and produces less amount of sludge. Anaerobic micro-organisms can be preserved unfed for long periods of time without any serious deterioration of their activity. The nutrient requirement for anaerobic treatment is low. It is less sensitive to toxic substances. Hence, it is proving to be a viable technology for pulp and paper wastewater treatment. It can remove about 75–85% of the BOD and 55–65% COD in pulp mill effluents. The major treatment methods include anaerobic lagoon, anaerobic contact processes, UASB, fluidized bed, anaerobic filters and hybrid processes. The comparison of the published data is difficult due to differences in the bleaching processes, nature of the bleach effluents and the proportion of the chlorination and extraction stage effluents are mixed. However it can be said that the efficiency of anaerobic lagoons is very low. The UASB and contact processes are the most widely applied anaerobic systems (Allen and Liu, 1998). Now-a-days, high rate advanced anaerobic reactors are being increasingly used. The review of the existing technologies shows that anaerobic treatment process is the only viable option for dechlorination of highly chlorinated compounds. It is resistant to shock loads and the efficiency is increased with addition of a cosubstrate. However, all anaerobic systems have been found to be highly unstable with respect to AOX loading rates. Moreover, higher AOX loading is inhibitory to methanogens in the digester. Also, the treatments are unable to remove fish toxicity of the effluents, in particular with the CTMP and TMP effluents. The poor removal of resin and fatty acids appears to be one of the important reasons for insufficient detoxification of pulp mill effluents. As a result, all the full scale anaerobic systems are currently used as primary treatment processes. To produce a non-toxic effluent and to further reduce BOD loading, two stage anaerobic–aerobic processes have been introduced for the pulp mill effluents. Anaerobic treatments may also be coupled to physical or chemical treatment such as ultrafiltration or reverse osmosis. These methods have been extensively tested for the treatment of recycling water in zero effluent operations and for kraft mill effluent colour and AOX removal (Allen and Liu, 1998). Hence, it could be said that, anaerobic treatment remains the most reliable and economically viable method of AOX removal at present. However, new strategies need to be used to improve biodegradation of chlorinated organics and hence AOX during treatment.

The generation of AOX measured in effluents from both rayon grade pulp and newsprint industries was below 1.0 kg AOX/t paper. The degradation of AOX in biological treatment plant observed is more than 70% and the level of AOX measured was further reduced below 0.50 kg/t paper in final discharge. The higher reduction of AOX in these categories of industries compared to writing and printing paper industries may be because of low initial concentration of AOX in influents. (v) The generation of AOX measured varies from 2.0 to 5.30 kg AOX/t paper. The lower value i.e 2.0 kg was measured in relatively modern industry (Unit-5) employing RDH pulping, oxygen delignification with chlorine dioxide in bleaching processes. In general, the generation of AOX in writing and printing paper industries varied from 1.92 to 5.32 kg AOX/t paper. The degradation of AOX in biological treatment plant varies from 44 to 65 % and the level of AOX in final discharge reduced from 2.0-5.3 kg to 1.0 - 2.65 kg of AOX/t paper in these category of industries. The variation in performance of ETP for removal of AOX may also be due to initial high concentration of

AOX in terms of mg/l due to varying quantity of water consumed per tone of paper. The main reason of high level of AOX may be because of use of high dosage of molecular chlorine due to high carryover of organic matter alongwith pulp to bleaching section and also requirement of high brightness of end product. The results of AOX assessed indicate that the generation of AOX at source is lower in the industries using modified pulping and bleaching processes, where the generation of AOX is about 2.00 kg which is further reduced to 1.00 kg/t paper in final discharge.

The performance of algal treatment for pulp mill effluent decreases with increasing color intensity and AOX content, which mainly originate from the chlorine bleaching of Kraft pulp, the separated CEH bleaching effluent was pre-treated by both the conventional and the heterogeneous catalytic ozonation processes. An increase in the BOD5/COD ratio from 0.11 to 0.28 and 87% color abatement in s of Pt–Co were achieved by catalytic ozonation, which had the best treatment performance. Biodegradability enhancement of the CEH effluent correlated well with a decrease in toxicity, high-molecular-weight-compound content, and AOX abatement. By the pre-treatment of the CEH bleaching effluent, the overall efficiencies of algal treatment of the combined pulp mill effluent in s of the fractional removal of COD and color were increased from 76% and 53% to 86–90% and 96–99%, respectively. Effects of both the conventional and the catalytic ozonation pre-treatments on subsequent biological treatment were close to each other and they reduced the filling period of the Sequential Batch Reactor (SBR) cycle from 8 to 5 days.(Merits of ozonation and catalytic ozonation pre-treatment in the algal treatment of pulp and paper mill effluents .The bench scale results of the first phase of this research demonstrated that the $NaBH_4$ reduction is a viable method for color elimination with no sludge produced. The batch kinetic study of $NaBH_4$ pretreatment indicated that 97% color decrease in 24 h followed first-order kinetics with respect to sodium borohydride consumption and the reaction rate constant was evaluated at 0.6 h−1. Subsequently in the second phase of the experiments, the pilot plant of an innovative chemical and biological reactor system was investigated. The plant consisted of two 20-l reactors operating in the batch mode for the overall residence time of 6 days. In the first reactor, chemical hydrogenation with $NaBH_4$ was performed for 1 day and resulted in a color and COD reduction by 97% and 35%, respectively, and increased BOD up to 85%. No significant change in TSS was observed. The chemically treated effluent was then subjected to a biological oxidation reaction in the second reactor for further treatment with a residence time of 5 days. The results indicated significant decrease in BOD (99%), COD (92%), and TSS (97%). Consequently, a combined chemical and biological reaction system appears to effectively decrease the color as well as BOD, COD and TSS, in contrast to the conventional techniques such as aerated lagoon and activated sludge systems in which color reduction is not observed. The economics of the pilot scale implementation of a NaBH4 color reduction treatment process for 97% color removal was estimated to be in the range of 0.001 US dollar per liter of the most highly colored wastewater sample.

Huge efforts have been made both in adopting more environmental-friendly bleaching processes, and in developing advanced oxidation processes and more effective biological treatments for the reduction of deleterious impacts of paper mill effluents. Even so, the success of such treatments is frequently reported in s of chemical parameters without a proper evaluation of the effluent's toxicity mitigation. This is the first study reporting an exhaustive evaluation of the toxicity of a secondary bleached kraft pulp mill effluent, after either tertiary treatment with the soft-rot fungi Rhizopusoryzae or with a photo-Fenton oxidation, using a battery of freshwater species. As it has been reported the photo-Fenton/UV treatment has proved to be the most effective in reducing the colour and the COD (chemical oxygen demand) of the effluent. Nevertheless, extremely low EC50 values were reported for almost all species, after this tertiary treatment. The treatment with R. oryzae was less effective in s of colour removal and COD reduction, but proved to be the most promising in reducing toxicity. The effectiveness of a biological treatment with Rhizopusoryzae and of a photo-Fenton oxidation in the mitigation of toxicity of a bleached kraft pulp mill effluent, Black liquor and bleach effluent from an agroresidue based pulp and papermill were treated anaerobically to reduce their high chemical oxygen demand (COD) and adsorbable organic halide (AOX) contents. Addition of 1% w/v glucose yielded 80% methane from black liquor with concomitant reduction of COD by 71%, while bleach effluent generated 76% methane and produced 73 and 66% reductions in AOX and COD, respectively. In the absence of glucose, black liquor and bleach effluent produced only 33 and 27% methane with COD reductions of 43 and 31%, respectively pulp and paper lignin and other color compounds are removed by chemical agents in bleaching process. Use of chlorine-based agents results in production of degradation products which include various chloro-organic derivatives. Since these new compounds are highly chlorinated, they cause a problem in the treatment of pulp and paper industry wastewaters. Chemical precipitation, lagooning, activated sludge, and anaerobic treatment are the processes used for treating pulp and paper effluents. Furthermore, a combination of these processes is also applicable. In this study, the effluent of Dalaman SEKA Pulp and Paper Industry was examined for its toxic effects on anaerobic microorganisms by anaerobic toxicity assay. Additionally, this wastewater was applied to a sequential biotreatment process consisting of an upflow anaerobic sludge blanket as the anaerobic stage and a once-through completely mixed stirred tank as the aerobic stage. Results indicated that: (1) Dalaman SEKA Pulp and Paper Industry wastewater exerted no inhibitory effects on the anaerobic cultures under the studied conditions, and (2) application of a sequential biological (anaerobic/next aerobic) system to treat the Dalaman SEKA Pulp and Paper Industry wastewater resulted in approximately 91% COD and 58% AOX removals at a HRT of 5 and 6.54 h for anaerobic and aerobic, respectively. The purpose of this present study is to investigate the removal efficiency of chemical oxygen demand (COD) from pulp and paper wastewater using laccase-polymerized membrane filtration process. The membranes with molecular weight cut-off (MWCO) of 5000 and 10,000, 30,000 and 54,000 were used in a cross-flow module to treat the pulp and paper wastewater containing high phenolic constituents and COD. With 2.98 IU/L of activated laccase applied at room temperature for 180 min, the contaminants in raw wastewater and second effluent were polymerized to form larger molecules with average molecular weight of 1300 and 900 Da (Dalton), respectively. With laccase polymerization prior to filtration, over 60% removals of COD by the four investigated membranes were observed, compared with low COD removal without laccase polymerization. Moreover, the addition of laccase resulted in 4–14% reduction of membrane permeability during the first 180 min filtration operation due to gel layer formation by the polymerization. No further flux decline was observed afterwards indicating the steady state was reached and the membranes could be used to remove the polymerized pollutants without significant fouling. The maximum apparent resistance occurrence for raw wastewater treated with laccase also supported the effectiveness for COD removal with laccase polymerization before membrane filtration. Additionally, pretreatment by inactivated laccase only caused further flux reduction without additional removal of COD.

Two basidiomycetous fungi (Meruliusaureus syn. Phlebia sp. and an unidentified genus) and a deuteromycetous fungus (Fusariumsambucinum Fuckel MTCC 3788) were isolated from soils affected with effluents of a pulp and paper mill over several years. These isolates were immobilized on nylon mesh and the consortium was used for bioremediation of pulp and paper mill effluent in a continuously aerated bench-top bioreactor. The treatment resulted in the reduction of color, lignin and COD of the effluent in the order of 78.6%, 79.0% and 89.4% in 4 days. A major part of reductions in these parameters occurred within first 24 h of the treatment, which was also characterized by a steep decline in the pH of the effluent. During this period, total dissolved solids, electrical conductivity and salinity of the effluent also registered marked decline. It is pertinent to note that this is the first report of bioremediation of pulp and paper mill effluent by an immobilized fungal consortium. Bioremediation of pulp and paper mill effluent by a novel fungal consortium isolated from polluted soil a, The research attempted to find the optimum condition for color and total COD reduction in wastewater from the pulp and papermill industry by using electrocoagulation techniques in batch and continuous modes. Six pieces of iron plates constructed in parallel configurations were used as electrodes. The effect of key parameters including the type of polyelectrolyte, current density, initial pH of the wastewater, and the circulating flow rate of wastewater in the reactor were investigated. The results indicated that the polyelectrolyte had no effect on pollutant removal. At optimum conditions, greater than 97% of color and 77% of total COD were effectively removed with a total operating cost of approximately 0.29 USD/m3 wastewater. First order rate kinetics best explained the reduction of color and total COD concentration, the model fitting the actual data very well. For the continuous mode, the treatment process reached the steady state condition within 2.15 h and the efficiency of color and total COD reduction was greater than 91% and 77%, respectively. The properties of wastewater including color, total COD, BOD5, TSS, TDS, pH and iron ions content were in the range of the acceptable values of current Thai Government standard

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